Photopolymers : environmentally benign technology for a variety of industries

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Photopolymers: Environmentally Benign Technology for a Variety of Industries

by

Tatyana Tarasevich

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ACKNOWLEDGEMENTS AND DEDICATION

“For My thoughts are not your thoughts, Nor are your ways My ways,” says the Lord. – Isaiah 55:8

This thesis is written with mercy and grace that I have found in you Lord.

This thesis would not have been possible without the support and encouragement of my research advisor and mentor, Dr. John T. Welch. Thank you for the many lessons you have taught me. You have showed extreme patience and allowed me as a student to find my strengths and work on my weaknesses. You have mentored on presentation of material and its discovery and strengthened my networking skills. The research in your lab was a very crucial time period that brought many valuable lessons. You have prepared me to think independently and in time of needing help, offered solutions on how to approach others to get answers that I required.

To Dr. Kelly Bonetti, Samadrita Biswas, Dr. Victoria Sokoliuk and Dr. Oksana Levchenko, thank you. You have been the best friend that a graduate student can ask for. Your encouragement, kindness, strong shoulders that bear my pains and joys will never be forgotten. Your presence in this time of my life will leave a lifelong impact full of memories that cannot be erased.

To Dr. Jason P. Seeley and Dr. Linbin Zhong I am grateful for the research techniques you taught me. To the Welch lab, thank you for being a home while I grew academically.

To my large family, thank you for your support and love.

This thesis is dedicated to you.
ABSTRACT

Photopolymerization is a well-known process with applications in a variety of industries. Photopolymers are formed by a reaction of monomers or oligomers, photoinitiators and in some cases crosslinkers. Upon irradiation with UV or visible light, monomers undergo conformational change to form polymers via a photochemical process. Several photopolymerization types will be discussed in this thesis. End products of photopolymerizations included epoxies, inks, coatings, photoresists, etc.

The common syntheses of photopolymers, such as Step-Growth Polymerization and Free Radical Polymerization, and the use of those approaches in commercial application will be explored. Both procedures employ UV irradiation, but the syntheses vary widely in regard to molecular weight of monomers or oligomers. The polymerization rate results in unique properties and features central to meet customer specifications for flexibility, stiffness, and scratch resistance.

Photopolymers are used in the preparation of coatings in many major industrial sectors such as Additive Manufacturing, Automotive, Aerospace and Aviation, and Microelectronics. The importance of coatings to those industries will be discussed in this thesis as well. Market share values for all discussed industries are several millions to billions of dollars. The advantages and disadvantages of photo coatings such as quick curing or curing at low temperatures, can profoundly impact, volume, quality, and speed at which materials are produced in many industries.
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1. BACKGROUND

Photopolymers are not novel materials. Sunlight induced cross-linking material in Judean asphalt was used in both mummification and for calking of wooden ships. Hardened by sunlight, this material was known to be insoluble upon polymerization.\textsuperscript{15} Today, photopolymerizations are used in a variety of commercial applications.\textsuperscript{23} Photopolymers are used in a variety of applications that include, but are not limited to the preparation of microchips, the development of photoresists, microprocessors, coatings, printing, and adhesives. Topics to be addressed include: what are the photopolymers, why are they significant and where can they be applied?

1.1 DEFINITIONS

In the mid 1960’s the US government issued a mandate to reduce volatile organic compounds in coating formulations which led to rapid development of the entire coatings industry. Today the use of UV curable formulations increased faster than that of the general coatings in annual growth.\textsuperscript{24} The following sections will define and describe the key components and properties of photopolymerizations.

1.1.1 Photopolymers

Light activated polymers will transform their properties upon exposure to a light source. Composition of monomers and oligomers undergo a unique structural transformation to a polymeric network at specific wavelengths that range from visible light to UV
radiation. Often times the photosensitive element is an additive that was added to the reaction or it can be built in the composition of the monomers. This polymeric network is utilized in variety of applications in different technologies from coatings, resin, sensors and many more. The development of these applications has aided technological enhancement of our society.

1.1.2 Monomers

Monomers are the building blocks of polymerization. Monomers are selected based on properties such as viscosity, curing speed, odor, and toxicity. Film properties, such as flexibility, hardness and adhesion, shell life and cost are inferred. Acrylates, one of the commonly used monomers, are most widely used in UV curing due to their flexibility and high reactivity. Acrylates cure at extremely rapid rates compared to other monomer systems (acrylic > methacrylic > vinyl > allylic). Acrylates are also a diverse class of monomers with the ability to have multifunctional substitutions. These multifunctional substitutions lead to enhanced features and variable of functionalities.

1.1.3 Additives

Additives are introduced to coatings to enhance the properties of select polymers. The properties include adhesion, dispersants for pigment spreading, color pigments and stabilizers for both thermal and UV protection. The most widely used additives are stabilizers, plasticizers, lubricants, and flame retardants. Stabilizers provide protection from thermal and light assisted oxidation. Plasticizers are used to make firm gels. Lubricants are added to create smooth surfaces and minimize cracking during
polymerization. Flame retardants are used to decrease exposure to oxygen or heat. Absorbers and fillers are often introduced to the synthesis to decrease light scattering and thus enhance printability and functionality.\textsuperscript{28}

1.1.4 Photoinitiator

Industrial photopolymerizations are usually solvent-free systems. Utilization of a solvent-free system generates a new era of syntheses that are economically and environmentally mindful. Photoinitiators allow the use of solar energy without requiring complex chemical mixtures.\textsuperscript{23} These initiators absorb UV or visible light and generate hypersensitive species that initiate polymerization processes.\textsuperscript{28} The hypersensitivity of these species is attributed to the excitation of electrons from ground state to the high energy state, thus generating energy to initiate polymerization processes. Radical photoinitiators absorb light to form a free-radical species that initiate rapid formation of high molecular weight polymers with crosslinkers.\textsuperscript{28} Most photoinitiators are water insoluble. Having a water soluble photoinitiator, however, is remarkable in photopolymerization, notably in synthesis of hydrogels or 3D printing.\textsuperscript{29}

Currently, fluorophores such as coumarins are utilized as photoinitiators. Coumarins can be characterized via spectroscopy in the visible or near UV regions in the light absorbing ability.\textsuperscript{30} In order for a photoinitiator to be effective, it must have a relatively high extinction coefficient in the region of the electromagnetic spectrum matching the output of the lamp source.\textsuperscript{24} Utilization of photoinitiators in photopolymerization abates the need for additional chemical reactants which would require removal via multiple purifications, thus, decreasing the yield. The principal limitation of photopolymerization
is that penetration of light energy through a dense layer of material is low. Cationic photoinitiators aid in formation of acrylate and methacrylate functional groups in polyether-type polymer chains. Through absorption of light, cationic sensitive species are broken down by cationic photoinitiators with the help of other co-initiators via a charge transfer system. One of the drawbacks of using cationic photoinitiators is that they are limited to usage of UV light sources.

Substitution of light sources by lasers is becoming crucial in applications that require higher intensity processes. This advantage leads to enhanced features that include higher reaction rates, enhanced imaging resolution, deeper penetration into substrates and better suitability of the emission spectrum of the light source to the absorption spectrum of the photoinitiator. Also, utilizing a high energy UV irradiation source is harmful to the operator. Utilization of visible light leads to a safer alternative for human health.

1.1.5 Crosslinking

Crosslinking is utilized to make materials more inflexible and is a process of connecting two polymer chains. Cross-linkers consist of multiple sensitive functional groups, that, upon activation change morphology and create product. There are three possible types of crosslinking: ionic, covalent, and via Van der Waals or hydrogen bonding. They are used to control polymerization in different environments. Crosslinking is also applied in situ to nano objects to yield more stabilized cross-linked nanoreactors. However, crosslinking has drawbacks as well. Sensor sensitivity can be damaged by crosslinking and polymerization of polymer composites. Crosslinking is also used in
epoxy resin synthesis. Epoxy resins or unsaturated polyesters become more rigid and reaching the hardness of glass. To modify the drawbacks of epoxies, liquid methacrylate, solid polymers or inorganic micro-and nanoparticles are added to uncured epoxy resin. One of the first examples in situ of UV radiation modification of epoxy resin is copolymerization processes of n-butyl acrylate with glycidyl methacrylate.\textsuperscript{41}

1.2 CATEGORIES OF PHOTOPOLYMERS

As depicted in Figure 1, there are several types of photopolymerizations. Each type yields unique products that have specific features and are utilized in different industries.

1.2.1 Type 1-Photopolymers that Undergo Photoinitiated Chain Growth
In Type 1, photopolymers with composition of low molecular weight monomers or oligomers with polymerizable functional groups undergo photoinitiated chain growth, also known as free radical process. This chain polymerization growth, with usage of a photoinitiator, can be radical, cationic, or anionic upon irradiation and will yield a crosslinked network polymer. Utilizing the energy source, these polymerizations often quickly cure small monomers or oligomers. These systems are used in UV curing of coatings, adhesives, printing inks, and some negative working photoresists.\(^{15}\) Similarly, in biomedical applications, hydrogels utilize chain growth polymerization to enhance 3D printing properties and decrease deformations during printing along with deficient mechanical properties.\(^{42}\) High performance composites often utilize glass-fiber-reinforced polymers. Synthesis of glass-fiber-reinforced polymers occurs at ambient temperatures or under UV light through photochemical curing.\(^{43}\) These composites are utilized in structural compositions of many industrial sectors including transportation, storage and plastics.

1.2.2 Type 2-Photopolymers That Undergo Step-Growth Polymerization

Type 2 system, in which photopolymers undergo step-growth polymerization, fundamentally differ from Type 1 due to photoactive functional groups which, upon irradiation dimerize or undergo coupling. Also known as condensation process, Type 2 utilizes monomers or oligomers with high molecular weight. Exposure to longer irradiation time increases the molecular weight of the polymers.\(^{44}\) This system is used in
negative photoresist technology and in the formation of network polymers. On exposure to light, polymer material in negative photoresists will become insoluble to the photoresist developer and leave behind a pattern from the that polymer on the surface. Dental industries utilize this method to substitute the most used methacrylate-based chain growth polymerizations when encountering revitalizing products. This system has a noticeably short curing process and has increased mechanical properties that are desired. Curing methacrylates by radical addition decreases control over its polymerization and often yield highly crosslinked and nonuniform networks. The curing process has been modified to use chain transfer agents to reduce shrinkage stress and enhance the toughness of the photopolymers. Step-growth polymerization is also exploited for in situ encapsulation of pancreatic β-cells using thiol-norbornene hydrogels. Reactive nanogels that are used in various applications such as polymer composites, tissue engineering, and drug delivery utilize step-growth polymerization to modify the chain length. This strategy can increase the capacity of nanogels in their chemical composition and function. These nanogels are soluble in aqueous solutions and are ideal for delivering nonpolar constituents as a vessel.

1.2.3 Type 3-Functional Polymers that Undergo Photoinduced Crosslinking

In Type 3 system, functional polymers undergo photoinduced crosslinking. Each of the constituents has a reactive function group. Reaction between the two monomers depends on the excitation of light by one of the reactive functional groups on the monomers and the use of a photoinitiator. This process is used to synthesize rigid
epoxies that are used in repair of composite plastics and fiberglass. Another application is synthesis of hydrogels utilized in the medical field as an embedding platform for drug delivery.

1.2.4 Type 4-Polymers that Undergo Functional Group Modification Under Irradiation

Type 4 system uses irradiation to create polymers that undergo functional group modification. Functional group X will transform to Y because of the fundamental reactivity of the X groups. Also, conversion may be guided by catalytically active species from photoactive compound. This modification will change the solubility of the polymer. Currently, this method is used in high performance positive tone photolithographic systems.¹⁵

1.2.5 Type 5-Polymers That Undergo Photoinduced Cleavage Reactions

The final category, Type 5, contains synthesis of polymers that undergo photoinduced cleavage reactions. Photoinitiator will act as an acid, base, or free-radical to execute a cleavage reaction. Occasionally, the group along the chain will break the bonds since they are photoactive. This cleavage will change the molecular weight to be smaller and subsequently lead to fragmentation of the polymer chain made by photolysis to be more soluble than initial high molecular weight macromolecule. This change in solubility permits these photopolymers to be used as positive tone photoresists.¹⁵
1.3 MARKET SIZE AND IMPACT

Photopolymers have high impact in many industries. Each industry may generate up to billions of dollars in the market per year. As seen in Figure 2, the global protective coatings market size is exponentially growing. It was estimated to be at USD 30.16 billion in 2018 and is expected to register a CAGR (Compound Annual Growth Rate) of 7.7% by 2025.\textsuperscript{10} Not depicted in the Figure 2 but will be discussed and subsequently depicted is the fact that solvent based coating is the largest formulator but has major disadvantage of being environmentally unsafe.\textsuperscript{10, 18}

1.3.1 Additive Manufacturing

Sometimes known as 3D printing, Additive Manufacturing has a diverse array of applications that range from simple, such as paper printing, to complex, such as extrusion, where molds are used to define a shape in 3D format. The global Additive Manufacturing materials market size was estimated at USD 845.7 million in 2018,
growing at a CAGR of 23.9% over the next ten year period. Different resins are used in the preparation of products. Variability in the features enable these resins to be used for many applications.

Most used resins are comprised of epoxies, alkyds, and polyesters as top leaders, as seen in Figure 3. Each of the listed resins has advantages and disadvantages in the features enabling them to be used for diverse applications.

Photopolymers are on the rapid rise in Additive Manufacturing. As seen in Figure 4, photopolymers are projected to have greatest impact on market share above metals and thermoplastics. Thermoplastics will be applied in industries such as aerospace and defense, along with automotive and medical. This is attributed to enhanced research and creation of more ecologically-friendly products. Polymer 3D printing is projected to generate $11.7 billion (about $36 per person in the US) in revenue in 2020, and grow to $24 billion (about $74 per person in the US) in 2024 and up to as much as $55 billion (about $170 per person in the US) yearly by 2029 with CAGR of 14.4%. Manufacturers are actively seeking to expand the usage of 3D printing.

Figure 3. Comparison of 3D printing materials with respect to the market.
Printing with intent to reduce production time, while enhancing product features and properties, and to reduce labor cost.\textsuperscript{11}

Additive Manufacturing has several applications as depicted in Figure 5. Each category is based on the method of printing the material and will be subsequently discussed. Additive Manufacturing will be directed by consumer products, connectivity to molds, and cast pattern applications.\textsuperscript{5}

Utilizing this fast-paced market, a variety of industries are trying to exploit it. Rather than using pure metals, alloys that contain diverse metals such as titanium, nickel, steel, aluminum, and cobalt are being utilized in production of high-performance parts in aerospace industry.\textsuperscript{49} In 2019,
material extrusion technology produced the most revenue. However, by 2029, vat polymerization and powder bed fusion are expected to surpass material extrusion.\textsuperscript{5}

1.3.2 Automotive

Photopolymers are used in automotive industry are often connected with Additive Manufacturing. Resin or any other type of form of polymers is utilized to make the body framework, coatings and parts that comprise the automotive. UV-cured technology segment is likely to grow with a CAGR of over 5% through 2026 as depicted in Figure 6.\textsuperscript{13} These coatings are in high demand since consumers are striving towards high performance coatings that protect against environmental stressors, hence reducing the maintenance costs. Several types of coatings are used in the Automotive industry and the leaders of the industry will be subsequently discussed.

1.3.3 Aerospace and Aviation
The Global Aerospace Coatings market was valued at $477 million in 2020 and it is expected to reach $1.02 billion (about $3 per person in the US) by the end of 2027, growing at a CAGR of 10.3% during 2021-2027.50

Polyurethane based coatings, as depicted in Figure 7, offer external protection to structural parts,7 while epoxies are less resistant to wear and tear that includes corrosion, cracking, and environmental breakdown.

2. HYPOTHESIS

2.1 NON-PHOTOPOLYMER ADVANTAGES AND DISADVANTAGES

Despite ease of handling and excellent properties, thermally cured solvent based and powder based coatings take long period of time to cure.21, 22

One of the advantages of non-photopolymer and a significant disadvantage of photopolymerization is that penetration of light energy diminishes with the a thickness of material.23 Thermal cure epoxy adhesives have high degree of cross-linking and glass transition temperature. 51
The advantages of photopolymerization over thermally cured polymerization include higher rates of polymerization and environmental benefits from elimination of volatile organic solvents. Also, photopolymerizations can be formulated for numerous applications since functionalized monomers and oligomers that can be used as building blocks with a wide range of properties. Additionally, wide range of viscosities that are present in the reactive monomers can also be formulated to meet the standards in some coatings applications.

### 3. SYNTHESES

There are multiple ways to synthesize photopolymers. Most photopolymers consist of monomers or oligomers, alkenes or alkynes, along with a crosslinker and a photoinitiator. Polymerization occurs upon irradiation with a light source, commonly with UV radiation and occasionally visible light. The most common ways are step-growth,
also known as condensation pathway, and chain-growth, also known as free-radical polymerization. As shown in Figure 8, main differences include adaptation of molecular weight size and concentration to determine the rate of formation. At low concentrations, step-growth is slow while free radical is fast. However, at larger molecular weight/concentration ratio, step-growth polymerization is preferred.

Depending on polymerization pathway, e.g. free radical curing or step growth processes, and market application, different ratios are used when curing with UV radiation as seen in the Table 1 (reproduced with permission) below. Monomers comprise more than half of the components in film preparation and are key components in viscosity control. Lamp source influences the process of curing and the intensity determines the speed of polymerization. Oligomer resin is a major component in composite industry.

![Figure 5. Difference between free radical and step-growth polymerization.](image)
3.1 STEP-GROWTH PROCESS

Commonly known examples of stepwise growth process are polyesters and polyamides. The first step-growth polymers synthesized for commercial purposes were achieved by Carothers and Dupon.\textsuperscript{52} Stepwise additions often progress without the use of catalysts. Monomers oligomerize with higher molecular weight polymers formed near the end of the reaction.\textsuperscript{23, 53} To enhance physical performance, higher molecular weight materials are utilized. Also, many techniques have been developed to improve the preparation of higher molecular weight step growth polymers.

The drawback of this polymerization is batch consistency and predictability in composition. Figure 9, is a visual representation of how two monomers come together to elongate the chain in a sequential process.\textsuperscript{23, 52}
3.2 FREE RADICAL OR CHAIN GROWTH POLYMERIZATION

Free-radical type of photopolymerization process is one of the most frequently encountered in current industrial applications.\textsuperscript{14}

To initiate a polymerization process, a free radical initiator is necessary in the radical addition pathway. As depicted below in Figure 10, the process begins with a generation of a radical which is then transferred to a monomer to create an active center. There are two pathways shown in the figure to depict nonequivalence of carbons of the alkene.

Upon generation of the radical, chain polymerizations advance by adding a single reactive monomer to the end of a polymer chain as seen in Figure 11.
A secondary radical is produced that generated from the terminal end of the growing chain until two radicals come together and terminate the growing chain. Reaction of the two radicals terminates the chain growth as shown in Figure 12. Fewer termination steps from low concentration of radicals results in higher molecular weight chains and polymers of similar identical weight. A drawback of this polymerization process is sensitivity to oxygen. To overcome this barrier, O₂ inhibitors are added, which increase the cost of adhesives prepared.²⁶

Table 2 has been adapted from Polymer Chemistry Database to summarize the differences between step-growth polymerization and free-radical polymerization.² Key differentiators are termination steps, active components which can react, and speed of reaction with respect to molecular weight increase.
TABLE 2. STEP-GROWTH VS CHAIN-GROWTH POLYMERIZATION

<table>
<thead>
<tr>
<th>Step-Growth</th>
<th>Chain-Growth</th>
</tr>
</thead>
<tbody>
<tr>
<td>All molecules present (monomer, oligomer, polymer) can react with any other molecule.</td>
<td>During propagation, only monomers react to the active site at the end of the growing chain.</td>
</tr>
<tr>
<td>Monomers exist throughout the reaction, but copious quantities of monomers are consumed early in the reaction.</td>
<td>Monomers exist throughout the reaction; its concentration decreases steadily with time.</td>
</tr>
<tr>
<td>There is no termination step, and the end groups of the oligomers and polymers are reactive throughout the polymerization process.</td>
<td>There are two distinctive mechanisms during polymerization; these are initiation and propagation. In most cases there is also a termination step.</td>
</tr>
<tr>
<td>The reaction proceeds rapidly at the beginning, but the molecular weight increases only slowly and high MWS are only attained at the end of the process by long oligomers reacting with each other.</td>
<td>The reaction speed depends on the concentration of initiator (and co-initiator) and high-molecular weight polymers form throughout the duration of the reaction.</td>
</tr>
<tr>
<td>Long reaction times are needed for the synthesis of long (high molecular weight) polymers.</td>
<td>Long reaction times have high degrees of conversion but do not affect (much) the (average) molecular weight.</td>
</tr>
<tr>
<td>Molecular species of any length (oligomers) exist throughout the reaction, with the length distribution broadening and shifting to higher MW with increasing reaction time.</td>
<td>The mixture contains primarily monomers and polymers, and only lesser amounts of growing polymer chains.</td>
</tr>
</tbody>
</table>

4. MARKET APPLICATIONS

Photocurable coatings have many applications in different markets. Summarized in Table 3, are some areas where they are used and potential areas of growth and expansion. As shown in Figure 13, there is
expected growth for all constituents of photopolymerization. Notable, monomers and oligomers will be the main constituents in the composition of the photopolymers.

**TABLE 3. APPLICATIONS FOR PHOTOCURABLE COATINGS**

<table>
<thead>
<tr>
<th>Application</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plastic Coatings</td>
<td>Rapid emerging space</td>
</tr>
<tr>
<td>Metal Coatings</td>
<td>Predominantly Epoxy Acrylates</td>
</tr>
<tr>
<td>Wire Coatings</td>
<td>Impending growth capacity</td>
</tr>
<tr>
<td>Textile Dressing and Coatings</td>
<td>Impending growth capacity</td>
</tr>
<tr>
<td>Wood Coatings</td>
<td>Conventional region</td>
</tr>
<tr>
<td>Paper Coatings</td>
<td>Rapid emerging space</td>
</tr>
<tr>
<td>Vinyl Floor Coatings</td>
<td>Dominated by UV curables</td>
</tr>
<tr>
<td>Fiberglass Laminates</td>
<td>High strength composites prospect</td>
</tr>
<tr>
<td>Photoresists</td>
<td>PC board and silicon chip manufacturing</td>
</tr>
<tr>
<td>Photocurable Inks</td>
<td>Curing of highly pigmented resins</td>
</tr>
<tr>
<td>Glass Fiber Coatings</td>
<td>Rapid emerging space</td>
</tr>
<tr>
<td>Contact Adhesives</td>
<td>Remarkable market potential</td>
</tr>
<tr>
<td>Furniture Coatings and Filler Boards</td>
<td>One of the first applications for UV curables</td>
</tr>
<tr>
<td>Conformal Coatings for Electronics</td>
<td>Excellent growth potential</td>
</tr>
</tbody>
</table>

4.1 ADDITIVE MANUFACTURING

There are seven categories of Additive Manufacturing, also known as 3D printing, processes according to the American Society for Testing and Materials (ASTM). The included are VAT Photopolymerization, Material Jetting, Binder Jetting, Material Extrusion, Powder Bed Fusion, Sheet Lamination, and Directed Energy Depositions.

4.1.1 Vat Polymerization
In vat polymerization, the model is built layer by layer using liquid photopolymer resin as depicted in Figure 14. UV light cures each layer as it is added on top of the previous hardened layer. After the desired object is made, the liquid resin is drained, leaving behind a hardened polymerized product. This method is used primarily because of the ability to use UV as the curing source. Vat polymerization utilizes photopolymers as the raw material of the process. These polymerizations have accuracy of 0.025 – 0.1 mm with even surface. Utilizing trifunctional methacrylates along with difunctional monomers increases viscosity and mechanical properties.

Ceramic slurry mixtures are utilized in the process and 50:50 wt. ratios of monomers were used. Vat polymerization has many advantages and disadvantages. It is a quick process with high accuracy but it is very expensive and has a long post formation processing time. Additionally, vat polymerization is used in avoidance of using support structures in printing of hollow structures. However, photopolymers that are used in this process are weak in structural composition, meaning in the chemical composition of the monomers used, and this leads to products being more prone to degradation and deformation over time.
Another limitation of this method is that this process is limited to photo-resin matters and the product can still be affected by UV light after it is printed.\(^4\) This method is most commonly used in stereolithography, direct light processing and masked stereolithography.\(^5\) There are two major variants of vat polymerization Digital Light Processing (DLP) and Stereolithography (SLA). SLA utilizes laser source and mirror, while DLP utilizes digital light projector.\(^5\)

Another popular usage of vat polymerization is in creation of Liquid Crystal Display (LCD) technology. Utilizing LED array as an additional energy source provides better pixel resolution at high speed of printing.\(^6\)

Vat photopolymerization is utilized in many industries, including the field of drug delivery and medical device fabrication.\(^5\)

### 4.1.2 Material Jetting

Material Jetting process forms objects by using either a continuous or Drop on Demand (DOD) approach. Material is jetted onto a build platform in a similar process as a two dimensional ink jet printer using thermal or piezoelectric method.\(^1\) Layers are built up from the previous layer and are cooled and hardened by UV light.\(^1\) The product is removed upon support material removal as depicted in Figure 15. The advantages of this product include multicolor usage along with high accuracy of droplet deposition. However, the disadvantage is that support material is required, and the method is only limited to usage of waxes and photopolymers. Using photopolymers as a building block creates a product as a material with hybrid properties such as flexibility and combining
rigidity. However, the photopolymers that are used exhibit properties that enables production of weak and brittle material. This limits the high accuracy. Waxes that are used make parts that are fragile. The process itself is a slow build process. Material jetting is used in visual prototypes and industrial tooling, is useful in the production of anatomical medical models for pre-surgical and education purposes, and is suitable for casting patterns.

4.1.3 Binder Jetting

Binder jetting is a process which involves two materials: a liquid sealant and a powder-based build material. As depicted in Figure 16, a print head moves horizontally along the x and y axes of the machine and deposits alternating layers of the build material and the sealant material. This print head resembles an overhead shower that spreads sealant by depositing it on the powder. Additional powder is added to the freshly
pressed layer and the object is formed only where the sealant meets powder, leaving behind loose powder surrounding the shape.

The advantages of using Binder jetting, aside from being a process that is faster than others, include flexibility of creating multicolored parts and using a range of materials that include metal, polymers, and ceramics. In some cases, sand is used as a powder base and does not require additional processing. Also, the unused powder based material can be reused in the next batch to avoid waste. Using the feature of two-material methods allows for diversification of the products that are being formed.

The drawback of this method includes unsuitability of creating structural parts and elongated post processing time. Also, this method needs addition of metals, most commonly bronze, during sintering process, also known as infiltration, to avoid significant shrinkage when making larger parts. Binder jetting is used in applications such as production of architectural models, packing, toys and figurines. This method is also less accurate than Material Jetting. Some of the

![Figure 13. Representation of the Binder Jetting Process, adapted from Gibson et al., 2010. Permission to use asked.](image-url)
markets that use this process include industrial applications, dental and medical devices, aerospace components, part casting, and luxury applications.\textsuperscript{64}

\textbf{4.1.4 Material Extrusion}

Fuse deposition modelling (FDM) is a common material extrusion process and is trademarked by the company Stratasys\textsuperscript{TM}. The nozzle contains the material that is heated before deposition of layer by layer. As depicted in Figure 17, the nozzle can move side to side horizontally and a platform moves vertically after each new layer is built.\textsuperscript{12} Material extrusion generally uses a continuous filament of a thermoplastic material as a base material.\textsuperscript{62} Upon building each layer, all the layers are fused together while the material is in melted state.\textsuperscript{12} Material extrusion process has accuracy on the span of 0.1-0.6 mm in formation of parts using polymers with low melting temperatures.\textsuperscript{55}

The advantages of using this method include wide selection of print material with easily comprehensive technique that does not require supervision and can be done using low temperatures.\textsuperscript{4} This is an unexpensive process that can use easily available ABS
(Acrylonitrile butadiene styrene) as its resin material. Also, unused resin can be recycled to produce more material and multi-material can be used in printing. Disadvantages of material extrusion are that layer lines are visible and the product is predisposed to warping and other problems associated with changes in temperature. 

Also, because of the limited range of motion of the nozzle, the final product has diminished quality. To maintain the quality of the product, consistent pressure must be applied to the material. Modifications have been made to material extrusion method to have two nozzles. With the addition of the second nozzle, constant strands of composite fiber are added to each layer, making a new hybrid material that is equivalent to parts made of metal. Material extrusion method is used for production of non-operable prototypes or rapid prototyping for multiple duplications of the same object to reduce cost.

4.1.5 Powder Bed Fusion

The Powder Bed Fusion (PBF) process includes the frequently used printing techniques such as:

- Direct metal laser sintering (DMLS),
- Electron beam melting,

Figure 15. Overview of the Powder Bed Fusion manufacturing process. Permission to use image asked.
(EBM), Selective heat sintering (SHS), Selective laser melting (SLM) and Selective laser sintering (SLS).\textsuperscript{12} PBF has four categories of energy sources: laser fused, electron beam fused, fused with agent and energy, and thermally fused. This process also uses two chambers, the build chamber and powder chamber, and a coating roller.\textsuperscript{4} As depicted in Figure 18, the energy system melts either the metal or plastic powder resin, which upon solidification forms a pattern. The roller spreads a fresh layer of powder which is then heated again by the energy source to melt it. The process is repeated until the desired shape is achieved. Loose powder that remains on the sides of the mold is cleaned up in the post processing step.\textsuperscript{12} The advantages of using PBF include usage of diverse materials simultaneously and reusage of the loose powder, low cost of machinery, and minimum or no required support of structures for the build, while creating perfect, complex and functional parts.\textsuperscript{4, 66} The disadvantages include usage of high power, dependance of powder grain size for finish, size limitations and slow speed.\textsuperscript{12} Moreover, thermal distortion is plausible for polymer parts.\textsuperscript{4} Applications of PBF are substantial, from jewelry and dental industry to aerospace and defense industry, along with the medical prosthetics.\textsuperscript{62} Each industry is dictated by the type and strength of the laser source being utilized and what type of resin grade is being employed in the types of printing techniques of the PBF mentioned earlier.

4.1.6 Sheet Lamination

Sheet lamination is used to produce products that are very pigmented and have high detailed resolution.\textsuperscript{67} There are seven types of Sheet lamination. The processes include
ultrasonic additive manufacturing (UAM), laminated object manufacturing (LOM), Plastic Sheet Lamination (PSL), Selective Lamination Composite Object Manufacturing (SLCOM), Composite Based Additive Manufacturing (CBAM), Computer-Aided Manufacturing of Laminated Engineering Materials (CAM-LEM), and Selective Deposition Lamination (SDL).4

To explain some of the differences, in Ultrasonic Additive Manufacturing process, ultrasonic welding is used to bind sheets or ribbons of metal together. LOM was first commercialized in 1991.68 Laminated object manufacturing uses the same process, except instead of sheets of metal, it uses paper as material and adhesives instead of welding.12,69 The precision of the desired product is based on the thickness of paper that is utilized. Average thickness of a sheet of paper is 50 to 100 microns.62 Typical metals that are used are stainless steel, aluminum, titanium, and copper.70

As depicted in Figure 19, sheet lamination process begins when material is placed on the cutting bed and bonded with adhesive. Using laser or knife, the desired shape is formed. Then the next layer is deposited, and the process is repeated until the desired shape is formed. Some of the advantages of this method include a larger...
working area, full-color prints, ability to layer multiple materials and incorporation of hybrid manufacturing systems at fast print rate without post-processing. The disadvantage of this method is that finishes of product can vary based on what starting material is used in the process. To achieve a specific finish, some post processing may be necessary. Also, limitation of material is a huge deficit of this method. Moreover, layer height cannot be changed without changing the material sheet thickness and removal of excess material after lamination can be difficult and very time consuming. This method also produces a lot of waste and has difficulties producing hollow objects.

Sheet lamination is one of the less accurate methods in Additive Manufacturing and is being used to produce non-functional prototypes and casting molds. It is also used to manufacture composite materials since build materials can be interchanged mid process.

4.1.7 Direct Energy Deposition

Directed Energy Deposition (DED) covers a range of terminology: Laser engineered net shaping, directed light fabrication, direct metal deposition, and 3D laser casing. It is a more complex printing process commonly used to repair or add additional material to existing components. DED manufacturing parts creates parts by precisely melting materials and ousting them on the workpiece, layer by layer. This additive manufacturing technique is primarily used with metal powders or wire source materials as depicted in Figure 20. DED uses polymers and ceramics, as well as the more commonly used such as aluminum, Inconel, niobium, stainless steel, tantalum, titanium and titanium alloys, and tungsten. A 4 or 5 axis arm with nozzle containing the
material moves around a fixed object. Layers create unique features or fix imperfections upon solidification of each layer.\textsuperscript{12} Advantages of DED include strong and dense parts which are built quickly, reduction of material waste, capacity to build large parts, and capability to make parts with custom alloys.\textsuperscript{4} In DED control of the grain structure to a high degree allows repair work of high quality and functional parts. High accuracy and programmed microstructure allows speed to be forfeited in pre-balance between surface quality and speed.\textsuperscript{12, 69} The disadvantages of DED are that the capital cost is high and support structures are not utilizable in the build. Secondary processing is required to overcome reduced surface finish.\textsuperscript{4} Moreover, fusion processes necessitate additional research to progress the process into a more mainstream positioning.\textsuperscript{12} Most commonly used applications for DED fall into three categories; near-net-shape parts, feature additions, and repair. Near-net-shape is used in aerospace and defense industry to make aerospace brackets, tanks, and ribs.\textsuperscript{72} DED is also efficient in fixing complex damaged parts, such as turbine blades or propellers.\textsuperscript{62}
Even though all of the seven methods of Additive Manufacturing vary in materials used and in the processing, the applications for end use are grand. Creating hybrid material allows flexibility and solutions for coatings to aid in problems such as corrosion and anti-fading. Moreover, reduction of weight restriction is now plausible along with elongation of lifespan of materials that are already on the market.

Hybrid materials and coatings aid in offering solution to problems in manufacturing methods that include low production rate, inaccurate dimensions, and limited maximum build size of components. As seen in Figure 21, Aerospace is a major end user of Additive Manufacturing comprising over 51 percent of the market share in 2019.

4.2 AUTOMOTIVE

Once the resin is formed in Additive Manufacturing, it is then converted to coatings that address multiple problem areas such as corrosion, paint chip, and pigmentation fading due to exposure of direct sunlight. Automotive market is moving away from solvent based paints to avoid high content of Volatile Organic Compounds (VOCs) and moving towards applications using powder-based paints. Currently, there is an increasing trend
for custom paint patterns and vinyls. Custom paint and vinyls increase visibility and lifespan of expensive paint customization by elongating the lifespan from general wear & tear and exposure to sun. As seen in Figure 22, North America contributes to one-third of market share in automotive industry. Coatings on metals contribute a sizable percentage of the market since metals are the major composition of vehicles. As seen in Figure 23, main constituents are basecoat and clearcoat. Those are coatings that are crucial in anticorrosion and antifading features of the vehicles. Basecoat is applied directly to the surface and is prone to corrosion. Clear coat is prone to pigmentation fading upon exposure to sun. Photopolymers are utilized in this industry to expedite curing time. Polyamides are used as main component for SLS due to the ability to of strong thermal resistance and are ability to withstand deformation and fracture of the material. Polymer nanocomposites are also used in Automotive market for their mechanical properties, thermal and chemical stability. To reduce corrosion rate, substitution of new parts that are more lightweight and durable is preferred over metal. Automotive body framework that is not comprised of metal has also more capacity for cargo.
Poor dispersal stability and inadequate weather resistance promotes the development of encapsulated pigments. Through soap-free mini-emulsion polymerization, reactive emulsifier uses advantages of covalent bonding and steric hindrance effect to increase dispersion stability. Shielding the effect of polymer in the core-shell structure, composite particles improve weather resistance and anti-ultraviolet weather resistance.  

Another application of Additive Manufacturing in Automotive market is the development of parts that decrease pollution. One of these parts is a catalytic converter. Catalytic converter transforms engine emissions into safer gases for the environment. Geometry of catalytic converters is under development to improve its efficiency. One of the proposed developments is to use ceramic stereolithography technology (CSL). CSL allows the synthesis of honeycomb and twisted honeycomb structures, which in its geometry achieve good physical strength and have a high surface area in printing.  

4.3 AEROSPACE AND AVIATION
Protective coatings are used in repair, maintenance, and painting for exterior surfaces of aircrafts. Efficient coatings reduce aircraft weight and increase fuel efficiency. To provide efficient camouflage and color, solvent-based topcoats are being utilized more.\textsuperscript{18} One of the technical requirements of space applications is temperature range of -120 °C (dark side) to +250 °C (solar side).\textsuperscript{79}

For example, A380 Airbus entails about 480 kgs of coating and requires maintenance every 5 to 8 years. This leads to downtime while those repairs occur.\textsuperscript{18} As seen in Figure 24, a solvent-based coating segment generates over 480 million dollars and is the most used method in coating utility due to simplicity of use and ease of application. Since the photocuring is fast and solvents evaporate quickly, it can be utilized anywhere. The drawback to utilizing a solvent system is that they are not environmentally benign. UV-responsive microcapsule-based coating is currently under development to fight cracks in the frame of the airplanes in-orbit. These microcapsules contain an inner polymeric shell and outer TiO\textsubscript{2} shell. Such microcapsules are synthesized by UV-initiated polymerization of Pickering emulsion in which the outer shell will break the inner polymeric shell upon impact.\textsuperscript{80} Microcapsules are then implanted into silicon resin.
matrices. When impaired, stress that is generated from the environment will break some microcapsules and aid unbroken microcapsules to be broken down by UV radiation. The breakage will release the encapsulated repair agents.

Additive Manufacturing is one of the key components in aerospace coatings. Carbon nanotubes are used as light absorbers to improve printing efficiency. Utilized in silicon-carbon-nitrogen ceramic coatings, carbon nanotubes aid in generating a stronger ceramic material that is used in areas where strong thermodynamic and stable physiochemical properties are required. Carbon nanotubes control the photocuring thickness. Structural adhesives such as self-adhesive tapes (SATs) are in high demand in aerospace. SATs thin films are comprised of epoxy acrylate copolymers with acrylate-based modifiers. Addition of modifiers, increases adhesion and strength of these thin films.

5. PROBLEMS TO SOLVE

5.1 ADDITIVE MANUFACTURING

One of the problems that still exists in Additive Manufacturing includes finding a photopolymer that can be cured by UV or visible light without the addition of a photoinitiator or addition of cross-linking agents. Often, the addition of such intrinsically important agents for photopolymerization will affect the yield and cause prolonged periods of purification for removal of them upon polymerization. As a result, specific
features take longer time to achieve at a higher cost. Developing a resin that can avoid addition of anything other than the oligomers or monomers, while projecting durability or flexibility, is an enormous potential and will solve time constraints and enhance the usage of resin for substitution of other substrates such as metals, toxic plastics, or endangered species of wood. Enhanced features can be strived for, and extrusion of surfaces can create a lightweight product.

5.2 AUTOMOTIVE

Some of the major problems that currently exist in automotive industry are corrosion and fading of paint from sunlight exposure. Exposed to the elements from the environment such as humidity and salt concentration in the air from the oceans in the coastal areas, the metal frame of the transportation rusts faster and needs replacement. Currently, automotive body parts are made with carbon fiber since it is more lightweight than metal. However, carbon fiber is more expensive than steel and aluminum since its synthesis is time consuming and energy intensive. Aluminum is lightweight and is preferred over steel, however, it is easily oxidized and corrodes faster. Also, coatings that cover headlights are not durable and with exposure to sunlight, lose the translucency and fade to a yellowish color. Changes in the color lead to fading of intensity of headlight function at night, and thus lead to potential safety hazard of humans operating the transportation.  

5.3 AEROSPACE AND AVIATION
Aviation and aerospace are actively seeking and have a strong growing need for constituents that are durable, lightweight, and environmentally friendly. There is a movement to move away from dense metals to be used in preparation of framework and parts for aviation. Just like in automotive industry, steel, which has robust functionality but is heavy in mass, is being substituted with lighter material such as carbon fiber, high performance epoxies or aluminum. Aluminum is lightweight but is prone to corrosion, while carbon fiber is prone to cracking and has lower durability. Placing an additive to epoxies increases the risk of lower yields and undesired byproducts that will need to be purified. Photopolymerization will aid with durability and longevity to expand lifetime of parts to reduce cost. Also, creating lighter parts will increase flight hours of airplanes and decrease weight limitations that currently exist. Secondly, solvent based coatings release VOCs and it is ongoing research to minimize outgassing into the environment.¹⁸

6. FURTHER DIRECTIONS

The photopolymerization of pigmented or highly filled thiol-epoxy thick composites remains a challenge due to the light screening effect derived from the competitive absorption, reflection, and scattering of the pigments or functional fillers.⁸⁵

Additionally, the market is globally striving for environmentally friendly products. Changing the chemistry of the monomers or oligomers or the process of polymerization
itself will yield a difference. Products will form with minimal or no outgassing. Plastics will become more biodegradable. Diminishing the corrosion by substituting for lightweight material, will expand the scope of how the product can be used and expand the longevity. One may ask how this can be done? There is a drive to create a product with simple chemistry, easy to handle, and with unique properties that will not degrade. Rather, this product will be a multimarket product due to many overlapping markets.

In Additive Manufacturing, there are several areas that need improvements. In the seven categories that make up the industry of Additive Manufacturing, there are several limitations that include durability while maintaining flexibility. Also, the type of material used in each subcategory is limited and further research is needed to broaden the specificity.\textsuperscript{4, 62, 63}

In Automotive industry, there is an increasing demand for vehicles with minimal maintenance and those that are light weight. By increasing aesthetic appeal of vehicles and decreasing maintenance cost, the automotive coatings market share will increase exponentially.\textsuperscript{13} Decreasing the weight of the vehicle will also increase cargo weight capacity.

In Aviation and Aerospace, there is currently a big emphasis on reducing the downtime of the planes. Airlines prefer advance coating solutions that will increase flight hours and reduces maintenance.\textsuperscript{18} Since solvent-based paints are easy to handle but have unwanted byproducts, research, and development of photopolymerized coatings that will act as a substitute, is a huge new segment for competitiveness in this market.
7. CONCLUSIONS

Photopolymerization is a process with a high impact on many industries. There are several categories of photopolymerizations, and each category generates a unique polymer with enhanced features. These features dictate which market is influenced by specific photopolymerization. Many industries are related by the products generated by a specific photopolymerization. For example, resin that is generated in Additive manufacturing is used in Automotive industry as well as in Aerospace and Aviation.

Each industry generates a multi-million-dollar market with projections of high percentage for growth and expansion. Photopolymers aid in production of coatings and other hybrid materials that are environmentally benign and increase production time without diminishing the quality of the manufactured material. Moreover, utilization of photopolymers allows solvent-free systems with the quick curing necessary for time constraints, in maintenance and repair.

Due to research limitations, many areas in different industries still have shortcomings that need to be addressed.
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