The 3d Printing Surge: Driven by Plastics

Summary

It can take a long time to become an overnight sensation. History is replete with tales of actors, singers, inventors, and the like whose apparent meteoric rise to stardom belied years or even decades of toil. Such is the case with additive manufacturing, aka 3d printing, which seems to have come out of nowhere the last few years, at least in terms of mass market attention. 3d printing is expected to enjoy a solid compounded annual growth rate (CAGR) for the foreseeable future – over 100 percent through 2018 according to one estimate[1] - and open up huge new markets for material providers particularly in the plastics arena. By 2019, 3d printing materials will top $1 billion[2] with two-thirds of that value coming from the plastics sector. Thermoplastic materials for 3d printing will become a $1 billion business in itself by 2025[3].

This paper examines the state of the 3d printing market, with an emphasis on the application and development of plastics as 3d printing materials. The terms "3d printing" and "additive manufacturing" are generally interchangeable and will be used interchangeably here unless otherwise noted.

Background

While 3d printing is still widely used for prototyping, it has increasingly been employed in large scale design modeling (e.g., automotive designs, wind tunneling) and full scale production of commercial, industrial, aviation and aerospace components, medical devices, live tissues and organs, consumer products and foods. 3d printing is performed with a wide variety of materials including plastics, metals, ceramics, glass, living tissue and even edible materials such as chocolate.

The seemingly sudden interest in 3d printing belies the technology's origins. Japanese researcher Hideo Kodama is credited with the first account of a working photopolymer-based rapid prototyping system back in 1981.[4] The photopolymer-based Stereolithography process was developed by 3d Systems founder Charles Hull in 1984[5] and Stratasys produced the first extrusion-based 3d printer in 1991.[6] Development of the first selective laser sintering (SLS) machines came a year later and the list of firsts just kept rolling: creation of the first functioning organ (1999), the first RepRap self-replicating machine (2008), first prosthetic leg (2008), first 3d printed blood vessel (2009), first 3d printed car and robotic aircraft and first 3d printing in gold and silver (2011), first 3d prosthetic jaw implant (2012).[7]

While industrial and medical usage and breakthroughs have steadily been advancing the technology, it's the recent promise of widespread consumer acceptance that seems to have catapulted 3d printing to the top of many minds. Service bureaus have started dotting the landscape, and several established industry names have jumped in. Staples, for example, offers 3d printing services in more than 50 locations. Following a successful testing of 3d printing services at six markets, shipping giant UPS expanded their program to over 100 locations by the end of 2014. Most service bureaus will turn your design into a finished product in a few hours and will then either ship the item or, if it was printed at a location near the customer, provide notification for pickup. On the hardware sales side, big box retailers such as Home Depot began putting the $999 Dremel Idea Builder on their store shelves at the end of 2014, while a search for "3d printer" on Amazon now turns up dozens of machines ranging from a few hundred to several thousand dollars.

The software driving 3d printing is generally Standard Tessellation Language (STL), developed by 3d Systems in the 1980s, or some variant. In very simple terms, STL takes a standard CAD (computer aided design) three-dimensional representation and digitally "slices" it into layers. These layer instructions are then sent to the 3d printer, which "prints" the object layer by layer. With recent and rapid advancements in the various 3d technologies and materials, objects with incredibly complex geometries and features can now be printed. 3d printed aircraft parts, candy, toys/games, cars and even houses have proven the scalability and versatility of the technology. At 3dshoes.com a customer can use a phone app to scan their feet, register their scan with the service, select a design and 3d printer filament, and order a custom pair of shoes without ever leaving home. The company offers a variety of colors in three different filament types – thermoplastic elastomer, flexible PLA and thermoplastic polyurethane, each offering a particular advantage for the shoe style and intended use.

On the artistic side of things, American painter and printmaker Frank Stella began experimenting with 3d printing as far back as 1990, and his 2014 "Scarlatti K" and "Circus" series of sculptures incorporate additive manufacturing.[8]

Perhaps signaling the start of the modern 3d printing revolution, Adrian Bowyer started the RepRap (Replicating Rapid Prototyper) project in 2005.[9] RepRap began and continues as an open-source self-replicating 3d printing project to advance additive manufacturing worldwide. A RepRap machine can produce half of its own parts; the other half are easily obtained items. With continued advancements in the field, RepRap open source contributors are expecting to produce a machine capable of creating an even higher percentage of its own parts, including electronic circuitry.

The Technology

Additive manufacturing is "a process by which digital 3d design data is used to build up a component in layers by depositing material," according to ASTM.[10] While industry professionals may draw distinctions, the terms additive manufacturing and 3d printing have come to be generally interchangeable. In consumer-oriented marketing there appears to be a preference for the phrase "3d printing," the implication perhaps being that "printing" is less intimidating and easier to understand and perform for most novice users than "manufacturing."

Additive manufacturing is distinct from most traditional manufacturing operations which are considered subtractive, i.e., removal of material is a key step in arriving at the finished object. The building of an item in layers yields comparatively less waste in additive manufacturing and the process has the potential to dramatically compress existing supply chains and cause a substantial disruption to long-established manufacturing industries. While a few distinct processes are driving 3d printing, it would be short-sighted to say that 3d printing consists of a finite number of technologies. The concept of additive manufacturing in theory provides for the creation *of* just about anything *from* just about anything. It stands to reason that with such limitless potential the field of available devices to accomplish additive manufacturing may grow to include processes or refinements not currently being considered.

The most popular additive manufacturing processes today can generally be categorized as Fused Deposition Modeling/Fused Filament Fabrication (FDM™/FFF), Stereolithography (SLA), Selective Laser Sintering/Direct Laser Metal Sintering (SLS/DLMS), Selective Laser Melting (SLM), Laminated Object Manufacturing (LOM) and 3d Inkjet Printing (3dP).

- SLA – uses a vat of ultraviolet-curable resin. A UV light traces the object pattern in the resin, curing a thin layer in the shape of the desired object. Successive layers are added until the final product is achieved.

- FDM/FFF – a filament supplies material to an extrusion nozzle to produce a part layer by layer. Note that FDM is a trademark claimed by Stratasys; FFF was put forth as a synonym by the open-source RepRap project.
- LOM - layers of adhesive-coated material are glued together and cut to shape with a blade or laser cutter.
- SLS/DMLS - uses a laser to sinter powdered material (metal, ceramic, plastic).
- SLM – similar to SLS/DMLS, the primary difference being the laser is used to fully melt the material.
- 3dP – similar to a standard two-dimensional inkjet printer but uses a curable liquid photopolymer instead of ink.

In a report following its 2013 Additive Manufacturing Workshop, The National Science Foundation provided this summary of several 3d printing technologies, manufacturers and materials:[11]

Type	Process/Technology	Material	Manufacturer	Machine
Vat Photopolymerization	SLA (Stereolithography)	UV curable resins	Asiga	Freeform Pico
			3D Systems	iPro
			3D Systems	Projet6000/7000
			EnvisionTEC	Perfactory
			Rapidshape	S Series
		Waxes	DWS	DigitalWax
		Ceramics	Lithoz	CeraFab 7500
Material Jetting	MJM (Multi-Jet Modeling)	UV curable resins	3D Systems	Projet 3500 HD/ 3510/ 5000/5500
			Stratasys	Objet
		Waxes	Solidscape	3Z
Binder Jetting	3DP (3D Printing)	Composites	3D Systems	Z Printer
		Polymers, Ceramics	Voxeljet	VX Series
		Metals	ExOne	M-Flex
Material Extrusion	FDM (Fused Deposition Modeling)	Thermoplastics	Stratasys	Dimension
				Fortus
				Mojo
				uPrint
			MakerBot	Replicator
			RepRap	RepRap
			Bits from Bytes	3D Touch
			Fabbster	Fabbster Kit
			Delta Micro Factory Corporation	UP
			Beijing Tiertime	Inspire A450
		Waxes	Choc Edge	Choc Creator V1
			Essential Dynamics	Imagine
			Fab@Home	Model
Powder Bed Fusion	SLS (Selective Laser Sintering)	Thermoplastics	EOS	EOS P
			Blueprinter	SHS
			3D Systems	sPro
		Metals	3Geometry	DSM
			Matsuura	Lumex Avance-25
			Phenix	PXL, PXM, PXS
	SLM (Selective Laser Melting)	Metals	EOS	EOSINT M
			SLM Solutions	SLM
			Concept Laser	LaserCusing
			3D Systems	ProX
			Realizer	SLM
			Renishaw	AM250
	EBM (Electron Beam Melting)	Metals	ARCAM	Arcam A2
			Sciaky	DM
Sheet Lamination	LOM (Laminated Object Modeling)	Paper	Mcor Technologies	Matrix 300+
		Metals	Fabrisonic	SonicLayer
		Thermoplastics	Solido	SD300Pro
Directed Energy Deposition	LMD/LENS (Laser Metal Deposition / Laser Engineered Net Shaping)	Metals	OPTOMEC	LENS 450
			POM	DMD
			Irepa Laser	EasyCLAD

3d printers come in a wide variety of shapes and sizes; most are measured by their build area which determines how large an object can be printed. Most consumer units measure several inches along each of the three build axes (length, width, height). Commercial units are usually larger and industrial printers are often sized to meet specific production requirements. Several manufacturers have recently pushed 3d printing to remarkable size capabilities:

- Stratasys claims its Objet 1000 is the largest multi-material 3d printer in the world, with a build area of 1000 x 800 x 500 mm (39.3 x 31.4 x 19.6 in.). The machine uses up to 14 distinct materials with 120 total possible material options.[12]
- Researchers at the Oak Ridge National Laboratory in Tennessee recently printed a replica of the classic Shelby Cobra sports car using their Big Area Additive Manufacturing machine (BAAM).[13]
- The world's largest 3d printer reportedly resides in China, and weighs in at 120 tons with a 12m build area along all three axes. Created to construct houses, the printer reportedly uses fiber reinforced plastic as its primary material.[14]

Industry Analysis

Issuing the company's first ever Hype Cycle for 3d Printing in 2014, Gartner, Inc. analysts estimated that enterprise adoption of 3d printing was 2-5 years away, while mainstream consumer adoption of the technology was still 5-10 years away.[15] "Today, approximately 40 manufacturers sell the 3d printers most commonly used in businesses, and over 200 startups worldwide are developing and selling consumer-oriented 3d printers, priced from just a few hundred dollars," said Pete Basiliere, research vice president at Gartner. "However, even this price is too high for mainstream consumers at this time, despite broad awareness of the technology and considerable media interest."[16]

Still, the race to bring extrusion-based printers to the consumer market is likely to remain a hotly contested one through 2015 as crowdfunded upstarts from 2014 move to deliver on their promises. (Crowdfunding is the process of raising funds from a large number of contributors, often using the Internet.) While price continues to be a strong driver, companies wishing to remain competitive beyond the initial consumer curiosity/hype phase will have to strike a balance between price and functionality. 3d printing analyst Land Grant notes that price is "most often the blunt-edge tool of unskilled entrepreneurs" and "as price goes down so must functionality."[17]

Regardless of any ultimate price/functionality balancing point, if 3d printing will take hold at the consumer level, innovation and funding toward that end might come from the very market that would benefit. Indeed, many upstarts have found early success through crowdfunding endeavors such as Kickstarter, Indiegogo and Microventures. Creators of the FLUX machine, for example, set a $100,000 fundraising goal on Kickstarter to get their design into production. Backers exceeded it the first day, eventually taking the crowdfunding effort over the $1.6 million mark. FLUX engineers tout an open source module format to encourage development community participation. The FDM/FFF unit includes a built-in 3d scanner and optional engraving module. Modules for the FLUX are attached via magnets so no tools are required. Additional components in development include separate extrusion modules for dual materials, ceramics and pastries. The base model FLUX starts at $499 and uses a standard 1.75 mm filament. Production is set for summer 2015.[18]

With over 12,000 backers on Kickstarter, developers of The Micro are well on their way to an expected 2015 first production run as well. The Micro weighs 2.2 lbs and uses 1.75 mm ABS and PLA filaments. Crowdfunding for The Micro topped $1 million the first day on Kickstarter; total funds raised exceed $3.4 million. The Micro is touted as an out of the box 3d printer anybody can use, with an anticipated price point of $199.[19]

Giving a perhaps ironic nod to traditional plastics manufacturing processes, creators of both the FLUX and The Micro said their greatest full-scale production concern is construction of the machine's plastic case. The Micro's Kickstarter page cites an injection molded case as the only real production risk noting, "…when making the specification for the seamless frame of The Micro, we demanded only the best quality surface finish."[20] The FLUX team expressed a similar concern, stating, "for a high quality machine, we require precise parts. Therefore, we decided to produce our parts with injection molding. Injection molding requires large capital expenses, which means that we need to secure a very reliable manufacture partner that will deliver great quality."[21]

Crowdfunding is influencing 3d accessories as well. Structur3d Printing's Discov3ry paste extruder attracted the support of over 500 investors, exceeding its $30k fundraising goal by 400 percent. The Discov3ry is touted as a universal paste extruder, compatible with almost every FDM/FFF 3d Printer on the market and able to deliver anything from polyurethane gaskets and custom orthotic insoles to cake icing.[22]

Grant questions if perhaps the crowdfunding rush for a low-cost home use 3d machine isn't "a suicidal race to the bottom" for 3d printing. He also notes that additive manufacturing could mirror one of the largest social/economic disruptors in US history – the automobile industry – which began as a handful of makers in the 19th century, quickly grew to over 200 players and was back down to less than 10 mainstays, all within a half century.[23]

With over 200 firms now competing in the 3d space, any consolidation that mirrors the auto industry of the 20th century may be close at hand. The feeding frenzy in crowdfunding is drawing a lot of attention to additive manufacturing, and behemoths like Google, GE, Autodesk and HP are stepping in as both users of, and investors in, the technology. GE is looking to introduce 3d printed parts into an aircraft engine by 2016, the same year HP's Multi Fusion Jet™ thermal inkjet is expected to be available.

Strategic private and institutional investment in additive manufacturing is arguably not yet on par with the hype/hope associated with the sector. Investment firm Mooreland Partners noted in a 2014 report that active private investment is "negligible."[24] The firm cites a number of reasons including long lead time for business development and lack of revenue or earnings to meet requirements. Mooreland's Brian Dow notes that "of the eight major investors in 3d printing only one – RRE Ventures – has made more than two investments."[25]

Following a summer 2014 selloff of 3d stocks, Dan Burrows at Investorplace cautioned that even those firms that dominate the space such as 3d Systems, Stratasys and ExOne can't hide the achilles that is common to many industries transitioning from breakout to shakeout. "3d printing companies are (or were) momentum stocks" noted Burrows following double digit losses for those companies. And "the promise of high-growth momentum names is that they will deliver whopping profit growth one day – and will grow into their valuations in the process. Of course by the time that happens the easy money will already have been made…"[26]

Portfolio managers for the 3d Printing and Technology Fund, incepted early in 2014, readily acknowledge the industry's volatility, even with much of the portfolio comprised of ten 3d printing and technology heavyweights - Stratasys, 3dSystems, Organovo, Autodesk, Dassault, Materialise, Hewlett-Packard, General Electric, Arcam and SLM Solutions Group. At the end of 2014 the 3dpfund.com portfolio was roughly equally split between 3d pure-plays (companies with a single product or industry focus) and technology-oriented firms. Fund managers Alan Meckler and John Meckler noted in their Q4 2014 shareholder newsletter that institutional class (minimum investment $100,000) shares closed out the first year off 24 percent.[27]

> *It is important to consider that stock price is not indicative of a company's operating results, but rather is a reflection of market expectations for said company's future performance. Heading into 2014 market expectations for pure-play 3d printing companies were highly inflated. Despite significant revenue growth across the board, 2014 was not a good year for pure-play 3d printing stock performance. In turn, 3d Printing and Technology Fund's performance languished.*[28]

Following the Las Vegas Consumer Electronics Show in January 2015, Bank of America/Merrill Lynch (BA/ML) issued a report on 3d Systems and rated the stock as "underperform," a valuation "predicated on the likely peaking of organic revenue growth and risks associated with the long term margin profile as recurring revenues will take much longer to build up relative to our original expectations." Citing shipment delays in 2014 that hurt revenue, BA/ML analysts said they "remain concerned that margin expectations could prove too high and Street estimates might need to be lowered."[29]

But looking at the big picture, BA/ML's Researched Investment Committee noted in February 2015 that technology remains its "most favored sector" for the year ahead, and investors should focus on eight key themes within the sector including the Internet of Things, wearable technology, cloud computing… and 3d printing.[30]

Even with the bumps of 2014, investment in the sector as a whole is clearly trending upward. From 3d printing's infancy in the late 1980s through 2010 approximately $300 million was raised by 3d firms through public offerings. From 2011 through 2014 that figure skyrocketed to over $4 billion.[31] Additionally, mergers and acquisitions appear to be on the upswing. Brian Dow reports that M&A activity has been accelerating, with 2014 seeing the most activity in the past five years and four out of every five deals closing since 2012 valued at $100 million or more. M&A buying is highest among service bureaus, and Dow notes that it is "highly likely that incumbent companies are making deals that aren't being publicized."[32]

The 3d Disruption Factor - Complement or Replacement?

3d printing is what's commonly referred to as a "disruptive technology." Essentially, any new technology that could adversely impact or displace an existing technology or market could be considered disruptive.

Any technology such as 3d printing that in theory decentralizes manufacturing and puts it within reach of just about every company and consumer in the world could be considered a serious threat to traditional manufacturing. Traditional plastics molding, for example, is a large-scale operation requiring a large physical and carbon footprint, substantial capitalization, and complex supply chain logistics. 3d printing poses a threat to all of that, at least on paper, with the possibility that smaller scale production-on-demand companies and individuals might be able to take on manufacturing themselves. But the economic disruption potential ripples far beyond a manufacturer's physical footprint and employment base. Imagine the possible effects on global transportation networks if large-scale manufacturing suddenly became decentralized. The relatively ordered and predictable march of supplies into an operation, and finished product out of that operation, would be substantially curtailed or eliminated. Large-scale transportation such as shipping, rail and air cargo would suffer economic impacts along with the affected industry.

Of course forecasts about the impact of 3d printing are as varied as the technology itself. Noting what digital technology has done to the newspaper and record store businesses, a GE Look Ahead report said 3d printing "is already disrupting business-as-usual in certain niche industries, prosthetics and medical implants among them, because 3d printing makes customization easier and design processes faster."[33] The report also noted "For standardized items, the cost advantage of additive manufacturing may be less significant since the technology does not yet allow high-volume production, while mass manufacturing decreases the average cost.[34]

McKinsey & Company noted in 2014 that additive manufacturing could have "implications for manufacturing-footprint decisions. While there is still a meaningful labor component to 3-D printed parts, the fact that it is lower than that of conventionally manufactured ones might, for example, tip the balance toward production closer to end customers. Alternatively, companies could find that the fully digital nature of 3-D printing makes it possible to produce complex parts in remote countries with lower input costs for electricity and labor."[35]

No matter the forecasts, many established manufacturers and manufacturing-reliant companies are hardly waiting around to see what happens. GE Chief Economist Marco Annunziata says that by 2020 "over 100,000 parts will be additively manufactured by GE Aviation, which could reduce the weight of a single aircraft by 1,000 pounds, resulting in reduced fuel consumption."[36]

Balancing the Upset

True, the digital revolution has crippled or buried some long established industries. But history has plenty of tales of technologies that put production capabilities in the hands of the masses, without eviscerating long-entrenched industries. Tax preparation software has gotten progressively broader appealing and better over the past two decades, to the point that more than 27 million self-prepared returns had been e-filed by the first week of March 2014 for that tax year, according to the IRS. Still, paid preparers including accountants and tax preparation firms e-filed more than 34 million returns for the same period. Overall, more than 144 million returns were filed that year, with 82 million of them handled by paid preparers representing over 38,000 firms. More than two decades into the self-prepare tax revolution, the paid preparer has adapted with the technology and remained viable.[37]

On a scale less serious than life's certainties (death and taxes), other mammoth industries have done just fine in the face of home-based manufacturing revolutions. The first hand-crank home ice cream freezer was patented by a Philadelphia woman in 1843; personal ice cream makers today are available just about anywhere in hand crank and electric models starting under $30. Yet they're hardly a threat to the $52 billion ice cream industry.[38] Similarly, if Prohibition had stuck perhaps home brewing kits would have upended large scale brewing and distribution. The commercial beer industry today is valued at over $100 billion.[39]

Perhaps the takeaway from history is that just because anybody *can* produce something they want… doesn't mean they *will*. Whether additive manufacturing upends traditional manufacturing on a global scale or simply complements it remains to be seen, but even if such change were to occur it would not happen overnight.

Driven By Plastics

While trade show highlight reels focus on the hardware, industry experts such as Gartner's Pete Basiliere are quick to point out that the key driver to effective, efficient use of additive manufacturing is material selection:

> *Organizations must begin with the end products in mind… determine the material, performance and quality requirements of the finished items first; second determine the best 3d printing technology; and third, select the right 3d printer.*[40]

The material of choice for most consumers, service bureaus and light commercial users, and the primary driver behind today's 3d printing surge is indeed plastic, for several reasons. Many of the early 3d technology patents have expired (most notably Stratasys' primary patent for FDM), leading to an open-source revolution in 3d printing. Numerous mid to large-sized firms have moved to fill the commercial/industrial demand, and a seemingly endless cavalcade of crowdfunded upstarts intent on driving price points down for mass market appeal have entered the industry.

FDM/FFM is also based on a proven, simple and highly adaptable manufacturing concept – extrusion. The extrusion material of choice, plastic, is readily available, comparatively inexpensive, well-established in a variety of extrusion processes and, perhaps most importantly… ubiquitous in everyday consumer life. Plastic parts, items, medical devices and objects are everywhere.

While the 3d printing industry may chart an uncertain track with hardware sales and consumer adoption, most analysts agree support for the overall sector in the form of materials will remain strong for the foreseeable future. Among the forecasts:

- Markets and Markets estimates (2014) the global additive manufacturing materials market will grow at a CAGR of 20.4 percent from 2014 to 2019 to $1.052 billion, with plastics accounting for $672 million of the total in 2019. Europe and Asia-Pacific combined accounted for more than half of the materials market in 2013; while North America was the single dominant geographical player. In a previous report (2013), Markets and Markets estimated the value of plastics revenue in 3d printing at $70.5 million and forecasted this figure will nearly triple by 2018 to $209.6 million. Analysts cited the 3d printing materials market as "moderately fragmented" with companies concentrating "on expanding their geographical reach." 3d Systems, Stratasys, Arcam AB and ExOne accounted for about 75 percent of the materials market share in production and supply.[41]
- Valuing the 3d printing materials market at $450 million in 2013 on global volume of 2,000 kilotons, Transparency Market Research expects a CAGR of 18 percent from 2014 to 2020, with the materials market valued at $1.432 billion by 2020.[42]
- IDTechEx notes that photopolymers dominate 3d printing with 56 percent of the materials market share. Solid thermoplastics comprise 40 percent followed by powdered thermoplastics (2), metal powders (1.4) and inkjet powders (0.6). The firm estimates in its 2015 report that solid thermoplastic filaments will be valued at over $1 billion by 2025, despite an expected decline in prices. Overall the 3d materials market is expected to reach $8 billion in 2025, overtaking the 3d printer market.[43]

Plastic considerations extend beyond basic polymer selection. Numerous material characteristics such as filament diameter/shape, rigidity, flexural modulus, melt point and even color dictate which filaments can be used with which machines. The most common plastics used in 3d printing are Polylactic Acid (PLA) and Acrylonitrile Butadiene Styrene (ABS), and these will likely continue to fuel demand for low-cost consumer oriented machines. Polyvinyl Alcohol (PVA) is used primarily to create support structures for complex geometries in dual-extruding printers. The printed object is submersed in water which dissolves the PLA. Polycarbonate, polyetherimide, polyamides and other plastics are also used in 3d printing though to a much lesser extent than PLA and ABS. Blended plastics such as PC-ABS, composites and digital materials continue gaining popularity on all fronts. Extensive research continues particularly in the medical and electronic fields.

Federal and state entities have waded into the 3d printing space, intent on fostering public-private-institutional collaboration. AmericaMakes, one of the institutes within the National Network for Manufacturing Innovation, was founded in 2012. Maryland created the Northeast Maryland Additive Manufacturing Innovation Authority in conjunction with the U.S. Army's Aberdeen Proving Ground in 2014, and the Center for Additive Manufacturing and Logistics at North Carolina State University is engaged in material development as well as research in the biomedical, automotive, aerospace and supply chain/logistics fields.

The National Science Foundation claims it has issued more than 600 grants amounting to more than $200 million for additive manufacturing research and related activities. NSF notes that "innovation in additive manufacturing has been dominated by the private sector, especially when it comes to the total number of patents and the continual advancement of the technology beyond initial invention. Still, the government, particularly NSF, has played a role in the early development of the AM field…" NSF notes that while the 3d printing industry is enjoying tremendous momentum in recent years, "…substantial challenges must still be overcome before the technology can become mainstream."[44]

> *These challenges include bringing down costs, developing new materials, achieving more consistency and standardization, developing new computeraided design tools, educating engineers, increasing process speeds, and advancing biological AM.*[45]

One of the obstacles already being confronted – with some success - is the effective integration of different materials, particularly on a nano scale. It's a "significant challenge that requires overcoming discrepancies in material properties in addition to ensuring that all the materials are compatible with the 3d printing process," according to researchers at Princeton. The research team recently 3d printed a contact lens with quantum dot LEDs embedded, as well as a cube of encapsulated LEDs. The marriage of micro LED technology with 3d printing was significant not just for the scale of the printed object but for the diverse array of materials involved - emissive semiconducting inorganic nanoparticles, an elastomeric matrix, organic polymers as charge transport layers, solid and liquid metal leads, and a UV-adhesive transparent substrate layer.[46]

Stratasys continues to push development of digital materials for use with its PolyJet technology. PolyJet printers function similar to traditional inkjets, using curable liquid photopolymers for the layer-by-layer 3d build. Digital materials are "composite materials with predetermined visual and mechanical properties" according to the company, and are created in the 3d printer by combining two or more base resins. Stratasys claims that "A single prototype 3d printed on our advanced Connex3 systems can contain as many as 82 distinct material properties, all created in one build."[47]

On the powder side, development of materials for selective laser sintering (SLS) has lagged behind the filament and liquid polymer explosion, likely due to the SLS machine's higher cost and perceived risks associated with a laser device. Germany's Diamond Plastics unveiled a new HDPE powder mid-2014 and a PP powder later the same year. As of early 2015, Quickparts was offering SLS services using nylon, glass-filled nylon, flame-retardant nylon and durable nylon. One of the advantages of a powder-based system is that material can be reused.

Much like the 2D printing space evolved, 3d companies are looking to generate as much proprietary material business as possible. Recognizing the potential market value of 3d printer materials, these firms are conducting their own R&D to develop new formulations and standards for their own machines and technologies. Because many thermoplastics aren't inherently compatible with 3d printing for a variety of reasons (e.g., melt temperature, warping without a mold), the R&D field is fairly wide open for 3d firms wishing to develop their own materials. ABS is one example – while it works well in filament-based extrusion printers, it doesn't fit as neatly with liquid photopolymer-based units. To bring the desired ABS qualities (toughness, heat resistance) to their PolyJet customers, Stratasys creates a "Digital ABS" by combining two materials (RGD15 and RGD35) at the print head.[48]

In early 2015, Stratasys unveiled its expanded line of ASA thermoplastic colors and digital materials. The ASA materials are recommended for specific Stratasys 3d printers including the Fortus 360mc, 380mc, 400mc, 450mc and 900 mc.

Material innovations are extending beyond just the polymers. At the 2015 CES show in Las Vegas, MakerBot announced its new line of PLA composites made with real metal, wood and stone. The filaments will be available in late 2015 and will be compatible with the company's SmartExtruder. In February, 2015 ColorFabb announced a new filament based on Eastman's Amphora 3d polymer. XT-CF20 is reinforced with 20 percent specially sourced carbon fibers. Because the filament is considered highly abrasive, the company recommends discarding brass extrusion nozzles in favor of steel or copper alloys.

The rapid development of proprietary 3d printing materials by the industry's largest firms hasn't gone unnoticed – or unchallenged. IdTechEx has called material development "possibly the most contentious issue in the 3d printing industry today."[49]

> *3d printer manufacturers are increasingly engaging in practices which are perceived by end-users as anti-competitive by locking customers in to their own materials supplies via key-coding and RFID tagging of material cartridges, an activity which is effectively enabling monopoly pricing of the materials concerned.*[50]

Any antitrust implications notwithstanding, providing plastic material to the mass market for 3d printing purposes may in many cases require a different approach than supplying the same or similar material for large scale extrusion molding operations. Even though the 3d printing materials space is in its infancy, service bureaus, 3d printer manufacturers and material suppliers have already recognized the need to convey material property information and relate polymer characteristics to certain desired end-user results. Storage and use of hygroscopic materials like PLA, for example, can become hyper-critical because the production environment may be less controlled. This would be particularly noteworthy when dealing with the consumer market, where novice designers, tinkerers and home manufacturers with little or no experience in polymer selection, use and handling could comprise a significant part of a material supplier's business.

Additional 3d printing material developments of note include:

- Shapeways, an e-based 3d printing service bureau, facilitates the customer interaction via a material selection interface focusing on four categories - Price, Detail Level, Strength and Smoothness. Customers select a low, medium or high value for each category and receive a material recommendation for their project. Shapeways then provides a cost and color choice breakdown for each, as well as material properties and characteristics such as whether it's food or dishwasher safe, watertight, recyclable, etc.
- Looking to break the limited color choice barrier, upstart Spectrom is working on a dye-based system that can impart color to any clear filament. As of early 2015 the Spectrom process can

produce 64 colors, but its developers say that through refinements and beta testing their system could provide thousands of color options.

- Billed as the first carbon fiber 3d printer, the Mark One "prints contours and curves in engineering nylon and fills each part with close-packed reinforcement in continuous carbon fiber, Kevlar or fiberglass. The printer actively switches between two nozzles during a print, creating fiber-reinforced plastic parts with a strength-to-weight ratio better than aluminum," according to a company data sheet.[51]
- In February, 2015 Formfutura launched its ClearScent line of colorless and nearly odorless ABS filaments.
- ProtoCrate offers a filament subscription service, providing customers with a 1kg spool for $49.99 each month.
- With an estimated availability of June, 2015, the Strooder is being touted as "the first truly consumer-ready filament extruder." Omni Dynamics, maker of the Strooder, says the machine "allows you to create your own custom filament for 3d printing at home" and also saves money "as raw pellets are on average five times cheaper than pre made filament. Strooder will also allow you to recycle your old prints for further cost saving as well as benefiting the environment."[52]

Risks and Downsides

Recognizing the untested waters of intellectual property (IP) in the new 3d printing world, toy maker Hasbro teamed up with Shapeways in 2014 with SuperFanArt, a website that gives customers and fans license to create their own expressions of Hasbro offerings such as My Little Pony. It's an interesting proactive partnership that nicely frames the daunting IP question facing 3d printing – how do you regulate the creation and/or sale of copyrighted or trademarked items if anybody can make the items themselves?

Fernando Sosa of Orlando, FL explained to CNN that he routinely prints politically themed objects and offers them for sale online. But when Sosa 3d printed replicas of a dancing shark that was part of Katy Perry's Super Bowl halftime show and offered them for sale - he was promptly served with a cease and desist order from Perry's lawyers.[53]

Moving beyond IP, the clarity of additive manufacturing's potential becomes even cloudier. Traditionally, when something goes awry with a product the consumer's recourse usually is with the supplier or manufacturer. When the consumer makes that product via 3d printing, the potential exists for liability to attach all the way down the production chain, from the designer to the resin maker, filament supplier, 3d printer manufacturer and so on. Even service bureaus could get dragged into lawsuits simply for using their machines to fulfill a customer's 3d print order.

Health and safety concerns also move to the forefront particularly with home-based additive manufacturing. Imagine being able to 3d print a bicycle safety helmet for your child or desserts and other foods. Standards for safety, cleanliness, hygiene, etc. will likely have to be developed in the coming years not just for the products that are produced, but for the processes and materials. For example, the melting or grinding of certain resins in an uncontrolled environment such as the home could lead to health risks.

Conclusions

Additive manufacturing/3d printing has begun to gain incredible momentum in markets around the world. While analysts may disagree on the timing and full impacts of the technology, it appears certain that 3d printing will at the least establish its own niche and complement traditional manufacturing particularly in the plastics sector, creating new opportunities for plastics suppliers, compounders and distributors.

Overall, the 3d printing materials market is expected to rise in support of increasing adoption of additive manufacturing technologies in home and industry. Given the technology's diverse application and expected manufacturing democratization, it's possible that some material sectors could actually serve to pull all or part of the overall 3d printing sector forward at times. Even if the dominant industry players continue to develop and push proprietary materials into the market, the sheer volume of institutional, public and private materials R&D means competition for the next great 3d printing material will likely remain healthy well into the future.

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Flame Retardants for Polymers

New Flame Retardants Deliver Safety Without Risk

Summary/Abstract

When decabrominated diphenyl ether or "decaBDE" is phased out by the end of 2012, the polymers industry could find itself at a crossroads. Mounting pressure from environmental and health agencies will have pushed the industry away from its most effective and economical flame retardant additive. At the same time, an expected surge in consumer plastics production will fuel an increased demand for fire-retardant additives. To meet this demand, plastics producers must quickly develop cost-effective, environmentally safe alternatives to a class of chemicals that has been saving lives for decades.

Background

Flame retardants have been a mainstay in the consumer goods landscape since the industrial revolution. Vinegar, gypsum, asbestos, borax and inorganic salts were among the earliest flame retardant materials in common use by industrialized nations to impart some degree of fire-resistance to products manufactured from wood, canvas and various fabrics.

Shortages of natural materials during World War II provided the impetus for development of numerous plastics including PE and ABS. By the 1950s, polymer research had begun to change the industrial landscape. Early "engineered thermoplastics" including acetal and polycarbonate were introduced. While these polymers began to supplant wood and metal enroute to revolutionizing the durable goods and fledgling consumer appliance/electronics industries, they carried an inherent fire risk – most common polymers are made from hydrocarbons, which tend to burn readily upon ignition.

As new polymers opened new markets and pushed plastics into the mainstream, consumer and government calls to improve fire resistance of plastic goods increased through the 1960s and 70s, leading to the development and widespread use of a variety of flame retardant copolymers and polymer additives. With the personal computer revolution of the 1990s, consumer technology and plastics – and by extension flame retardant additives -- solidified a relationship that would drive global economies into the 21st century.

The Chemistry of Flame Supression

Fire retardants fit into a variety of classifications depending on their chemical composition and use. Inorganic flame retardants such as aluminum trihydrate, magnesium hydroxide and various phosphorous and boron based compounds work well in clothing and textiles. Inorganic flame retardants are added as fillers into the polymer, and they represent about half of the global flame retardant production by volume.[1]

For the polymers industry, the flame retardant (FR) of choice has been an organobromide, selected from a group of halogenated flame retardants known as polybrominated diphenyl ethers (PBDEs). Three specific PBDEs – pentaBDE, octaBDE and decaBDE – dominated the FR additives market because they were inexpensive to produce and easily incorporated into existing production lines. Regardless of their composition, flame retardants all serve the same basic purpose – to inhibit combustion through one or more chemical or physical mechanisms.

Flame retardant properties can accrue to polymers in two basic ways. First, the FR can be chemically bonded to the polymer, resulting in a modified polymer with a different molecular structure than the original. This resulting copolymer is inherently flame retardant and will maintain its FR properties for a significant length of time because the FR compound has formed a molecular bond with the original polymer. Because of the high processing costs, copolymerization is usually reserved for thermosets such as polyesters, epoxies and polyurethanes.

A second, more economical approach is to use a fire retardant *additive*. Additives make up the majority of the flame retardant market due to the relatively low cost of incorporating these chemicals into flame retardant polymers. FR additives work well across a broad spectrum of plastics. Since they do not copolymerize in production, FR additives may leach out over time, compromising the flame retardant properties of the plastic and possibly accumulating to toxic levels in the environment.

In order to function effectively, any flame retardant additive must be as compatible as possible with the original polymer, meaning it should have a minimal impact on key polymer properties such as tensile strength, color and UV stability. PBDEs proved effective in meeting this criterion, with variants such as decaBDE imparting fire retardant qualities at very low addition rates. In a polyolefin or polyamide product, for example, the amount of PBDE needed is one-half to two-thirds less than the amount of inorganic (e.g., aluminum trihydrate, antimony) needed to achieve the same FR properties.[2]

Additive flame retardants can be incorporated into the polymer prior to, during, or after polymerization, so they are especially practical for use in thermoplastics.

The FR Hyper-Demand Driver – Personal Electronics

One of today's key drivers in fire-retardant plastics is the consumer technology segment. Even in countries experiencing stagnant growth or recession, the demand for televisions, smartphones, personal computers and tablets is expected to be strong in 2012.[3] By 2015, shipments of media tablets are expected to rise to 262.1 million units, a 15-fold increase over 2010. Smartphone shipments are expected to skyrocket from 294 million in 2010 to over one billion in 2015.[4]

With a rising global demand for plastics in general and forecasts for a particularly robust consumer electronics market, the worldwide demand for flame retardant additives is expected to reach 2220 metric tons in 2014, up 45 percent from 2010. The Asia/Pacific region alone will account for half of the global total by doubling its FR demand over the same time period, from 547 to 1090 metric tons.[5]

Deca-BDE in the Environment: Guilt by Dissociation?

Signed by nearly 150 scientists representing two dozen countries around the world, the San Antonio Statement of October 2010 is "a call for attention to a continuing pattern of unfortunate substitution," according to its authors in an accompanying editorial.[6,7] The editorial specifically cites the use of a succession of PBDE congeners following a ban on chemically-similar PBBs (polybrominated biphenyls) in the early 1970s.

> *After PBBs were restricted, the use of poly-brominated diphenyl ethers (PBDEs) as flame retardants in consumer products increased dramatically over the next several decades. PBDEs are structurally similar to both PCBs and PBBs and have the potential for similar behavior. However, in 2004 two commercial mixtures -- PentaBDE and OctaBDE (the name reflecting the average number of bromines present) -- were banned in the European Union (Cox and Efthymiou 2003) and voluntarily withdrawn from production by the sole U.S. manufacturer (Great Lakes Chemical 2009). PBDEs contained in these two mixtures were subsequently adopted as persistent organic pollutants (POPs) by the Stockholm Convention (Stockholm Convention Secretariat 2010). The cause for concern is now well recognized. However, the resistance to degradation continues to result in high concentrations of PBDEs in the environment, wildlife, and people (de Wit et al. 2006; Frederiksen et al. 2009; Su et al. 2007).*

In recent years, scientists have measured PBDEs in human adipose tissue, serum and breast milk, fish, birds, marine mammals, sediments, sludge, house dust, indoor and outdoor air, and supermarket foods.[8] In general, levels of PBDEs in humans and the environment are higher in North America than in other regions of the world, a finding that is often attributed to the greater use of pentaBDE in North America. About 49 million pounds of decaBDE, or nearly half the world's production, was added to consumer products in North America in 2001. DecaBDE can comprise 10 to 15 percent of the plastic casing of a television and 18 to 27 percent of upholstery fabrics by weight.[9]

While decaBDE has not been found in the same concentrations as the penta and octa congeners, scientists attribute this inequity to debromination – the loss of bromine atoms which effectively turns decaBDE into a lesser congener such as octa or pentaBDE. Research suggests that the lower congeners of PBDE tend to bioaccumulate more readily than higher congeners like decaBDE.[10]

Although the environmental pathways of PBDEs are not entirely known, they're likely to include manufacturing of PBDE chemicals and products containing those chemicals, particularly plastics and textiles. Additionally, exposure may occur during disposal, dismantling, and recycling of plastic products, including computer equipment, via inhalation of dust and ingestion while eating, drinking or smoking.[11]

Environmental groups and government agencies continued to monitor PBDEs following the elimination of the penta and octaBDE congeners. In its 2006 PBDE Project Plan, EPA summarized animal studies of various commercial mixtures and individual congeners which suggested potential concerns about liver toxicity, thyroid toxicity, developmental toxicity, and developmental neurotoxicity.[12] These findings, and the presence of PBDEs in house dust and breast milk, raise particular concerns about potential risks to children. In 2008, EPA published peer reviewed Toxicological Reviews of four PBDE congeners: tetraBDE, pentaBDE, hexaBDE and decaBDE, to support summary information on EPA's Integrated Risk Information System (IRIS)3 database.

In 2009, the Institute for Reference Materials and Measurements (IRMM) released two certified reference materials, ERM-EC590 and ERM-EC591, to help analytical laboratories better detect PBDEs and PBBs. The two reference materials were custom made to contain all relevant PBDEs and PBBs at levels close to the legal limit set out in the RoHS Directive of 1 g/kg for the sum of PBBs and PBDEs.

By the end of 2009, the U.S. EPA had seen enough. Voluntary phase-out agreements were secured with the two primary decaBDE manufacturers in North America – Chemtura and Albermarle, as well as ICL Industrial Products, the largest U.S. importer of decaBDE. Under these agreements, decaBDE will no longer be produced for consumer product use after 2012.

DecaBDE Alternatives: Already in Production

In January 2011 the EPA’s Flame Retardant Alternatives for DecaBDE Partnership released a list of more than two dozen Alternative Flame Retardants. But chemical manufacturers, including some steeped in decades of PBDE production, were well into their own decaBDE alternatives research by the time the EPA released its list.

Plastics Color Corporation says it has developed flame retardant systems for polypropylene and polyethylene and will soon introduce FRs for acrylic, polystyrene, PVC and other resins. PCC, based in Calumet City, Ill., says its new FlamaSol FR™ flame retardant system yields superb extinguishing performance without the use of decaBDE.

> *FlamaSol FR is ideal for use in construction materials (electrical conduit, junction boxes, switch boxes), warehousing products (shelving and pallets), personal electronic equipment (computers, printers and televisions) and other applications where flammability or ignition is a concern. FlamaSol FR surpasses in-house testing standards comparable to UL 94 and ANSI 4996 for plastic pallets.*
>
> *FlamaSol FR is appropriate for use in injection molding, extrusion and blow molding applications.*[12]

Conclusion

The phase-out of decaBDE in 2012 will signify a sea change in production of flame retardant additives. With the stalwart PBDEs that carried FR polymer production through four decades now off the table, the next generation of FR additives will have to prove themselves as quickly and cleanly as possible. Polymer producers and modifiers in developed nations have joined with the scientific community and regulatory agencies in recognizing that PBDEs as a group might lead to environmental and health concerns. With today's R&D capabilities, polymer scientists are developing FR additives that were not possible with 20th century technology. An industry-wide shift away from PBDEs altogether can help assure that a growing global demand for flame-retardant plastics is met in the most environmentally and biologically responsible manner possible.

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Antimicrobial Plastics
Reducing Infections and Protecting Products

Abstract

This paper examines the development and application of antimicrobial plastic resins as a response to public, private and institutional demands for plastic products and product components that inhibit microbial growth. In the U.S. alone, 1.8 million hospital-associated infections lead to 99,000 deaths each year, killing more people annually than aids, breast cancer and automobile accidents combined. While medical research continues to target constantly-evolving microbes including so called "super bugs," advances in resin-compatible antimicrobial additive technology have drawn the plastics industry into the germ battle on several fronts. Plastic products with enduring antimicrobial properties include medical devices and equipment, food preparation surfaces, household appliances, automobile interior parts, computers, phones and other personal electronic devices, sports equipment, construction supplies and other contact surfaces. Typical antimicrobial resin formulations include silane, N-butyl-1, 2-benzisothiazolin-3-one, copper, zinc and silver. Incorporation of these proven antimicrobials into a variety of plastic resins is generally performed to achieve either biostabilization (preservation) of the plastic article or to impart active biocidal properties to the plastic article. While there may be some overlap in these two primary purposes, producers, compounders and product manufacturers must distinguish their antimicrobial intent carefully to ensure proper product classification under, and compliance with, the appropriate regulatory framework.

Background

Microbes have been around since our earth took her first breath. The oldest known fossilized microbes date back 3.5 billion years. So resilient are these tiny single-celled organisms (millions of them could fit in the eye of a needle) that scientists claim to have successfully "revived" a dormant bacteria estimated to be 250 million years old.[1] Microbes include bacteria, fungi, protista, viruses and archaea (which until recently were thought to be bacteria). Because of their high-profile and seemingly constant influence on human life and health, bacteria and viruses are perhaps the most well-known categories of microbes.

Most bacteria living in and on humans are harmless; some are actually beneficial such as those that reside in the intestinal tract and aid in digestion. The fermentation mechanism of certain microbes was harnessed by humans for creating such things as bread, wine, beer, yogurt and cheese long before those organisms were first observed via microscope in the 17th century. Prior to that time food spoilage had also been a mystery and was attributed to a widely held belief that life somehow arose from non-living things in a process dubbed "spontaneous generation." The work of several scientists, culminating with Pasteur in the 19th century, put to rest the spontaneous generation theory and gave rise to scientifically-supported germ theory as the reason for food spoilage, infection, etc.[2]

There are an estimated 10 trillion to 100 trillion cells in and on the average person, with microbes outnumbering "human cells" by 10 to 1. So great is the number of microbes - scientists estimate the number of bacteria alone at 5 nonillion or 5,000,000,000,000,000,000,000,000,000,000 – that the mass of all microbes combined would exceed that of all animals on earth. With as many as 10 million different species of bacteria, it's noteworthy that the same handful (e.g., E. coli, S. aureus or "staph") are able to grab human headlines year after year – and not in a good way.[3]

For a humorous yet nonetheless scientific glimpse into microbial life on humans, researchers conducted the Belly Button Biodiversity study in 2012. Swabbing the navels of some 500 volunteers, they discovered over 2,300 distinct microbes living in the average belly button.[4]

Microbes have also been employed to speed decomposition of waste matter. Researchers at North Carolina State University recently isolated one species of anaerobic bacteria they believe is responsible for production of methane gas in landfills.[5] So-called biodegradable plastics rely on microbes as well, and the task of digesting plastic can be specialized. One study showed that several strains of a pseudomonas bacteria have a particular appetite for polyethylene terephthalate (PET) plastic commonly used to produce drink bottles.[6] While the benefits of these "good" microorganisms make them a welcome addition to human life, it's a microbe's pathogenic role in human health that garners the most attention from scientists and researchers in all parts of the world. And rightly so. The Spanish Flu in 1918 is credited with killing over 20 million people.[7] Other bacterial and viral pandemics and epidemics such as the plague/black death of the 14th century remain etched in human history hundreds of years after they occurred. Ebola, HIV, Swine Flu, Avian Flu, cholera, tuberculosis, smallpox, gonorrhea, meningitis, ear infections and the common cold all result from the proliferation of bad microbes in or on the human body.

While advances in microscope technology beginning in the 17th century started bringing these pathogens to light, it would take several hundred more years of research before the scientific community would be able to combat microscopic health threats on a large scale.

Fighting microbes with microbes

During the second half of the 19th century microorganisms were discovered to be responsible for many of the infectious diseases that had been plaguing humanity for centuries. Scientists began to formulate treatments for these diseases based on destruction of these organisms. The first antimicrobial agent used to treat disease was Salvarsan, a remedy for syphilis created in 1910. This was followed by the class of drugs known as sulfonamides in 1935.[8] However, these drugs were synthetic compounds, with limitations in safety and efficacy. Penicillin, a natural compound produced by Penicillium mold, had the safety and efficacy that synthetic antimicrobial agents lacked. It was discovered in 1928 by Alexander Fleming and came into clinical use in the 1940s. Penicillin was used to save the lives of many wounded soldiers during World War II.[9] During the next twenty years, new classes of antimicrobial agents were developed one after another, many from natural sources such as soil bacteria. Some of these bacteria-fighting "antibiotics" included streptomycin, chloramphenicol, tetracycline, macrolide, and glycopeptide (e.g., vancomycin).[10]

As new and more powerful antibiotics were developed through the mid-20th century, it may have seemed for a time that eradication of most if not all bacteria-caused diseases was close at hand.

But pathogens don't survive hundreds of millions of years without the ability to adapt. Many bacteria have quickly evolved in response to antibiotics, developing resistance to even the most powerful drugs. One of the most well-known examples is Methicillin-Resistant Staphylococcus Aureus (MRSA). Most MRSA infections occur in people who have been in hospitals or other health care settings, such as nursing homes and dialysis centers.[11]

While MRSA has been among the most feared bacterial adaptations to antibiotic therapy, the CDC is now warning of an even more lethal threat. A strain of enterobacteriaceae has evolved with resistance to carbapenem, a so-called "last resort" antibiotic. The Carbapenem Resistant Enterobacteriaceae (CRE) bacteria kill half of patients who become infected. **"**In addition to spreading among patients, often on the hands of health care personnel, CRE bacteria can transfer their resistance to other bacteria within their family," according to the Centers for Disease Control. The CDC adds that this type of spread can create additional life-threatening infections for patients in hospitals and potentially for otherwise healthy people. Currently, almost all CRE infections occur in people receiving significant medical care in hospitals, long-term acute care facilities, or nursing homes. "CRE are nightmare bacteria. Our strongest antibiotics don't work and patients are left with potentially untreatable infections," said CDC Director Tom Frieden, M.D., M.P.H. "Doctors, hospital leaders, and public health, must work together now to implement CDC's 'detect and protect' strategy and stop these infections from spreading."[12]

MRSA, CRE and other so-called super bugs seem to thrive in hospital and long term care environments. Approximately 1.7 million healthcare-associated infections (HAIs) were estimated to have occured in 2002, with nearly 6 percent of these infections resulting in the death of the patient. These infections are not limited to the most vulnerable patients. While approximately 500,000 were in newborns, children, and adults in ICU settings, the other 1.2 million infections were in patients in non-ICU areas of the hospital.[13]

Although they may be the site of most super bug infections, the spread of pathogens is hardly limited to health care settings. A recent University of Arizona study demonstrated how illness spreads in an office environment when researchers took a group of 80 office workers and placed water droplets on the hands of all but one of them. One person received droplets containing artificial viruses that mimicked cold, flu and stomach bug. When researchers sampled commonly touched surfaces in the office, as well as the hands of all 80 volunteers, roughly half of the tested surfaces and participants were contaminated with at least one of the viruses. This translated to a 40-90 percent chance of infection with one of the three viruses by the end of one eight-hour work day.[14]

While health care settings are certainly the frontline for major infection battles, the Arizona study and others like it point to an opportunity to skirmish with pathogens at home and in the office as well. Although many pathogens are transferred from host to host via air and direct personal contact, the prevalence of microbes on common surfaces and the ease with which these microbes appear to be transferred from person to person on contact indicate a possible need to address microbial activity on a much broader scale.

Antimicrobials in Plastics

Antimicrobials are added to plastics for two primary purposes – as an active biocide to kill germs and as a biostabilizer/preservative for the plastic. The main difference lies in the antimicrobial activity profile.[15] Plastics with active biocides are often formulated for use in implantable medical devices and items with known high infection potential such as catheters.[16] But with the spread of pathogens tied more closely to regular contact with contaminated surfaces on common items such as desks, tables, keyboards, towel dispensers and trays, biostabilized plastics are becoming more prominent not only in medical settings but in home, industrial and office applications as well.

Frost & Sullivan predict that by 2015 the global antibacterial plastic industrial applications market will reach 1.4 billion pounds.[17] Global antimicrobial coatings demand was worth $1.6 billion in 2012 and is estimated to reach $3.3 billion in 2018, expanding at a compound annual growth rate of over 12 percent from 2012 to 2018, according to a report from Transparency Market Research.[18] The U.S. is reportedly the global leader in antimicrobial coatings and dominates the demand for these products.

Why plastics?

The sheer ubiquity of plastics in modern society makes them a logical candidate for antimicrobial use. It would be difficult in a developed nation to go through an average day without contacting a plastic surface in your car, home, work or virtually any other public or private setting. To the extent that contact with plastic is practically unavoidable, efforts to minimize the spread of pathogens via that contact are clearly worthwhile.

Imparting antimicrobial properties to plastics also serves to protect the product against the ravages of microbial action. The ability of a microbe to degrade a plastic depends not just on the type of microbe but on the type of plastic. In some cases, microbes that might normally find a plastic inhospitable could readily colonize on the surface because of additives. For example, plasticizers, fillers and lubricants tend to make PVC susceptible to fungal attack, while some polyurethanes, particularly those that are ester-based (e.g., dioctyl phthalate and dioctyl acetate), are inherently vulnerable even before compounding/processing.[19]

The risk of microbial degradation is substantial in common household plastic items, particularly those that are prone to moist conditions. Building products are also prime targets for microbial degradation.

Microbes that degrade plastic (including Aureobasidium pullulans, Aspergillus paecilomyces, Penicillium, and Verticillium*)* are capable of utilizing one or more ingredients in the plastic as their sole carbon source, and, to a smaller extent, a source of nitrogen. The most common plastic ingredients that can be used as a carbon source are epoxidized oil (a plasticizer-stabilizer) and calcium-zinc stearate. A common source of nitrogen is stearamide. Utilization of these components by microbes can result in brittleness, discoloration, and loss of mass in the plastic "host."[20]

While some microbes are able to eat plastic by colonizing on the surface, others can insert fibrils into the material in order to access nutrients. In these cases, they can mechanically destabilize the plastic and add another component to the degradation. Extensive microbial activity on plastics can result in a breakdown of critical physical/mechanical properties resulting in brittleness, dimensional changes, increase in gas permeability and loss of structural integrity. Other common adverse effects include staining, odor and changes in electrical properties such as resistance due to colonization on plastic wire insulation coatings.[21]

In addition to the obvious consumer goods impact, the degradation of plastic items via antimicrobial action has cultural significance as well. In *Microorganisms Attack Synthetic Polymers in Items Representing Our Cultural Heritage*, Francesca Cappitelli and Claudia Sorlini note that "As museums keep acquiring objects that reflect both everyday life and technological and historical events, the proportion of plastics in museums is increasing dramatically."[22] Additionally, the authors explain that synthetic polymers (e.g., adhesives, consolidants, protective coatings) are often employed to preserve many artifacts from further deterioration. Ironically, the polymers used for preservation are themselves prone to several forms of bio-deterioration including:

- biological coating masking surface properties
- increased leaching of additives and monomers that are used as nutrients
- production of metabolites (e.g., acids)
- enzymatic attack
- physical penetration and disruption
- water accumulation
- excretion of pigments[23]

Barbie dolls, toys and numerous other scientific and pop culture items found in museums are made from PVC which is highly susceptible to fungi that consume plasticizers found on the surface of the object. PVC products are also susceptible to a loss of plasticizers from bacteria such as Pseudomonas aeruginosa. Polyurethane materials suffer enzymatic degradation at the hands of fungi such as Chaetomium globosum and bacteria such as Bacillus subtilis, while nylons can suffer physical damage from wood-degrading fungi such as Bjerkandera adusta and bacteria such as Bacillus pallidus. Even space technology isn't immune from microbial attack on earth. At the National Air and Space Museum in Washington, DC, fungi belonging to the genera *Paecilomyces* and *Cladosporium* have been cultured from two synthetic polymers in Apollo-era space suits. [24]

Microbial action on plastic items increases the risk of damage not just to the item itself, but to any information the plastic item might contain or encase. "Plastics have allowed novel ways of recording information; audiotapes, computer diskettes, and compact discs are now commonly stored in archives and libraries," explain Cappitelli and Sorlini. "Also, photographic materials, binders, and supports can be made of plastics. Plastic audiovisual material, including compact discs, can be subject to biodeterioration. Initial fungal colonization of plastics in audiovisual materials generally means failure because of interruption of the signal." [25]

Regardless of the object/product or type of plastic, the onset of degradation by one type of microbial can yield smaller organic compounds that invite additional microbes to join and accelerate the rate and type of bio-deterioration and compromise multiple characteristics of the plastic and ultimately shortening the product life. In addition to microbes that can break down plastics and use certain components as food sources, secondary microbial colonies may form well after the initial colony has formed. These secondary colonies are not able to break down the plastic themselves, but are able to utilize the components after they have been broken down, which can accelerate the rate of deterioration.[26]

Resistance in numbers

Microbes have four basic needs for survival: moisture, suitable temperature, a food source and a suitable surface for growth and replication.[27] Because of their composition and exposure to moisture, many plastic products provide an ideal surface for the formation of complex microbial colonies called *biofilms*. A biofilm is "a complex aggregation of microorganisms growing on a solid substrate. Biofilms are characterized by structural heterogeneity, genetic diversity, complex community interactions, and an extracellular matrix of polymeric substances."[28]

Biofilms are common in nature, as bacteria commonly have mechanisms by which they can adhere to surfaces and to each other. Dental plaque is a common biofilm. Bionewsonline explains that in industrial environments, "biofilms can develop on the interiors of pipes and lead to clogs and corrosion. In medicine, biofilms spreading along implanted tubes or wires can lead to pernicious infections in patients."

> *Biofilms can also be harnessed for constructive purposes. For example, many sewage treatment plants include a treatment stage in which waste water passes over biofilms grown on filters, which extract and digest harmful organic compounds. Bacteria living in a biofilm can have significantly different properties from free-floating bacteria, as the dense and protected environment of the film allows them to cooperate and interact in various ways. One benefit of this environment is increased resistance to detergents and antibiotics, as the dense extracellular matrix and the outer layer of cells protect the interior of the community.* [29]

Biofilms are not only resistant to many antimicrobial agents and disinfectants, they can acquire enhanced resistance through the transfer of resistance plasmids. Such resistance could be especially acute in the health-care environment for patients with urinary catheters and collection bags. Many of the enteric organisms shown to colonize urinary catheters carry plasmids encoding resistance to multiple antimicrobial agents. Resistant organisms such as MRSA have also been shown to form biofilms. [30]

Even with increased awareness about the dangers of contaminated surfaces, and the widespread availability of antimicrobial agents (e.g., disinfectants) within the home and health care settings, pathogens continue to flourish. "Many disinfectants contain nonvolatile antimicrobial agents such as quaternary ammonium compounds (QACs) that can leave an antimicrobial residue on treated surfaces," according to Dorjnamjin, Ariunaa, and Shim in the *International Journal of Molecular Science*. "The potential of these agents to prevent bacterial colonization is limited because of their lack of persistence on surfaces after some environmental insult, such as water contact or rubbing. These moist environments and physically contacted surfaces are the most likely to be contaminated, to allow bacterial proliferation, and to act as a pathogenic reservoir."

The authors conclude that "For a given disinfectant technology to realize a significant residual antimicrobial benefit, it must persist under such conditions."[31]

Antimicrobial plastics – fighting on all fronts

Pharmaceutical approaches to pathogen control (e.g., antibiotics) have succeeded to some degree. But the ability of microbes to mutate and re-emerge even stronger is a clear indicator that drugs alone will not control the spread of pathogens. Topical measures such as disinfectants may help in the battle but are of little use against particularly stubborn free-floating pathogens and entrenched biofilms. However, the proliferation of plastic items in virtually all settings subject to human contact provides an opportunity to address all of these concerns by engaging microbes proactively on the surfaces where they colonize and are spread via contact. Using select antimicrobial formulations matched to appropriate resins, the plastics industry is producing a wide variety of antimicrobial polymers for use in medical, industrial, commercial, marine and home applications.

Among the most common antimicrobial agents incorporated into plastics are quaternary ammonia compounds (QACs), silanes and metals including silver and zinc. While a much broader scale of antimicrobial additives may be available, plastics manufacturers and compounders must be careful in their selections to ensure that any additives/masterbatches are resin-compatible and able to maintain their antimicrobial efficacy through every stage of the manufacturing process. To be effective, antimicrobial agents in general must have broad spectrum antimicrobial activity (equally effective against a wide variety of bacteria, fungi, and algae), pose little risk to the product or to the people applying the product, must easily fit current production systems, must be environmentally friendly, and must be compliant with all relevant biocidal regulations.[32]

Generally, antimicrobial additives can be classified as either leaching or non-leaching depending on their mechanism of action. Leaching antimicrobial agents are defined as agents that must come off the treated substrate in order to exert the antimicrobial properties. Any antimicrobial agent that must enter the cell to work is considered a leaching agent. Non-leaching agents are fixed to the treated surface (usually by covalent bonds) and subsequently do not need to leave this surface to provide antimicrobial action. As these agents are physically attached, there is generally no means for removal and therefore no means to diminish the overall strength.

Use of antimicrobial additives has been expanding rapidly into polyolefins, TPEs, nylons, and acrylics in consumer, industrial and healthcare applications.[33]

Mechanisms of action

Silane-based QACs or "Si-Quats" act as antimicrobials by disrupting the ionic charge of the cell wall in these single-celled organisms. The Si-Quat polymer consists of a long uncharged carbon chain interspersed with positively charged ammonium moieties. The charge differential of the treated surface interferes with the integrity of the cell wall or cellular membrane, resulting in the rupture of and death of the microorganism. These agents also prevent the formation of biofilms through the same mechanisms. In addition, the hydrophobic properties of the polymerized carbon chain interfere with the adhesion of microorganisms to the substrate surface.[34]

Zinc pyrithione (also known as Zinc Omadine® or Zinc 2-pyridinethiol-1-oxide) is used to preserve a wide variety of food/drinking water contact, and non-food contact articles, and is the active ingredient in many anti-dandruff shampoos. It kills microbes by interfering with the microbe's proton pump activity. Proton pumps are used by the cell to open pores in the cell wall, allowing the transport of nutrients into the cell and waste products out of the cell. Without this capability, the microbe is unable to grow or thrive and dies as a result.[35]

Zinc pyrithione is incorporated into various polymers and plastics as a liquid, powder, or aqueous dispersion during the manufacturing process of these materials, and during the manufacture of finished articles from these materials. Zinc pyrithione is added usually by metering pump if it is a liquid, and by open pouring if it is the powder form. It is added at a point where thorough mixing will take place.[36]

The antimicrobial mechanism of action for Isothiozolanones such as 10,10'-Oxybisphenoxarsine (OBPA) and 4,5-dichloro-2-n-octyl-4-isothiazoline-3-one (DCOIT) is enzyme inhibition. Enzymes regulating cellular respiration, energy production, and cellular growth are destroyed. Protein destruction, and the subsequent production of free radicals, is the actual cause of cell death.[37]

A silver lining?

Silver has long been employed as an antimicrobial, although its specific mechanism of action was unknown throughout centuries of usage. Hippocrates referenced the use of silver in wound care. At the beginning of the twentieth century surgeons used silver sutures to reduce the risk of infection and physicians used silver-containing eye drops to treat ophthalmic problems, various infections, and sometimes internally for diseases such as epilepsy, gonorrhea, and the common cold. During World War I, soldiers used silver leaf to treat infected wounds. With the development of modern antibiotics in the 1940s, the use of silver as an antimicrobial agent diminished.[38]

Silver and most silver compounds have an oligodynamic effect and are toxic for bacteria, algae, and fungi in vitro. The oligodynamic effect is typical for heavy metals such as silver, lead and mercury, but silver is considered the least toxic for humans. The antibacterial action of silver is enhanced by the presence of an electric field. Applying an electric current across silver electrodes enhances antibiotic action at the anode, likely due to the release of silver into the bacterial culture. The antibacterial action of electrodes coated with silver improves in the presence of an electric field.[39]

Silver has multiple mechanisms of action that lead to the death and destruction of microbial cells. Silver reacts with the cell wall of microbes to inhibit essential functions of the cell wall, including cellular respiration and nutrient uptake. Silver can also interfere with the structural integrity of the cell wall/cellular membrane, leading to proton leakage, cytoplasmic leakage, or complete rupture of the cell wall all resulting in cell death. Silver ions can also interfere with enzymatic functions within the cell. The enzymes affected are responsible for a wide range of intracellular activities, such as the breakdown of nutrients, production of proteins, and DNA replication. These effects are secondary, however, as the effects on the cellular membrane are the primary mechanism of antimicrobial action.[40]

In 2012 researchers at Rice University were able to isolate silver ions from nanoparticles and demonstrate the mechanism of antimicrobial action. They discovered that the silver nanoparticles themselves were ineffective in killing microbes. It was only upon oxidation – when the nanoparticles released silver ions – that bacteria were effectively killed. The experiment in an anaerobic environment demonstrated that silver ions were 7,665 times more toxic to bacteria than the nanoparticles. "These findings suggest that the antibacterial application of silver nanoparticles could be enhanced and environmental impacts could be mitigated by modulating the ion release rate, for example, through responsive polymer coatings," researcher Zongming Xiu said.[41]

Antimicrobial regulation in the U.S.

According to the U.S. Environmental Protection Agency (EPA), approximately one billion dollars each year are spent on a variety of antimicrobial products, and more than 5000 antimicrobial products are currently registered with the EPA and sold in the marketplace. Nearly 60 percent of antimicrobial products are registered to control infectious microorganisms in hospitals and other health care environments. Because antimicrobials are considered pesticides, regulation of antimicrobial plastic additives in the U.S. is generally the domain of EPA under the Federal Insecticide, Fungicide and Rodenticide Act (FIFRA). If certain dental uses are claimed, or if the plastic or product containing the plastic is intended for use on or in humans or animals, it could be classified as a drug and regulated by the Food and Drug Administration (FDA).[42]

Though rare, there are some antimicrobial additives for which the proposed use makes them both a food additive and drug (e.g., a no-rinse hand sanitizer used by food handlers). In this case, the product may have to comply with the requirements of FIFRA applicable to both food additives and drug products.[43]

According to the EPA, antimicrobial pesticides have two major uses:

1. disinfect, sanitize, reduce, or mitigate growth or development of microbiological organisms;
2. protect inanimate objects, industrial processes or systems, surfaces, water, or other chemical substances from contamination, fouling, or deterioration caused by bacteria, viruses, fungi, protozoa, algae, or slime.

The EPA regulatory framework also considers antimicrobial articles/products as belonging to one of two categories – public health products and non-public health products. Public health products are intended to control microorganisms infectious to humans in any inanimate environment. Non-public health products are used to control growth of algae, odor-causing bacteria, bacteria which cause spoilage, deterioration or fouling of materials and microorganisms infectious only to animals.[44]

Because antimicrobials can't discern whether their purpose is to preserve an article or protect human health, EPA provided a carve-out known as the Treated Articles Exemption. Under the TAE, articles (products) that employ broad spectrum antimicrobials as a biostabilizer/preservative can be exempt from EPA registration as long as no claims are made regarding the ability of the article to provide a human health benefit. To qualify for the exemption, treated articles must display appropriate clarifying statements. If an article claims to be effective in controlling specific microorganisms (e.g., E. coli, S. aureus, Salmonella) it must be registered as a pesticide because EPA considers this a public health claim that goes beyond the preservation of the treated article itself. In these cases EPA requires chemical data supporting the claims. Upon review, EPA could still determine that the product is exempt from registration as a pesticide and limit the manufacturer to claiming only that the product contains a pesticidal preservative to protect the product itself.

Any pesticide-treated product that is not registered by EPA must not make public health claims, such as *fights germs, provides antibacterial protection,* or *controls fungus*. EPA's policy is predicated on the fact that no scientific evidence exists that these products prevent the spread of germs and harmful microorganisms in humans. [45]

Penalties for making unsubstantiated claims can be severe. In 2010 the EPA levied the following penalties, among others:

- VF Outdoor (parent company of The North Face), $207,500 for unsubstantiated antimicrobial claims related to shoe products
- Califone International, $220,000 for unproven antimicrobial claims related to headphones
- Component Hardware Group and John S. Dull Associates, $98,000 for unsubstantiated antimicrobial claims related to certain plumbing and electrical products[46]

The EPA provides the following classification guidance for some of the more commonly used public health antimicrobial products:

- *Sterilizers (Sporicides):* Used to destroy or eliminate all forms of microbial life including fungi, viruses, and all forms of bacteria and their spores. Spores are considered to be the most difficult form of microorganism to destroy. Therefore, EPA considers the term Sporicide to be synonymous with "Sterilizer." Sterilization is critical to infection control and is widely used in hospitals on medical and surgical, instruments and equipment. Types of sterilizers include autoclaving, ovens, low temperature gas (ethylene oxide), and liquid chemical sterilants which are used for delicate instruments which cannot withstand high temperature and gases.
- *Disinfectants:* Used on hard inanimate surfaces and objects to destroy or irreversibly inactivate infectious fungi and bacteria but not necessarily their spores. Disinfectant products are divided into two major types: hospital and general use. Hospital type disinfectants are used on medical and dental instruments, floors, walls and bed linens. General disinfectants are used in households, swimming pools, and water purifiers.
- *Sanitizers:* Used to reduce, but not necessarily eliminate, microorganisms from the inanimate environment to levels considered safe as determined by public health codes or regulations. Sanitizers include food contact rinses for dishes, cooking utensils and food processing plants as well as non-food contact products such as carpet sanitizers, air sanitizers, laundry additives, and in-tank toilet bowl sanitizers.

  - *Antiseptics and Germicides:* Used to prevent infection and decay by inhibiting the growth of microorganisms. Because these products are used in or on living humans or animals, they are considered drugs and are thus approved and regulated by the Food and Drug Administration (FDA).
  -
- When EPA registers a disinfectant product for use in a hospital or other public health setting, the product effectiveness must be demonstrated against a target organism concentration that significantly exceeds concentrations typically found on surfaces in hospitals or other public health settings. For example, a product's effectiveness against Pseudomonas aeruginosa is demonstrated against a minimum concentration of a million microorganisms. This level is 1,000 to 10,000 times higher than the contamination level that is typically found on surfaces in healthcare facilities. This rigor in the Agency's registration requirements provides an added margin of effectiveness for real world use of disinfectant products. Nevertheless, EPA cautions that antimicrobial products alone are never relied on to control infectious processes in health care settings.[47]

Food contact surfaces and the EPA/FDA tug of war

The Food Quality Protection Act of 1996 (FQPA) amended FIFRA as well as the Federal Food, Drug and Cosmetic Act (FFDCA), changing the definitions of "food additive" and "pesticide chemical" to the extent that "These changes had a significant impact on the regulatory authority for many antimicrobial products that are used in food-contact applications," according to the U.S. Food and Drug Administration (FDA).[48]

The federal government sought to clarify the antimicrobial oversight confusion that arose under FQPA with the Antimicrobial Regulation Technical Corrections Act of 1998 (ARTCA), which amended the definition of a *"pesticide chemical"* and "corrected the unintended transfer of regulatory authority, from FDA to EPA, that resulted from the passage of FQPA, for certain food-contact antimicrobials," according to the FDA. "Specifically, ARTCA reestablished FDA's traditional regulatory authority for certain antimicrobials that are used in or on food-contact articles."

FDA currently regulates antimicrobial substances incorporated in, or applied to, food packaging materials regardless of whether the substance is intended to have an ongoing effect on any portion of the packaging. FDA does not regulate "antimicrobials that are incorporated in, or applied to, objects that have a semi-permanent or permanent food-contact surface, other than food packaging, to provide a sanitizing effect on such surface."[49]

Regardless of the regulatory framework under which an antimicrobial additive may fall, there are uniform testing standards to benchmark performance. These include:

  - ISO 22196, *Measurement of antibacterial activity on plastics and other non-porous surfaces*
  - AATCC Test Method 147-2004, ***Antibacterial Activity Assessment of Textile Materials: Parallel Streak Method***

- JIS Z 2801 (Japan), ***Antimicrobial products – Test for antimicrobial activity and efficacy***
- QB/T 2591 (China), *Antimicrobial Plastics, Test for Antimicrobial Activity*
- ASTM E2149-10, 10 *Standard Test Method for Determining the Antimicrobial Activity of Immobilized Antimicrobial Agents Under Dynamic Contact Conditions*

Conclusion

While antibiotic and antiviral advancements have eradicated some diseases and limited the impact of many others, pathogens continue to plague societies around the world, with some developing resistance to even the most potent drug therapies. Research and development efforts continue as the pressure to find new and more powerful response options is unrelenting. Meanwhile, the contact-based spread of pathogens throughout medical, home, office and industrial environments presents a continuing risk to personal health as well as product performance and longevity.

Antimicrobial plastics bring proven broad spectrum germ-fighting capabilities to thousands of common use items and public area plastic surfaces. Antimicrobial additives and masterbatches also serve to protect plastic items and surfaces from microbial degradation thus maintaining their performance and prolonging their service life. Given the pervasiveness of plastics in developed nations and the ability of manufacturers and compounders to impart antimicrobial properties across a variety of formulations, plastic products and components could play a key role in keeping pathogens at bay in both medical and non-medical settings for years to come. U.S. manufacturers and compounders involved in the production of antimicrobial plastics need to understand the complex dual agency regulatory scheme in order to appropriately classify their formulations and products.

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Plastics Color
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Solutions for sustainability

The Paradox of Biodegradability

Summary/Abstract

As scientists, environmentalists and manufacturers continue to push biodegradability to the forefront of the plastics disposal debate, the "paper or plastic" grocery store dilemma of yore may soon be replaced with consumers mulling over the question, "compost or landfill?"

The "correct" answer lies in the ultimate disposal of the product - a fate that is unknown to the manufacturer and depends in large part on consumer location, politics, public perception and, above all, cost.

And therein lies the modern plastic paradox – how does the polymers industry create more environmentally-friendly products when the ultimate disposal environment is unknown until the consumer is finished using the product. And how much are consumers willing to pay – in dollars as well as convenience – to address the problem of plastics disposal. Compounding this uncertainty is the mixed messaging consumers are receiving from the convergence of science and sales. While terms such as *bioplastic*, *biodegradable plastic*, *degradable* and *compostable* are often interchanged in consumer advertising, the chemical and biological processes those words describe are distinct and occur only under certain conditions in certain environments.

Background

According to the University of Hannover in Germany, there are over 300 types of "bioplastic" today made from renewable resources such as corn, sugar cane and soy. But "bioplastic" has a particular meaning that may or may not relate to a polymer's biodegradability. The distinction between a plastic that is degradable and one that is biodegradable is significant. A degradable plastic will simply break down into smaller fragments, often microscopic in size, through chemical and mechanical processes. *Biodegradation* is "the process by which organic substances are broken down into smaller compounds using the enzymes produced by living microbial organisms. The microbial organisms transform the substance through metabolic or enzymatic processes." While the term is obviously appropriate in reference to plant and animal matter, biodegradation can also include "artificial materials that are similar enough to plant and animal matter to be put to use by microbes."[1]

It is this similarity to organics that makes it possible for otherwise stubborn hydrocarbon-based and synthetic plastics to undergo biodegradation – with a little help from additives.

The Packaging Recovery Organization of Europe (E-PRO) notes that the term bioplastics is often used as a catchall for different plastic types, creating confusion about two critical aspects of a polymer - its composition and its end-of-life. "The composition and the end-of-life are independent aspects that should not be confused. The biodegradability of plastic is independent of its composition… bio-based plastics are not always biodegradable," and "biodegradable plastics are not always made of renewable resources. Traditional petroleum based plastics can be biodegradable. Moreover, it should be noted that not all biodegradable materials are compostable."[2]

Because biodegradability "is an end of life option and harnesses microorganisms present in the selected disposal environment, one must clearly identify the 'disposal environment' when discussing or reporting on the biodegradability of a product – like biodegradability under composting conditions (compostable plastic), under soil conditions, under anaerobic conditions (anaerobic digestors, landfills) or under marine conditions," explains Ramani Narayan, Department of Chemical Engineering and Materials Science at Michigan State University.[3]

Even when a product's intended disposal environment is clearly evident to consumers, making proper disposal a habit requires good marketing – and good science to support it. "Ever since the introduction of "biodegradable plastics" in the late 1980s, confusion and skepticism about claims and product performance have prevailed," notes the Biodegradable Products Institute. "Although touted as 'environmentally friendly,' several so-called biodegradable plastic products did not biodegrade as expected. And yet manufacturers of these products were able to make claims of biodegradable because no scientifically based test methods and standards existed."[4]

While an apparent rush to market hampered the plastics industry's early biodegradable efforts, things began to change in 2002, says BPI, when specifications and tests were developed to separate scientific fact from marketing fiction. In granting use of its Certified Compostable label, BPI says it uses independent laboratories to test products, and its scientists "check the data to verify that the products meet requirements in ASTM Specifications D6400 or D6868. The ASTM Specifications used by the BPI resulted from eight years of intensive work by leading scientists, resin producers and the composting industry."[5]

As the science of biodegradable plastics has evolved, so too have testing and certification protocols. ASTM subcommittee, D20.96, *Environmentally Degradable Plastics and Biobased Products,* now boasts a total of 21 active and eight proposed standards. ASTM standards D6400 and D6868 pertain specifically to the labeling of plastic items and plastic packaging designed for disposal in a municipal or industrial composting facility, with D6400 including a provision for post-degradation eco-toxicity testing consistent with the Organisation for Economic Co-operation and Development's OECD 208, *Terrestrial Plant Test: Seedling Emergence and Seedling Growth Test*.[6]

According to E-PRO, "A distinction needs to be made between plastics that can be composted at home and those which require an industrial process. A certain level of temperature, heat, water and oxygen is required by active micro-organisms for efficient and effective biodegradation. A product is compostable according to the internationally recognized standard EN 13432 only when specific conditions (temperature, humidity level, time) are met in the composting system. These conditions are significantly different in home composting than in industrial facilities. Many products which meet EN13432 in industrial composting facilities will not do so in home composters."[7]

While the focus in composting has obviously been on the commercial/industrial sector, standardization and testing efforts are beginning to include the home consumer. ASTM's D20.96 subcommittee recently initiated work item WK35342, *Specification for Home Composting of Biodegradable Plastics*. Such a standard makes sense from both an economic and an education perspective, according to D20.96 member Robert Whitehouse, Ph.D., senior customer applications development manager, Metabolix Inc. "Home composting reduces the amount of volume of trash for curbside collection and associated landfill fees," says Whitehouse. "Municipalities have the same interest since their served costs are reduced from less trash collection and landfill options. Education is equally important, because the home consumer may have very little knowledge regarding plastic materials that can be biodegraded through the home composting process, hence they need to have the packaging marked by the brand owners so that items can be distinguished from non-biodegradable materials." Whitehouse says the proposed standard will have several types of potential users, including resin producers, packaging converters, retailers/brand owners and consumers.[8]

Marketing a compostable plastic product demands a great deal of clarity, cautions environmental attorney Elizabeth Poole. **"**Unqualified compostable claims should only be used on a product that breaks down into, or otherwise becomes part of, usable compost in a safe manner in approximately the same time as the materials with which it is composted. Such claims should be qualified if composting facilities are required and not available to a substantial majority of consumers where the product or service is sold. (The FTC informally considers a substantial majority to be 60%.)"[9]

At the same time it is considering home composting standards for the first time, ASTM is also reevaluating a longstanding plastics recycling education effort. Recognizing that the stalwart Resin Identification Code (RIC) classification system has confused consumers and not kept pace with changing plastics disposal options, ASTM's D20 committee initiated work item WK37080 - *New Practice for Marking Plastic Manufactured Articles for End of Life Purposes*. According to the work item abstract, "The recycling community has for 20 years attempted to use the Resin Identification Code system to help educate consumers on which products are accepted in municipal waste programs. Unfortunately, the RIC system was never intended for that purpose. In response to the request of the municipal recycling organizations, we are proposing a practice that will more efficiently assist public education."[10]

Developing a Taste for Petroleum-Based Plastics

Biodegradation of a plastic material occurs when microbes in a particular environment metabolize the molecular structure of the plastic polymer. While the process is natural and fairly rapid for plant-based materials, petroleum-based plastics had historically been written off as non-biodegradable. The problem, quite simply, is that microbes just don't have a taste for conventional plastic. Thus, for the better part of the last two decades, scientists have worked to make traditional plastics a more appealing meal for microbes. The result has been numerous proprietary organic formulations that, when added to hydrocarbon-based plastics, make the entire plastic item biodegradable through microbe activity.

Regardless of their type or application, biodegradable plastics are created in one of two ways:

- Polymers are produced from renewable plant-based resins or a combination of plant and petroleum resins.
- An additive, usually a proprietary chemical formulation, is added to traditional petroleum-based resins.

In both cases, biodegradation begins when one or more environmental conditions are present such as heat, pressure, moisture, mechanical stress or UV exposure. The ultimate biodegradation of a plastic – and its impact on the environment in the process – depends on both its chemical composition at manufacture and its final resting place after consumer use. A fully-compostable bag derived from PLA sources requires the high-heat and oxidative conditions of a commercial compost facility to fulfill its promise. Bury that same bag in a predominantly anaerobic landfill and its decomposition may be dramatically slowed or completely halted. Similarly, a petroleum-based plastic bottle with a biodegradation additive formulated for metabolism by anaerobic microorganisms might linger in a compost facility for decades or even centuries. Depending on the formulation, this can be overcome.

Depending on the polymer and additives, biodegradation can either be direct to humus, water and carbon dioxide, or it can be a two-step process where the material must disintegrate prior to biodegradation. This step – initiated by organic additives - breaks down plastic's characteristic long monomer chains through hydrolysis, allowing microbes to colonize in the material and initiate the biodegradation process.

Because plastic packaging and other consumer products have an expected shelf life and service life and must exhibit certain physical properties consistent with their intended use (e.g., strength, temperature range), the biodegradable compound is often just one component in a masterbatch additive. Unlike traditional commonly recycled plastics such as HDPE, biodegradable plastics must be designed with a critical eye toward shelf life and biodegradation rates. "Designing plastics and products to be completely consumed (as food) by such microorganisms present in the disposal environment in a short time frame is a safe and environmentally responsible approach for the end of life of these single use, short life disposable packaging and consumer articles," says Narayan. "The key phrase is 'complete.' If they are not completely utilized, then these degraded fragments, which may even be invisible to the naked eye, pose serious environmental consequences."[11]

For plastics producers, there's no easy way around this all or nothing proposition. Depending on the masterbatch used in production, consumers who might want to play it safe and dispose of a biodegradable plastic (e.g., PLA and other starch-based materials) in a municipal recycling stream could unwittingly contaminate the recycling stream. With no control over the consumer's end-game and no single biodegradable solution, the plastics industry risks undermining recycling efforts as well as polluting the environment further if biodegradables don't reach a post-consumer location that is consistent with their composition.[12]

A Little Trash Talk

Regardless of its origin, use or composition, practically every plastic item eventually ends up as some form of waste somewhere on the planet. In the United States alone, plastics accounted for about 12 percent of the 250 million tons of municipal solid waste generated in 2010, making plastics the fourth highest waste category behind paper, food scraps and yard trimmings. About 136 million of the 250 million tons of total MSW were landfilled in 2010, with the remaining 114 million tons going to recycling, composting and energy recovery (incineration).[13] Looking just at plastics in the U.S.:

- 31 million tons of plastic waste were generated in 2010, representing 12.4 percent of total MSW.
- In 2010, the United States generated almost 14 million tons of plastics as containers and packaging, almost 11 million tons as durable goods, such as appliances, and almost 7 million tons as nondurable goods, for example plates and cups.
- Plastics also are found in automobiles, but recycling of these materials is counted separately from the MSW recycling rate.[14]
- 51 million tons of plastic resin were produced in 2010.[15]

While solid waste generation increased from 3.66 to 4.43 pounds per person per day between 1980 and 2010, the recycling rate skyrocketed from less than 10 percent of MSW to about 34 percent over the same three decades. Correspondingly, disposal of waste to landfills dropped from 89 percent of MSW generated in 1980 to about 54 percent of MSW in 2010 with actual landfill tonnage staying nearly flat across those three decades.[16]

In terms of waste stream recovery efficiency, automotive batteries led the charge in 2010 with a recycling rate of 96 percent, followed by newspapers (72 percent), steel cans (67 percent), yard trimmings (58 percent), aluminum cans (50 percent), tires (36 percent) and glass containers (33 percent). While 29 percent of PET bottles and jars and 28 percent of HDPE bottles were recycled in 2010, plastics overall achieved a recycling rate of only eight percent. You don't have to dig very far in a landfill to figure out why – beyond bottles, plastic packaging is seldom recovered, and in many cases it's simply not commercially recyclable. This is significant considering that nearly one-third of all MSW in the U.S. came from packaging-related materials in 2010.

Of the six primary container/packaging materials cited by EPA, plastics were recycled the least with a recovery rate of 13.5 percent, trailing paper/paperboard (71 percent), steel (69 percent), aluminum (36 percent), glass (33 percent) and wood (23 percent). Yet, plastic ranked second only to paper in terms of total weight in the packaging/container segment of the overall municipal solid waste stream. Given the comparatively light weight of most plastic packaging, there's clearly a huge volume of plastic items in the MSW stream.[17]

The Dangers of Degradation

Plastics seem to have undergone a uniquely notorious evolution among items that end up in the waste stream. With the birth of the modern environmental movement in the 1970s, activists successfully branded plastics as a non-degradable, permanent blight on the global landscape. Once produced, they would simply exist forever. "Plastics in daily use are generally assumed to be quite stable," explains Katsuhiko Saido, Ph.D. But Saido and others have found that "plastic in the ocean actually decomposes as it is exposed to rain and sun and other environmental conditions, giving rise to yet another source of global contamination that will continue into the future." Saido explained that polystyrene begins to decompose within one year, releasing components that are detectable in the parts-per-million range. Those chemicals also decompose in the open water and inside marine life.[18]

According to Saido, "Each year as much as 150,000 tons of plastic debris, most notably Styrofoam, wash up on the shores of Japan alone. Vast expanses of waste, consisting mainly of plastic, float elsewhere in the oceans. The so-called Great Pacific Garbage Patch between California and Hawaii was twice the size of Texas and mainly plastic waste."[19]

Saido, a chemist with the College of Pharmacy, Nihon University, Chiba, Japan, said his team found that when plastic decomposes it releases potentially toxic bisphenol A (BPA) and PS oligomer into the water, causing additional pollution. "Plastics usually do not break down in an animal's body after being eaten. However, the substances released from decomposing plastic are absorbed and could have adverse effects. BPA and PS oligomer are sources of concern because they can disrupt the functioning of hormones in animals and can seriously affect reproductive systems."[20]

"About 44 percent of all seabirds eat plastic, apparently by mistake, sometimes with fatal effects. And 267 marine species are affected by plastic garbage – animals are known to swallow plastic bags, which resemble jellyfish in mid-ocean, for example," according to a 2008 study by oceanographer and chemist Charles Moore of the Algalita Marine Research Foundation.[21]

Modern Science Embraces an Old Idea

While polymer and additives manufacturers continue to develop, evaluate and tweak proprietary eco-friendlier plastics options, some of the biggest names in global consumerism have already invested millions in the science – and marketing – of biodegradable plastics. Coke introduced its *PlantBottle*, comprised of 30 percent plant sugars, in 2009. Not to be outdone in any aspect of the century-old cola wars, Pepsi unveiled its own green bottle two years later. Comprised of switch grass, pine bark and corn husks, the 100-percent renewable feedstock bottle marked the beginning of what Rocco Papalia, Senior Vice President, PepsiCo Advanced Research, said would be a successful symbiotic relationship between the company's beverage and food businesses. "This bottle far surpasses existing industry technologies and helps us address the petroleum issue because we anticipate being able to manufacture the bottle for our beverage business by using the agricultural waste from our foods business. For example, our Tropicana business generates 1.3 billion pounds of orange peels every year. Eventually, we'll use this and other agriculture waste to make our beverage bottles and other packages."[22]

Pepsico subsidiary Frito Lay set the snack packaging eco bar rather high in 2009 with the launch of its Sunchips fully compostable packaging, which the company says will completely biodegrade within 14 weeks in a suitable compost operation.[23] And several major U.S. automobile manufacturers now incorporate partially bio-based plastics in many of their interior components.[24]

Sharing a ride with plant-based plastics may strike modern consumers as a remarkable 21st century concept, but it's actually a throwback to the 1930s when, in the midst of building his namesake automobile empire, Henry Ford found time to construct numerous plastic parts out of agricultural materials. His renewable plastic efforts culminated in 1941 with the "soybean car", a vehicle with a steel frame enclosed by 14 plastic panels made from common agricultural sources. The car weighed 33 percent less than a conventional all-steel vehicle. In a 1934 *Modern Mechanix* article, Ford explained his penchant for agri-plastic. One day "we shall grow annually many if not most of the substances needed in manufacturing. When that day comes… the present unnatural condition will be naturally balanced again. Chemistry will reunite agriculture and industry. They were allowed to get too far apart and the world has suffered by the separation."[25]

While today's auto industry – and the global proliferation of plastics - are both attributable to the rise of petroleum, natural materials such as rubber and shellac have been used to make plastic items for centuries. In the 1850s, Alexander Parkes of Birmingham, England developed the first thermoplastic, *Parkesine*. New York printer and inventor John Wesley Hyatt followed in 1869 with the first commercially successful thermoplastic, patented as the now-ubiquitous "celluloid" that gained widespread use in early photo and cinema applications.[26] By this time the industrial revolution was on, and petroleum was quickly becoming its primary fuel source. By the mid-20th century petroleum-based plastics were the rule, and plant-derived polymers faded quietly into obscurity.

With environmental awareness on the upswing, rising oil prices and growing concerns over the sustainability of a petro-plastic economy, renewable resources are once again being considered for wholesale plastics production. Viewed through the lens of modern science and industry, bio-based plastics may be much more appealing today than they were a century ago.

Today's plastics producers are recognizing the need to approach biodegradability with the end user – and end of product life – in mind. ENSO Bottles has developed a biodegradable PET bottle that it claims is recyclable and will biodegrade in both landfill (anaerobic) and composting (aerobic) environments. ENSO account manager John Barnes in a 2009 *Plastics Today* article said his firm's product, which uses a proprietary additive called EcoPure®, has the same physical properties as traditional PET so it won't contaminate the recycling stream.[27] Additionally, John Lake, chief executive officer of BioTec Environmental, owners of the EcoPure technology, has stated, "we've blended EcoPure with a number of resin systems and done ASTM D-5511 testing that shows very promising results."[28]

Skeptics, including the Association for Postconsumer Plastics Recycling, say that even if biodegradable PET bottles pose no contamination threat to the recycling stream, their biodegradability puts them at odds with a recovery effort based on consumer behaviors that took decades to mold. Giving the consumer the choice to either recycle a PET bottle or discard it could reverse what the recycling industry and many environmentalists consider a good habit. Further, material that would be reused in a recycling effort drops permanently out of the plastic supply chain when it biodegrades. In a 2008 position statement, APR noted that "repeated use of molecules through recycling leads to less environmental burden than single use of molecules. Repeated use of molecules should lead to more efficient use of natural resources and complement overall sustainability efforts."[29]

Sustainability might not be as clearcut as recycling advocates hope, since many plastics suffer degradation during both their useful product life and while in the recycling stream. Additionally, polymers that are recycled don't boomerang in the recycling stream forever - they may eventually comprise a product that is not recyclable or they can permanently drop out of the recycling stream for any number of reasons, including improper disposal.

Common Ground – the Need for Standards

While recycling proponents and biodegradable advocates may not see eye-to-eye on the future impact of biodegradable plastics, they do agree on one key point – the need for quality assurance testing through applicable, objective standards. In the United States, the American Society for Testing and Materials (ASTM) has provided several standards for biodegradable plastics, including ASTM 6400/6868 which stipulate pass/fail tests for compostability, a minimum 60 percent biodegradation within 180 days in specified composting conditions, and third-party certification.[30]

ASTM 6954 provides a standard testing guide for oxo-biodegradables, where "Each degradation stage is independently evaluated to allow a combined evaluation of a polymer's environmental performance under a controlled laboratory setting. This enables a laboratory assessment of its disposal performance in, soil, compost, landfill, and water and for use in agricultural products such as mulch film without detriment to that particular environment."[31]

Additional ASTM performance standards include:

- ASTM D7475-11, Standard Test Method for Determining the Aerobic Degradation and Anaerobic Biodegradation of Plastic Materials under Accelerated Bioreactor Landfill Conditions
- ASTM D5988-03, Standard Test Method for Determining Aerobic Biodegradation in Soil of Plastic Materials or Residual Plastic Materials After Composting
- ASTM D5526-94, Standard Test Method for Determining Anaerobic Biodegradation of Plastic Materials Under Accelerated Landfill Conditions

In Europe, the most widely-cited authority is EN13432, which stipulates requirements for packaging recoverable through composting and biodegradation as well as a test scheme and evaluation criteria for the final acceptance of packaging. EN 14995 broadens the scope of plastics when used in non-packaging applications and provides for the evaluation of compostability.[32]

Some say biodegradation can pose an air pollution risk. Plastics that end up in a landfill – if encouraged to biodegrade anaerobically – would release methane, a greenhouse gas, as part of the biodegradation process. If the landfill boasted a waste-to-energy system, the methane could be captured and used to generate electricity. With no recovery, a greenhouse gas estimated to be 21 times more potent than CO_2 could be released into the atmosphere during anaerobic biodegradation.[33]

With new greenhouse gas regulations on the horizon, proponents of biodegradation argue that not only can landfill methane be captured, it can become an enduring and efficiently produced fuel source. According to the EPA, 576 of the 2,400 municipal solid waste landfills in the U.S. capture methane for energy production, and another 510 "could turn their gas into energy, producing enough electricity to power nearly 682,000 homes."[34]

Science and Salesmanship

Separating science from marketing is rarely easy. Remember the cola giants' bio-bottle wars? Consumers may have the impression that Pepsi's 100 percent bioplastic green bottle is also 100 percent biodegradable. While it is recyclable – no small feat for a plant-based PET bottle – PepsiCo says it is not biodegradable in its current composition.

For those plastics that are bona fide biodegradables, Adam Lowry of *Treehugger.com* urges that a failure to link these plastics with the ability to recover them only reinforces "a false sense of responsibility that we are doing good by the environment when we really aren't. If the composting infrastructure is not in place to recover the bio-material from that corn-based cup, it's really no better than the ubiquitous red plastic keg cup. Here's the problem: Most biodegradable cups are made from PLA (polylactic acid) plastic. PLA is a polymer made from high levels of polylactic acid molecules. For PLA to biodegrade, you must break up the polymer by adding water to it (a process known as hydrolyzing). Heat and moisture are required for hydrolyzing to occur. So if you throw that PLA cup or fork in the trash, where it will not be exposed to the heat and moisture required to trigger biodegradation, it will sit there for decades or centuries, much like an ordinary plastic cup or fork."[35]

Steve Mojo, executive director of the Biodegradable Products Institute, explains that there are two primary misconceptions driving consumer confusion. "Eighty-five percent of consumers think that bio-based/renewable also means biodegradable, and 60 percent think biodegradable products magically disappear when you throw it away," he said.[36]

"The challenge all companies will face will be finding a way on the packaging to convey their message — especially when people are buying the product, not the packaging," he added. "It is confusing to consumers and it is going to get more so as many people don't understand what those words really mean."[37]

To help consumers wade through the confusion, the plastics industry has to do more than provide information. It needs to instill confidence in the technology. The Plastics Environmental Council (PEC) is one of several diverse groups working to this end. The consortium of businesses, independent scientists and academics, engineers, landfill/compost operators and environmental groups is studying landfill degradation rates of plastics treated with biodegradable additives. The study is expected to yield a new landfill biodegradability standard in 2013 that Board Chairman Robert McKnight says "will inspire confidence in these additives from businesses, consumers and regulators."[38]

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