CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

In this chapter, the basic concept of biopolymers is introduced. Polyhydroxyalkanoates (PHA) and its derivative, polyhydroxybutyrate (PHB) are discussed including their properties, synthesis route, advantages and challenges in the application. Then, additive manufacturing or 3D printing especially vat-photopolymerization part are also being explained and discussed. Lastly, the implementation and utilization of 3D printing in medical sector is also discussed at the end of this chapter.

2.2 Biopolymers

Biopolymers are polymeric substance that are biologically or naturally synthesized from living organisms such as plants and microorganisms (Velde & Kiekens, 2002). They are made up from repetitive blocks composed of several monomers such as polysaccharide, protein and nucleic acid that are derived from renewable resources (Lisitsyn et al., 2021). They can be categorized into three major classes which are natural, synthetic and microbial derived polymers (Ibrahim et al., 2019). In other aspect of categories, they could also be distinguished from their polymer backbone; polysaccharides, polyamides, polycarbonates, vinyl and polyesters polymers. There are various ways to segregate types of biopolymer. Since they are produced from renewable resources, they are the most promising alternatives to the petroleum-based polymers due to their advantages such as biocompatible, abundance in nature and non-toxic (Baranwal et al., 2022). Sustainable management and efficient usage of natural resources have been envisioned by the United Nations by 2030 which is aligned with the 12nd of Sustainable Development Goals (SDGs); Responsible consumption and production (Lenzen et al., 2022). Thus, the utilization of biopolymers in accordance with the SDGs to promote greener environments.

2.2.1 Classification of Biopolymer

Biopolymers can be categorized into several ways based on different perspectives. They can be sorted according to their origin, type of monomers, degradability, and polymer backbone. Figure 2.1 shows different classification of biopolymers based on their origin.

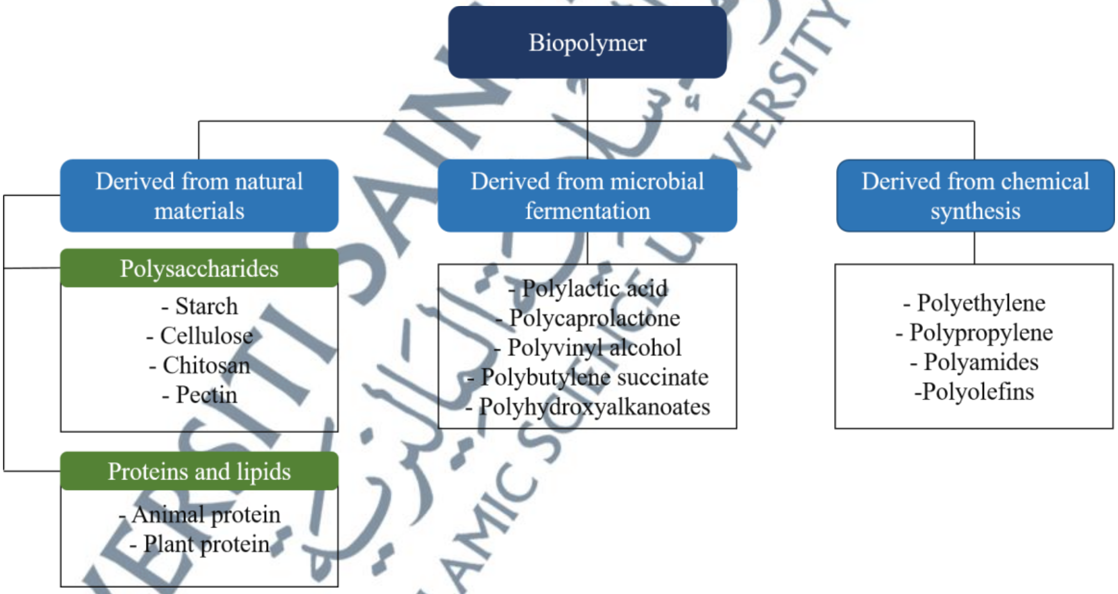


Figure 2.1: The Classification of Biopolymer (Ibrahim et al., 2019).

2.2.2 Polyhydroxyalkanoates (PHA)

Among the ideal candidates of biopolymers, polyhydroxyalkanoates (PHA) have gained significant interest among researchers to explore and utilize this polymer. PHA are microbial polyesters that are derived from specific microorganisms under certain circumstances such as deprivation of nutrients and excess of carbon sources (Riaz et al., 2021). The survival mechanism of this bacteria or microbes urges them to produce PHA for their energy storage purposes. They are many types of PHA producing bacteria such as Azotobacter, Bacillus and Pseudomonas where each family of these microorganism creates different kinds of PHA (Yoshida et al., 2022; S. M. Lee et al., 2021; Sabarinathan et al., 2018). They are being classified into three major categories which are short-chain length, medium-chain length and lastly long-chain length; consisting of 3-5 carbons, 6-14 carbons, and more than 15 carbons respectively (D. Li et al., 2021).

2.3 Polyhydroxybutyrate (PHB)

Polyhydroxybutyrate (PHB) that falls under scl-PHA family is a typical type of PHA which is being studied progressively among researchers due to its mechanical properties that resemble polypropylene (PP) and polyethylene (PE) that are derived from petroleum-based (McAdam et al., 2020). Generally, PHB is created in the cell of PHB-producing microorganisms when subjected to deficient of nutrients and excess of carbon sources whether in positive or gram-negative bacteria (Susianingsih et al., 2020). The extraction and recovery of this polymer have been greatly discussed as the selection of bacteria and extraction approaches used could synthesize different forms of PHB. Figure 2.2 shows the chemical structure of PHB.

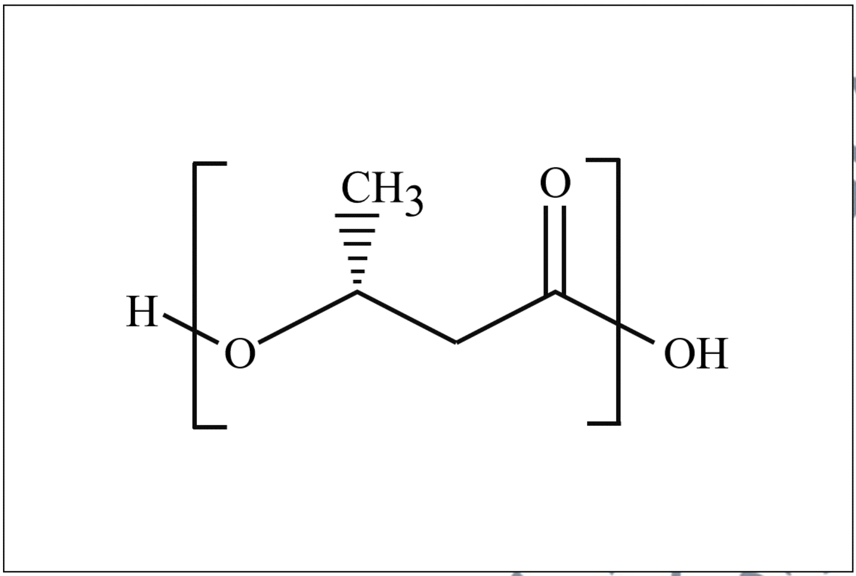


Figure 2.2: The Chemical Structure of PHB.

2.3.1 Properties of PHB

PHB is considered as highly crystallized polymer due to its special stereo-chemical regularity of structure, having up to 70% of crystallinity (Smith et al., 2020). This unique characteristic is portrayed by its excellent mechanical properties by having modulus of elasticity ranging from 3 to 3.5 GPa and tensile strength about 20 – 40 MPa (Yeo et al., 2018). The brittleness occurs due to the secondary crystallization during inherent physical aging (Rastogi & Samyn, 2020). It has also low tensile strain ranging from 5–7%, attributed to the large spherulites formation during the slow crystallization process, thus, could easily lead to crack and fracture (Majerczak et al., 2022). PHB could also degrade at temperature ranging from 170 – 200 °C, hence limiting the thermal processing temperature (Silva et al., 2022). The methyl functional group (CH_3) and ester linkage group (-COOR) that are present in the molecular structure of PHB contributed towards its thermoplastic, hydrophobic, high crystallinity and brittle characteristics (Das et al., 2021). Table 2.1 shows the comparison of properties between PHB, PP and LDPE.

Table 2.1: Properties of PHB, PP and LDPE.

Properties	PHB	PP	LDPE
Tensile strength (MPa)	20 – 40	30 – 35	0.4 – 1.2
Elongation at break (%)	5 – 7	330 – 350	200 – 800
Young’s modulus (GPa)	3 – 3.5	3 – 4	0.2 – 0.6
Impact strength (kJ/m2)	3	8.8	15 – 50
Density (g/cm3)	1.24	0.946	0.910 – 0.940
Glass transition (°C)	−5 to 5	−25	−100 to −80
Melting point (°C)	170 – 200	150 – 171	100 – 130

2.3.2 Synthesis Route of PHB

There are three synthesis routes in the production of PHB which are: ring-opening polymerization by utilizing β-butyrolactone reagent, natural/transgenic plants and bacterial fermentation (Dobrogojski et al., 2018). The synthesis of PHB involves three main stages that include different enzymatic reactions. Initially, the condensation process occurs when two acetyl coenzyme A are combined together to form acetoacetyl-CoA, catalyzed by β-ketothiolase (PhaA). Next, acetoacetyl-CoA undergoes hydrogenation process by PHA-reductase enzyme (PhaB) to create PHB monomer which is (R)-3-hydroxy-butyryl-CoA. Lastly, PHB monomer starts to combine together through polymerization process, catalyst by the PHA-synthase enzyme (PhaC) to form PHB polymer (Yu, 2006). The illustration of the whole process is shown in Figure 2.3.

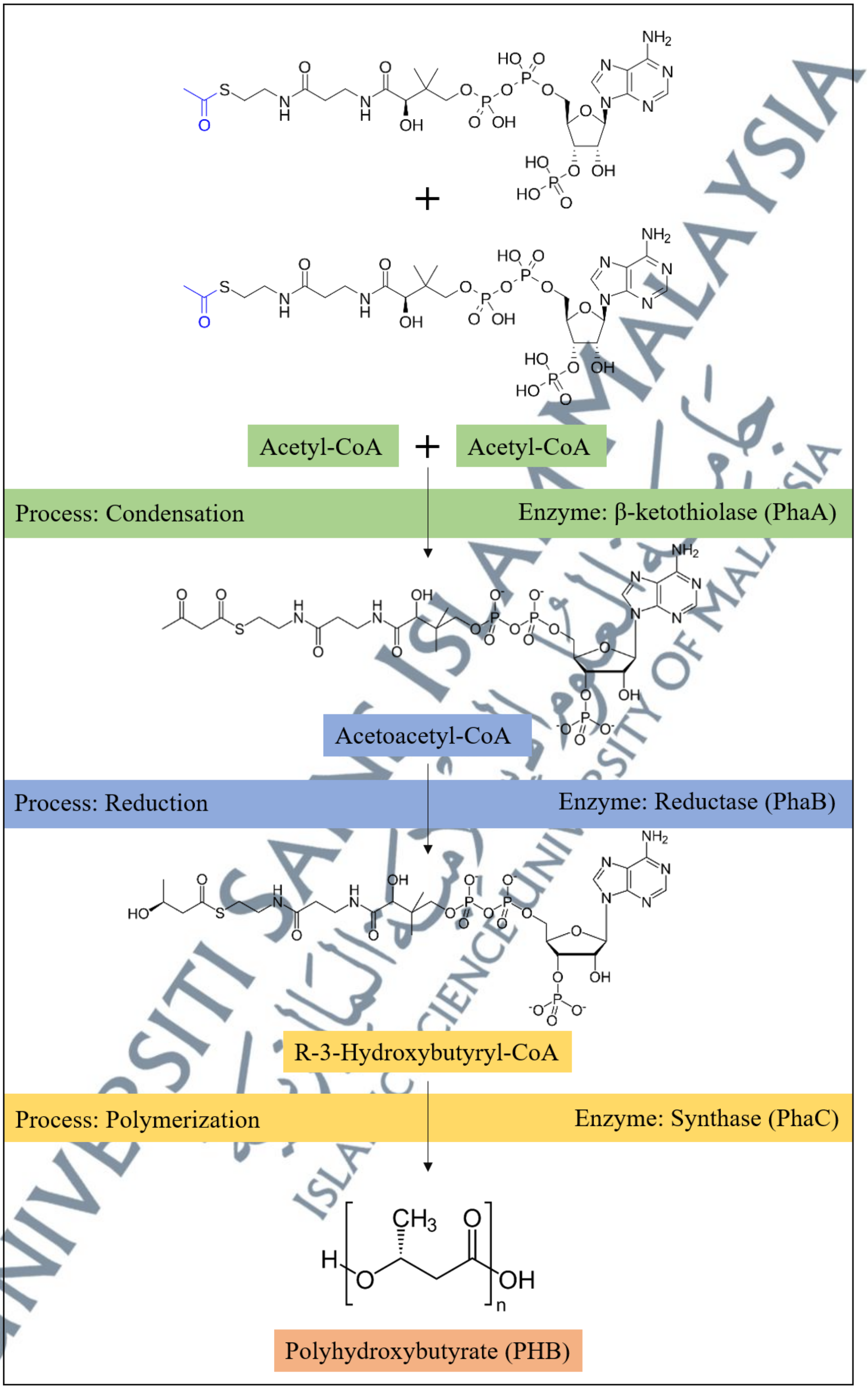


Figure 2.3: The Synthesis Route of PHB.

2.3.3 Advantages of PHB

Over the decades, PHB has gained significant interest among researchers and industries attributed to its versatility in application as it has many benefits. The biodegradability and biocompatibility of PHB are the dynamic duo of its characteristic that entice scientist to fully utilize this biopolymer. PHB could undergo both aerobic and anaerobic degradation (Iglesias-Montes et al., 2021). PHB degrades much faster under anaerobic conditions compared to aerobic. According to a previous study, PHB were degraded anaerobically around 83% in just 77 days and meanwhile aerobic degradation took up to 177 days (García-Depraect et al., 2022). The biocompatibility of PHB has been proven as it does not trigger any immune response to the human body (Bonartsev et al., 2019). Thus, it has been utilized and applied in the biomedical application such as vascular grafting, drug delivery and cartilage tissue engineering (Pulingam et al., 2022).

Apart from that perfect combination, the production of PHB by PHB-producing microorganism could be supported by the renewable and sustainable resources for their carbon sources intake. PHB could be produced in an event where nutrients are lacking such as nitrogen, phosphorus and oxygen, with the presence of excess carbon sources such as glucose and fructose (Jiang et al., 2016). They can be extracted from the food waste such as sugarcane bagasse, rice straw and wheat (Saratale et al., 2021; J. Y. Lee et al., 2023; Soto et al., 2019). Moreover, the utilization of bioreactor system in PHB production by using bacterial fermentation has at least reduced the environmental impacts compared to petrochemical-based plastics (Manikandan et al., 2021).

2.3.4 Challenges in the Application of PHB

Apart from all the benefits shown by PHB, the utilization of this polymer at the industrial-scale production is still restricted due to some obstacles. The production cost of PHB is still higher compared to the conventional polymer as it is still in its infant stage for the mass production (Aydemir & Gardner, 2020). Despite all of these disadvantages, developed countries such as German, India and China has taken a proactive measure to produce PHB for commercialization purposes since they can see huge potential of this polymer in the future (Bhalerao et al., 2020).

PHB is considered as a highly semi-crystalline polymer. It is a material of high stiffness and low deformation capacity. The presence of large spherulites in pure PHB, has initiated the tendency of crack and fracture to happen during secondary crystallization. The continuous crystallization phase has restricted the molecular segments, resulting molecular conformation changes are difficult. In conjunction with that issues, a study was conducted to study the correlation between crystallinity, morphology and mechanical properties of PHB (El-Hadi et al., 2002). The findings found that smaller spherulites enhance the mechanical properties with the incorporation of nano-clay as nucleating agent (Mohamed El-Hadi, 2014).

The utilization of PHB is also limited due to its narrow thermal processing window. The thermal instability of PHB is attributed from the ester linkage bond that degrades by random scission above its melting point typically between 170 – 200 °C (X. Li et al., 2023). PHB exhibits low mechanical performance compared to other petroleum-based plastics such as high density polyethylene (HDPE), polyester and polytetrafluoroethylene (PTFE) (Turco et al., 2021). Thus, it limits its applications in high-stress environments. Lastly, PHB has poor abrasion resistance compared to other biodegradable polymer (Karbasi et al., 2022). Thus, it cannot withstand with the wear and tear during the usage since it can lead towards surface scratching and cracking.

Various ways have been devised to toughen the PHB so that it can be explored further for desired applications including drawing and thermal treatment, blending with materials from natural resources and synthetic polymers, inclusion of natural fibers or rigid fillers and lastly modification by chemical functionalization as illustrated in Figure 2.4 (Yeo et al., 2018). However, blending is much convenient and economical-approach compared to other techniques (Abdelwahab et al., 2012). It is a process of combining different types of existing polymers aiming to achieve an intermediate or better properties while preserving the major characteristics of the two pure components. Nevertheless, the blending technique could be integrated with additive manufacturing methods can be a good solution to improve the mechanical performance of PHB blend.

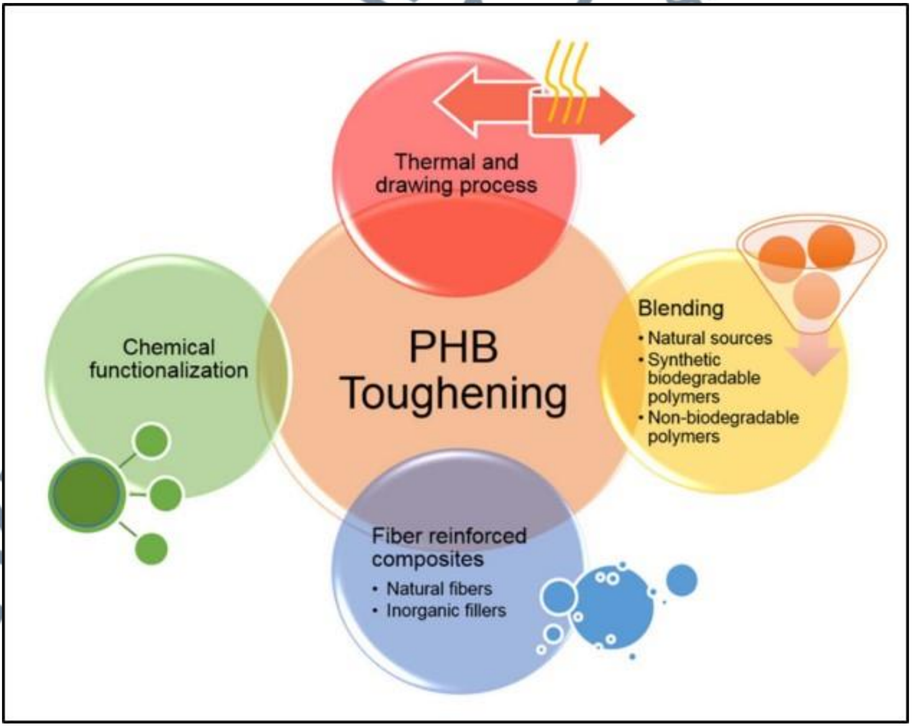


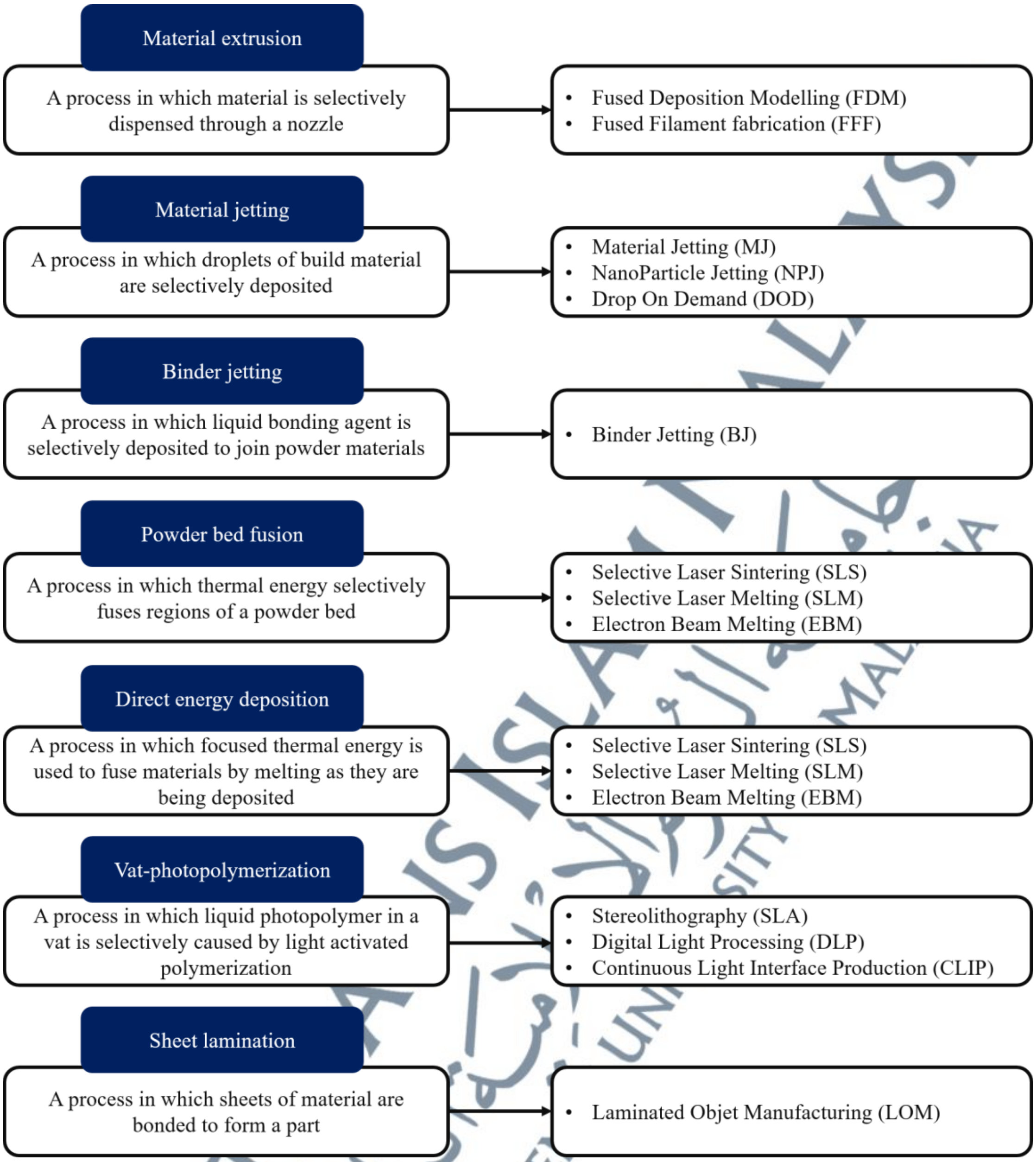
Figure 2.4: Different of PHB Modification Techniques (Yeo et al., 2018).

2.4 Additive Manufacturing

Additive manufacturing (AM) is defined as a continuous process of layering materials on top of each other to form a 3D structure by using a control aided design (CAD) software (Sun et al., 2021). AM or better known as 3D printing was introduced in the early 1980s. Chuck Hull was the first person that invented stereolithography (SLA) which was the first commercial of AM technology in 1983. He coined the word stereolithography in his patent application entitled “Apparatus for production of three-dimensional objects by stereolithography” on 8th August 1984 before being approved on 11st March 1986.

2.4.1 Classification of Additive Manufacturing

AM process could be made suitable for various application due to its versatility of techniques using a variety of materials such as metallic, ceramic, and polymeric materials in different physical states, for instance, solid, liquid and viscoelastic. Therefore, it could be classified in different perspectives according to the context. American Society for Testing and Materials (ASTM) has formulated a set of standards that categorized AM into seven classes based on the methodology involved during the fabrication of 3D structure. The list breaks down into materials extrusion, material jetting, binder jetting, powder-bed fusion, direct energy deposition, sheet lamination and vat-photopolymerization. Figure 2.5 shows the seven categories of AM process and their technologies.



Material extrusion
A process in which material is selectively dispensed through a nozzle
- Fused Deposition Modelling (FDM)
- Fused Filament fabrication (FFF)

Material jetting
A process in which droplets of build material are selectively deposited
- Material Jetting (MJ)
- NanoParticle Jetting (NPJ)
- Drop On Demand (DOD)

Binder jetting
A process in which liquid bonding agent is selectively deposited to join powder materials
- Binder Jetting (BJ)

Powder bed fusion
A process in which thermal energy selectively fuses regions of a powder bed
- Selective Laser Sintering (SLS)
- Selective Laser Melting (SLM)
- Electron Beam Melting (EBM)

Direct energy deposition
A process in which focused thermal energy is used to fuse materials by melting as they are being deposited
- Selective Laser Sintering (SLS)
- Selective Laser Melting (SLM)
- Electron Beam Melting (EBM)

Vat-photopolymerization
A process in which liquid photopolymer in a vat is selectively caused by light activated polymerization
- Stereolithography (SLA)
- Digital Light Processing (DLP)
- Continuous Light Interface Production (CLIP)

Sheet lamination
A process in which sheets of material are bonded to form a part
- Laminated Objet Manufacturing (LOM)

Figure 2.5: Additive Manufacturing Classification Based on ASTM F-42 (Zhang et al., 2018).

2.5 Vat-photopolymerization

Vat-photopolymerization is the first ever 3D printing process that had been introduced by Dr. Hideo Kodama in 1980s, who published an article regarding the rapid prototyping process using photosensitive resin (Gupta et al., 2019). The exposure of the ultraviolet light towards the liquid resin that is contained in a vat/tank induced the polymerization to occur. Thus, the resin hardened to form a 3D structure. However, this process is divided into three systems depending on their mechanism and light sources such as stereolithography (SLA), digital light processing (DLP) and continuous liquid interface production (CLIP) (Yao et al., 2020).

2.5.1 Digital Light Processing (DLP)

Digital light processing (DLP) technology is equipped with the light source that can illuminate the surface layer of photopolymer resin all at once. This feature comes in to reduce printing time while preserving high resolution of printing, thus compensating its precedent technology which is stereolithography (SLA) (Bagheri Saed et al., 2020). The light source is projected at the bottom of the photopolymer resin that is contained in a vat/tank, followed by the dipping of the building platform continuously into the resin bath. These steps will be repeated layer by layer until a 3D structure is formed. The utilization of DLP-based 3D printing has become a norm in research field such as fabrication of customized dental model/molds, sculptures or figurines, electrically conductive objects and medical devices (Yoo et al., 2021; Liu et al., 2021). Figure 2.6 shows the illustration of DLP 3D printer.

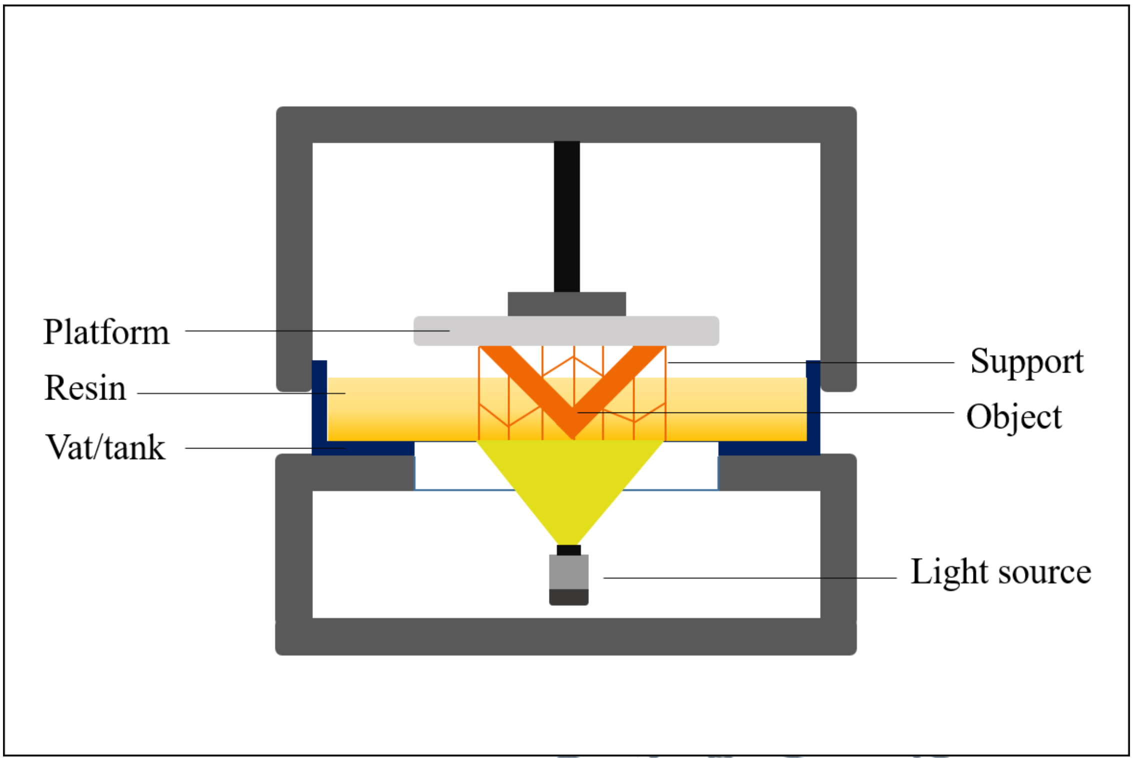


Figure 2.6: Illustration of DLP 3D Printer.

2.5.2 Continuous Liquid Interface Production (CLIP)

A group of innovators, led by Joseph DeSimone and his team, reported a new technique of 3D printing that has been patented under EiPi Systems that utilized photopolymerization to form a high resolution of 3D structure. CLIP operates by projecting a series of cross-sectional images below a photopolymer resin that only allows ultraviolet light to pass through an oxygen-permeable membrane called UV-transparent "window". Above the window, a region called the dead zone is located, where it maintains the liquid interface from attaching to the window. The curing part of the 3D structure is drawn out slowly from the photopolymer resin bath (Rungrojwittayakul et al., 2020). Figure 2.7 shows the illustration of CLIP 3D printer.

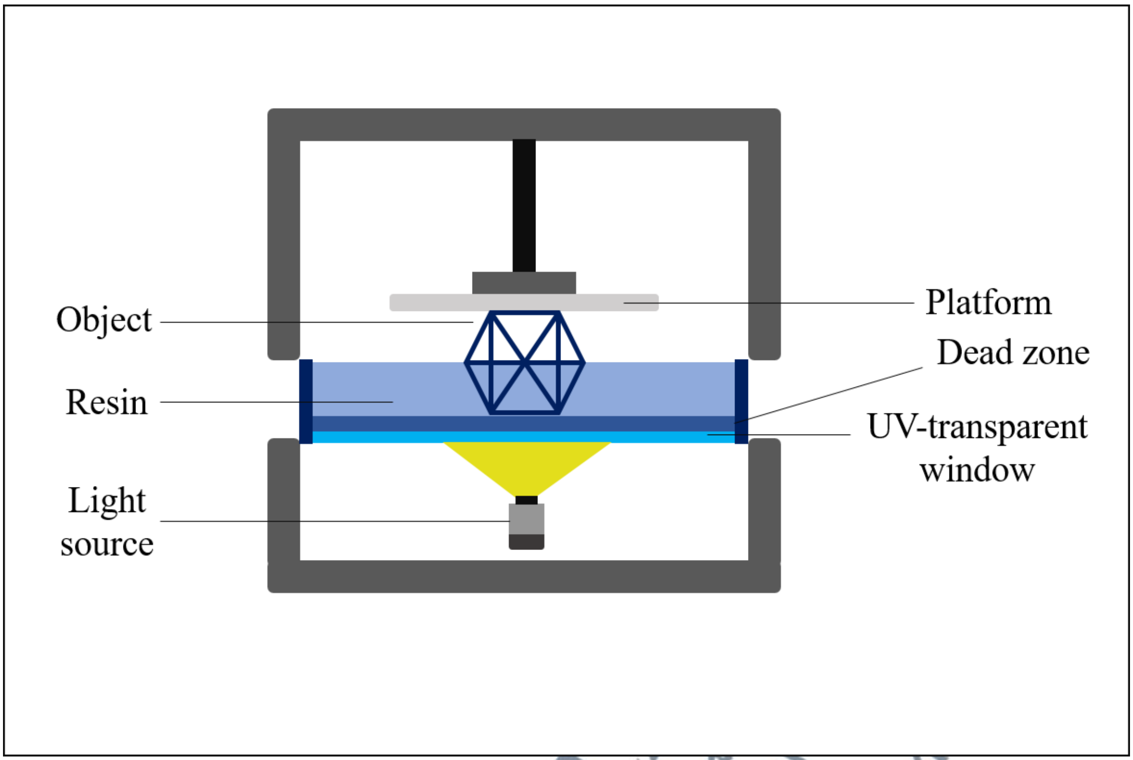


Figure 2.7: Illustration of CLIP 3D Printer.

2.5.3 Stereolithography (SLA)

Stereolithography (SLA) belongs to the family of vat-photopolymerization that uses UV light, as mentioned before, to create a 3D structure. It comprises of several components including 3D printer, photopolymer resin and computer-aided design (CAD) file. The UV laser is emitted onto the surface of photopolymer vat according to desired 3D CAD file or familiar with standard-triangulated language (STL) (Norjeli et al., 2022). The wavelength of laser for SLA 3D printer emits, typically in the UV spectrum, ranging from 380-405 nm (Smirnov et al., 2022). However, SLA 3D printers are commonly equipped with 405 nm wavelength of laser since the optics are much cheaper than the shorter wavelength due to their availability (Riccio et al., 2021). However, shorter wavelength can give higher precision and accuracy (Sanli et al., 2022). Aside from its pre and post-processing that require large capital, another drawback of this kind of techniques is their reliance on the selection of photopolymer resin as the ability to absorb the photon's energy where it must match with the properties of the material itself (Safaee et al., 2022). Figure 2.8 shows the illustration of SLA 3D printer.

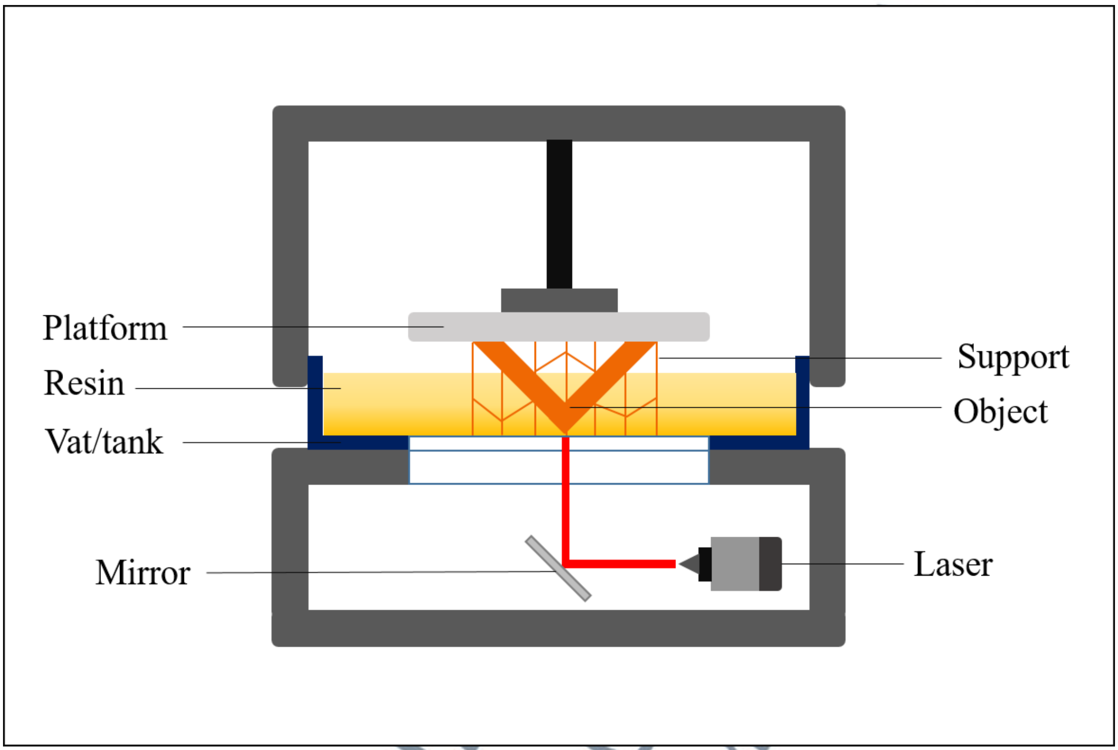


Figure 2.8: Illustration of SLA 3D Printer.

2.6 Photopolymerization Mechanism in Vat-photopolymerization

The polymerization mechanism involves the selective curing of a liquid photopolymer resin to solidify it and form a three-dimensional object. The photopolymer resin contains specialized molecules called photoinitiators, which are sensitive to the UV light and play a crucial role in the polymerization process. Thus, the mechanism of photopolymerization typically depends on the type of monomers and photoinitiators used. Therefore, the photopolymerization mechanism is divided into two types which are cationic photopolymerization and free radical photopolymerization (Sangermano et al., 2018; Metral et al., 2019).

2.6.1 Cationic Photopolymerization

Cationic photopolymerization is a process of transferring charge to a monomer when light irradiation is present, making it unstable/reactive with other monomers, thus a chain growth of polymerization could occur (S. Liu et al., 2021). In 1977, Crivello discovered that cationic photopolymerization occured when diaryliodonium salts (Ar2MtXn−) generate high acidic solutions upon being irradiated with UV light. All the steps of this mechanism is similar with the radical system but this system utilize different kind of photoinitiator and monomeric materials (Hola et al., 2020). During cationic photopolymerization, once the acid species have been generated, it is still active even if light irradiation has been stopped (Pierau et al., 2022). It is the most significant difference between radical photopolymerization. Volume shrinkage is the fatal weakness for photopolymerization because it could induce strong internal stress which led towards deformation of materials. However, cationic photopolymerization has proven to has lower volume shrinkage compared to the free radical photopolymerization.

Cationic photoiniator are usually in form of salts such as sulfonium and iodonium (Kocaarslan et al., 2019). They are comprised of cationic and anionic pair where each one has specific role in the polymerization reaction. The cationic parts is responsible for the absorption of UV radiation while anion determines the strength of acid formed during the photolysis. As the cationic photoinitiator absorbs UV radiation, the initiator molecules will undergo a series of decomposition reactions and will be converted into a strong acid species, either a Lewis or Brönsted acid. The ring opening polymerization takes place by protonation of the monomer, followed by the addition of further monomer molecules, resulting in a chain growth reaction. A schematic process of cationic photopolymerization of an epoxy monomer in the presence of a generic diaryliodonium salt is shown in Figure 2.9.

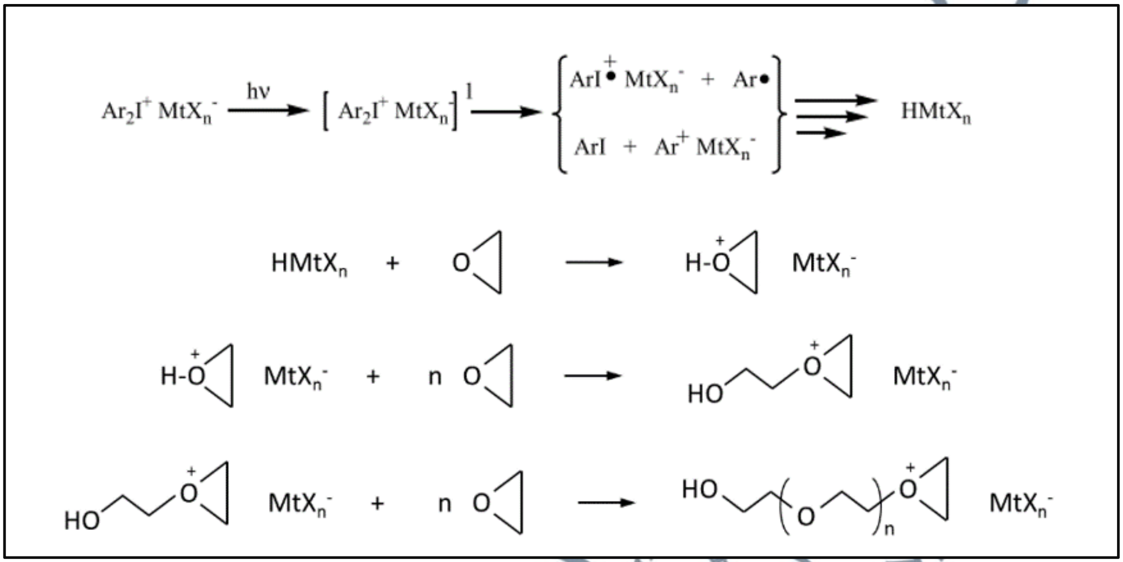


Figure 2.9: The Mechanism of Cationic Photopolymerization (Vitale et al., 2014).

2.6.2 Free Radical Photopolymerization

Free radical photopolymerization (FRP) is a synthesis route of cross-linking between monomers and oligomers to attain a polymeric substance of unsaturated compounds by using light irardiation to initiate the polymerization (Metral et al., 2019). The mechanism only applies to those monomers that have olefinic double bonds (Basbug Alhan et al., 2020). There are three fundamental steps in this mechanism which are initiation, propagation and termination. During the formation of free radical, light irradiation will be bombarded to the photoinitiator to create reactive species. Then, these species will react with the carbon double bonds of unsaturated compounds (oligomers). During the propagation step, the polymerization starts to occur as the reactive species will continue to propagate and react with another oligomer to create a new radical. Finally, the process of cross-linking will be stopped at termination process when two oligomer chains react with each other (Bagheri & Jin, 2019). Acrylate and methacrylate monomers are typically found in the free radical photopolymerization (Nowak et al., 2017). Figure 2.10 shows the mechanism of free radical photopolymerization.

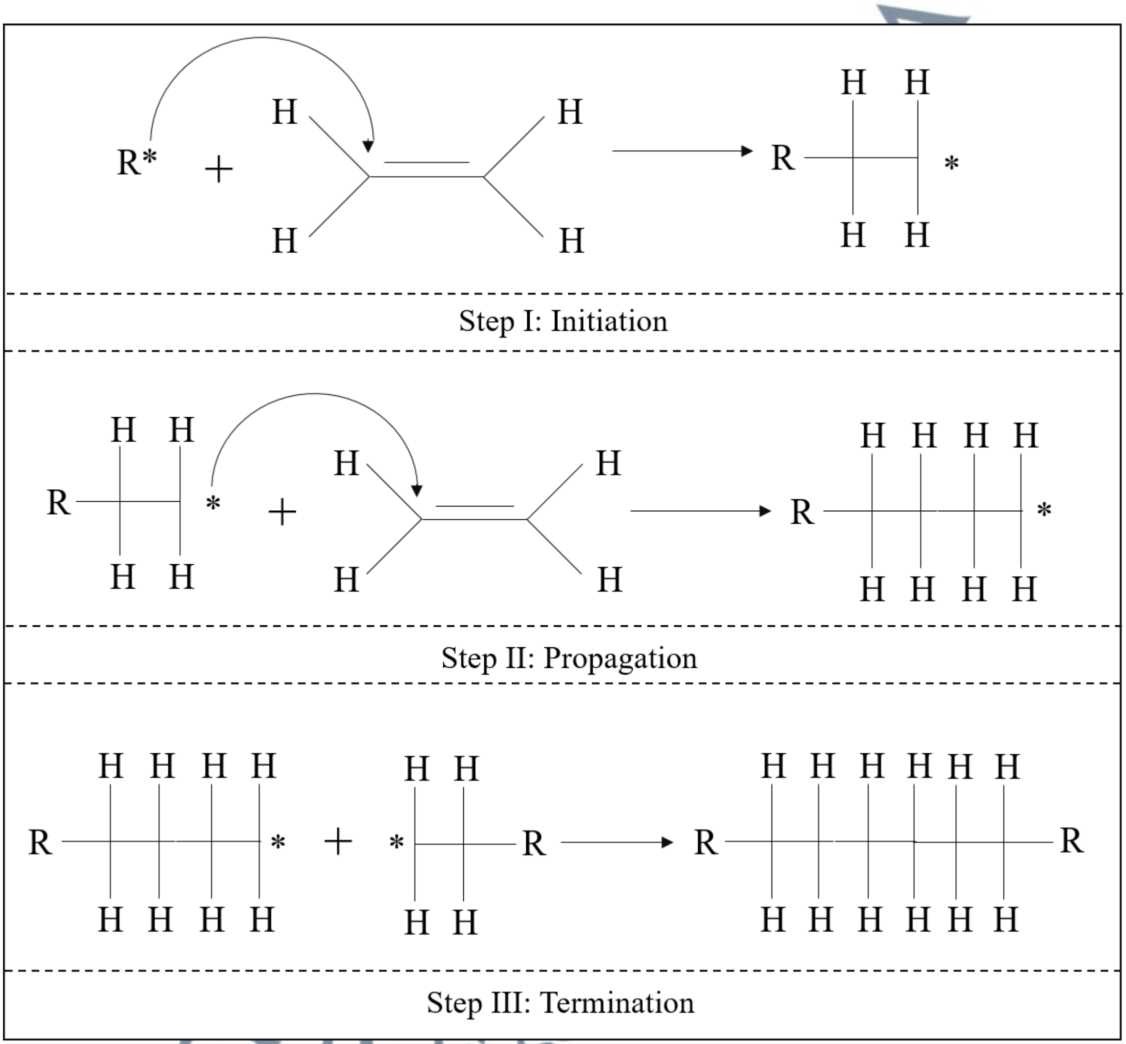


Figure 2.10: The Mechanism of Free Radical Photopolymerization.

2.6.3 Monomers for Photopolymerization

Resin formulation that are being commercialized in the market offer variety of low and high molecular weight of multi(meth)acrylates and monoacrylates. They exhibit their own properties and both are suitable for certain applications. Briefly, polymethacrylates typically portray higher tensile stress, lower tensile strain and much stiffer compared to polyacrylates attributed from its methyl group that cause steric hindrance (Raszewski et al., 2022). Contrary, the latter one commonly displays lower tensile stress, higher tensile strain and much flexible (Snyder et al., 2007). The most commonly used monomer/oligomers in 3D printing is bisphenol A-glycidyl dimethacrylate (Bis-GMA), bisphenol A ethoxylated dimethacrylate (Bis-EMA), urethane dimethacrylate (UDMA) and triethylene glycol dimethacrylate (TEGDMA) (Borges et al., 2019).

Bis-GMA has several significant benefits among others including relatively low shrinkage polymerization, higher modulus and reduced toxicity due to lower volatility (Pratap et al., 2020). However, it has lower degree of double bonds conversion (DC) and higher viscosity, thus the mixing with other monomers that less viscous is required such as reactive diluents (Sarosi et al., 2021). For instance, TEGDMA is typically used for this objective to compensate the higher viscosity and also increase the DC (Jagtap & More, 2022). Conversely, the addition of TEDGMA causes the increasing of shrinkage and reduced mechanical performance (He et al., 2019). Bis-EMA has been developed to overcome both monomers' flaws aforementioned, which led to a lower viscosity, higher mechanical properties and increasing in DC (Perea-Lowery et al., 2021). However, the only thing that becomes a great concern is that the after-products degradation of Bis-GMA and Bis-EMA, is generate bisphenol A (BPA). BPA has been recognized to has an estrogenic effect towards human health (Barszczewska-Rybarek et al., 2020). BPA is almost everywhere in our environment and is released from common goods. It may enter human body through different routes including dermal and oral exposure or only through inhalation. Even though, the primary route exposure is through dietary exposure, direct paper contact, toys and medical devices against skin through non-dietary exposure could not be simply ignored (Manzoor et al., 2022).

Hence, BPA free monomer has been formulated through research and development to avoid using substances that may trigger immune response. Figure 2.11 shows the humans exposure to BPA via different sources and exposed roots.

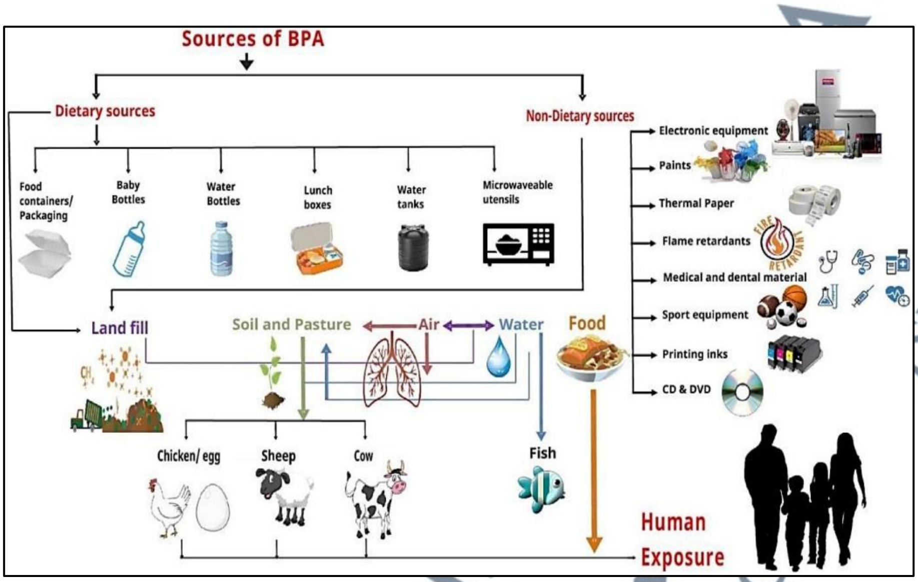


Figure 2.11: The Human Exposure to BPA via Different Sources and Exposed Roots (Manzoor et al., 2022).

Currently, urethane dimethacrylate (UDMA) has been introduced as the only commercial alternative to those BPA-based dimethacrylates (De Nys et al., 2021). Reactive diluents are still required even though the viscosity of UDMA significantly lower than Bis-GMA. However, UDMA can also be used alone in certain application. UDMA exhibits the highest mechanical properties such flexural strength and modulus of elasticity compared among other monomers instead of not having the highest degree of conversion (Szczesio-Wlodarczyk et al., 2021b). Typically, mechanical properties of polymer highly depend on the degree of conversion and 3D structure of polymer network. However, in UDMA, stronger hydrogen bonding formed by the urethane proton donor group contributes towards better mechanical performance (Marianela T.

Lemon, Melissa S. Jones, 2006). Table 2.2 shows the properties of Bis-GMA, Bis-EMA, TEDGMA and UDMA, meanwhile Figure 2.12 shows the molecular structure of each monomer.

Table 2.2: The properties of Bis-GMA, Bis-EMA, TEDGMA and UDMA (Gajewski et al., 2012)

Monomer	Molecular weight (g/mol)	Viscosity (Pa.s)	Degree of double bonds conversion (%)	Flexural strength (MPa)	Flexural modulus (GPa)
Bis-GMA	512	1200	34.5	72.4	1.0
Bis-EMA	540	0.9	75.5	87.3	1.1
TEDGMA	286	0.01	82.5	99.1	1.7
UDMA	470	23	72.4	133.8	1.8

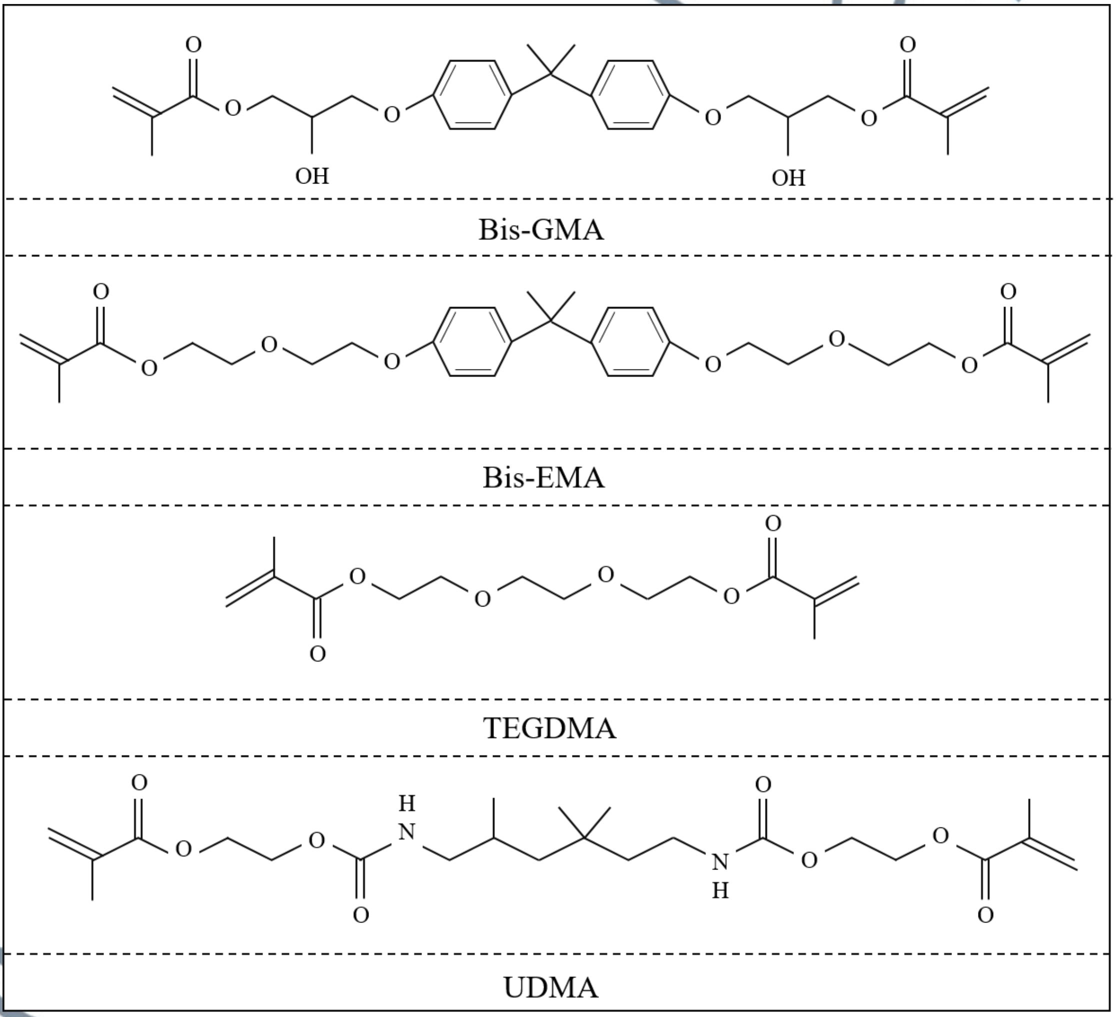


Figure 2.12: The Molecular Structure of Bis-GMA, Bis-EMA, TEDGMA and UDMA.

2.6.4 Degree of Double Bond Conversion (DC)

Photo-activation is the most used method to initiate the polymerization reaction of photopolymer resin. Degree of double bond conversion (DC) is defined as the percentage of carbon-carbon double bonds (-C=C-) converted to single bonds (-C-C-) to form a polymeric structure. During polymerization, monomers are transformed into complex polymer chains, although not all monomers will be converted into polymer structures, resulting in some unreacted monomers that remain as methacrylate pendant groups (Bin Nooh et al., 2021). This is because of the gelation, vitrification, immobilization and steric isolation that prevent the polymeric network (Moldovan et al., 2019). Several factors for instance, the chemical structure of monomer, photo-initiator concentration and polymerization conditions have a significant effect towards the final DC.

A high DC is associated with high polymerization shrinkage while a low DC is associated with low mechanical properties, low color stability and low biocompatibility (Yılmaz Atalı et al., 2022). Under ambient conditions, the limiting conversion due to vitrification of polymeric networks in resins based on commonly used dimethacrylate monomers can range from less than 50% to more 80% (Stansbury, 2012). Many studies have investigated the effect of filler load, size and geometry on DC of the resin-composite. DC was found to progressively decrease linearly with the increasing of opaque filler content (Alshali et al., 2013). This is attributed to the scattering effect of fillers on penetrating light during the photopolymerization. Table 2.3 shows the properties of dimethacrylate monomers and the limiting degree of conversion for corresponding dimethacrylate networks.

Table 2.3: The Properties and Limiting Degree Conversion of Corresponding Dimethacrylate Networks (Barszczewska-Rybarek, 2009).

Monomers	**Molecular weight**	**Concentrations of double bonds (mol/kg)**	**Viscosity (Pa.s)**	**Limiting degree of conversion (%)**
Bis-GMA	510.6	3.90	1200	39.0
TEDGMA	286.3	6.99	0.011	75.7
UDMA	470.0	4.25	23.1	69.6

2.7 Application of PHB via Stereolithography (SLA) in Medical Application

PHB is a very attractive class of biopolymers for the fabrication of tissue enginereed heart valves due to its biodegradibility, thermo-processability, biocompatibility, mechanical properties, non-toxicity, and environmental origin (Kovalcik, 2021). The creation of tissue-engineered heart valves is another extremely appealing application for PHB (G. Q. Chen & Wu, 2005). The primary factor is the diverse range of mechanical characteristics, which make it appropriate for both hard and soft tissues (Jana et al., 2014). It is also biodegradable, which makes it an excellent choice for making heart valves and other bio-based goods.

SLA printing is a promising and precise technique for creating tissue engineering scaffolds and other healthcare devices (Skoog et al., 2014). In fact, it serves as a helpful tool in orthopaedic and reconstructive surgery so that anatomical structures can be modelled, typically using computed tomography scanning (CT-scan) or magnetic resonance imaging (MRI), and fabricated using these techniques (Sodian et al., 2007). Therefore, it can be tested as a simulation before the surgery. For instance, a study reported that this biopolymer was used to fabricate a heart valve by utilizing SLA technology (Sodian et al., 2002). In order to produce a three-dimensional scaffold employing P4HB and polyhydroxyoctanoate (PHOH) biopolymers, they first used x-ray tomography to create the CAD model. Figure 2.13 depicts the process flow for the fabrication of SLA-printed subclavian artery. Eventhough there are not many research on SLA printing of PHB biopolymers in the literature, there was a succesful synthesis of PHB-based curable resin that could potientially print biomedical devices such as porous scaffolds and implants using SLA (Foli et al., 2020).

Figure 2.13: The Potential and Future Applications of the Additive Manufacturing of PHB.

2.8 3D Printed Arm Cast

There are many clinical trials that had been considered successful for the utilization of 3D printing technique to develop casts (Schwartz & Schofield, 2021). Casts are being used to encase an injured limb within a stipulated period of time during the rehabilitation process. It is also used to protect and support the broken bones and joints. A personalized hand-wrist-arm cast had been developed via Fused Deposition Modelling (FDM) 3D printer (Buonamici et al., 2020). The whole process started from data acquisition of patients' wrist to cast manufacturing which only required four to nine hours based on five case studies. Significant reduction period of time had been demonstrated by this technique. Contrary with the conventional cast that needs up to 48 to 72 hours just to ensure the plaster is fully dried (Guida et al., 2019). In addition, 3D printed arm cast offers great benefits such as lightweight, has good-ventilated structures, comfortability and washable (El Khoury et al., 2022). All of these advantages allow of 3D printed arm casts to act as an alternative towards conventional cast. Figure 2.14 shows the 3D printed arm cast was worn by a model patient.

Figure 2.14: 3D Printed Arm Cast in the Five Case Studies (Buonamici et al., 2020).

Another previous study has also prepared two qualitative questionnaires based on their initial experience among 10 patients with age ranging from 5 to 78 years (Y. Chen et al., 2020). 3D printed arm casts were developed and applied to them and the follow-up sessions were done within six weeks by the orthopedic surgeons. All of them opted for 3D printed arm cast instead of the conventional cast due to less pressure sores, no compartment syndrome and very comfortable even when they perform their daily tasks. Figure 2.15 shows the 3D printed arm cast fabricated using FDM 3D printer.

Figure 2.15: 3D Printed Arm Cast Developed using FDM 3D Printer (Y.-J. Chen et al., 2017).