

**DEVELOPMENT OF PHOTO-CURABLE PMMA-
BASED LIQUID RESIN: DISPERSIBILITY
STUDY OF GO AND AGO IN PMMA-BASED
LIQUID RESIN AND MECHANICAL ANALYSIS
OF COMPOSITES**

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**DEVELOPMENT OF PHOTO-CURABLE PMMA-BASED LIQUID RESIN:
DISPERSIBILITY STUDY OF GO AND AGO IN PMMA-BASED LIQUID
RESIN AND MECHANICAL ANALYSIS OF THE COMPOSITES**

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled “Development of Photo-curable PMMA-based Liquid Resin: Dispersibility Study of GO and AGO in PMMA-based Liquid Resin and Mechanical Analysis of The Composites”. I also declare that it has not been previously submitted for the award of any degree and diploma or other similar title of this for any other examining body or University.

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LIST OF SYMBOLS

°	Degree
°C	Degree Celcius
wt%	Weight percent
%	Percent
nm	Nanometer
cm ⁻¹	Wavenumber
mV	milli Voltage
mm	Millimeter
s	second

LIST OF ABBREVIATIONS

UV	Ultraviolet
3D	Three-dimensional
SLA	Stereolithography Apparatus
MMA	Methyl methacrylate
PMMA	Polymethyl methacrylate
ACH	Acetone cyanohydrin
GO	Graphene oxide
AGO	Aminated graphene oxide
PS	Polystyrene
PVA	Polyvinyl alcohol
PP	Polypropylene
AM	Additive manufacturing
CAD	Computer-aided design
CAM	Computer-aided manufacturing
DIW	Direct ink writing
SLS	Selective laser sintering
FDM	Fused deposition modelling
CLIP	Continuous liquid interface production
DLP	Digital light processing
LED	Light-emitting diode
IR	Infrared
H	Hydrogen
BF ₃	Boron trifluoride
N ₂	Nitrogen
ArF	Fluoro aryl group
-NH ₂	Amine group
ISO	International standard organization
PDI	Polydispersity index
DOC	Degree of curing

**PEMBANGUNAN RESIN CECAIR PMMA FOTO-BOLEH DIAWET:
KAJIAN KETERSERAKAN GO DAN AGO DALAM RESIN CACAIR PMMA
DAN ANALISIS MEKANIKAL KOMPOSIT**

ABSTRAK

Kefungsian amina graphene oksida telah dilakukan dengan pencampuran dan pemanasan graphene oksida dan ethylenediamine untuk menghasilkan amina graphene oksida. Analisis FTIR dijalankan untuk mengesahkan kejayaan tindak balas kimia antara graphene oksida dan ethylenediamine. Resin cecair PMMA foto-boleh diawet telah dihasilkan dengan hanya mencampurkan serbuk PMMA ke dalam cecair MMA dengan kaedah pemanasan. Kemudian, larutan tersebut dicampurkan dengan pemula-foto (Irgacure 819) dan campuran tersebut dapat dipolimerasi oleh sumber cahaya UV. Selepas itu, serbuk GO dan AGO dengan peratus berat 0.1%, 0.2% dan 0.5% ditambahkan ke dalam resin cecair PMMA yang mempunyai kelikatan paling rendah untuk kajian seterusnya. Hasil kajian menunjukkan bahawa untuk 0.2wt% GO, nilai positif potensi zeta resin PMMA adalah paling tinggi dan untuk 0.2wt% AGO, nilai negatif potensi zeta resin PMMA adalah paling rendah, menunjukkan koloidal PMMA paling stabil, dan kestabilan adalah disebabkan oleh tolakan elektrostatik antara zarah. Kemudian, 0.2% GO dan AGO dipilih untuk fabrikasi komposit PMMA di bawah sumber cahaya UV yang berbeza. Polimerisasi dilakukan dengan tiga sumber cahaya UV yang berbeza iaitu dengan pencetak resin 3D Creality Halot-one, ruang penyinaran UV dan Cure Spot. Walau bagaimanapun, hanya kaedah Cure Spot yang berjaya memolimerisasi resin cecair PMMA. Tahap penukaran monomer kepada polimer dianalisis untuk menilai tahap penyembuhan PMMA pada jumlah pemula-foto (Irgacure 819) yang berbeza. Kesimpulannya, jumlah Irgacure 819 yang lebih tinggi memberikan tahap penukaran monomer kepada polimer yang lebih tinggi. Selepas itu, ujian tegangan dilakukan dan hasilnya dibandingkan. Hasil kajian menunjukkan

bahawa kekuatan tegangan komposit PMMA/GO and PMMA/AGO lebih tinggi daripada PMMA, kekuatan tegangan GO lebih tinggi daripada AGO dan kekuatan tegangan 0.5 wt% Irgacure 819 lebih tinggi daripada 0.2 wt% Irgacure 819 pada jumlah PMMA dan MMA yang sama.

DEVELOPMENT OF PHOTO-CURABLE PMMA-BASED LIQUID RESIN: DISPERSIBILITY STUDY OF GO AND AGO IN PMMA-BASED LIQUID RESIN AND MECHANICAL ANALYSIS OF COMPOSITES

ABSTRACT

Amine-functionalization of graphene oxide (GO) was performed using ethylenediamine (EDA) under heating to produce aminated graphene oxide (AGO). The successfulness of AGO produced was confirmed by using FTIR analysis. The photo-curable PMMA liquid resin was successfully produced by simply mixing the PMMA powder into MMA liquid with some heating. Then, the solution was added with photo-initiator, Irgacure 819 at room temperature. After that, 0.1wt%, 0.2wt% and 0.5wt% of GO and AGO were dispersed into the most dilute PMMA liquid resin which then used to study the dispersibility of GO and AGO inside the PMMA liquid resin. The result showed that for 0.2 wt% of GO and AGO, the zeta potential value of PMMA resin was the highest, indicating the PMMA colloids were highly charged, and the stability was caused by the electrostatic repulsion between the particles. Then, 0.2 wt% of GO and AGO was chosen for fabrication of PMMA composites under different UV light source. The polymerization was done by three different method which were by Creality Halot-one 3D resin printer, UV irradiation chamber and Cure Spot. However, only Cure Spot method successfully polymerized the PMMA liquid resin. The degree of conversion was used to evaluate the degree of curing of PMMA at different loading of Irgacure 819. It can be concluded that the higher amount of photo-initiator gives higher degree of conversion at fix curing time and irradiation source. After that, tensile test was done and the result was compared. The result showed that tensile strength of PMMA filled with GO and AGO higher than unfilled PMMA, tensile strength of GO higher than

AGO and tensile strength of 0.5 wt% Irgacure 819 higher than 0.2 wt% Irgacure 819 at same amount of PMMA and MMA.

CHAPTER 1

INTRODUCTION

1.1 Background of Research

The definition of UV curing or photopolymerization is the photochemical process of generating crosslinked network with the presence of photo-initiators and specific UV light source. Since photo-initiator is very sensitive to light, when it irradiates with correct light source, it decomposed into reactive species which will react with monomer to form polymers.

UV curing mechanisms of monomer can be categorized into radical or cationic system, depending on the type of initiator used. For radical photopolymerization system, three main steps dominant which are initiation, propagation and termination. First, initiation start when the photo-initiator with the presence of monomer is irradiated with light source which produced free radicals. The free radicals react with monomer, forming reactive monomer. Then monomers continue to add and eventually form an end-active polymer. The termination steps can be done either by combination or disproportionation (Selimis & Farsari, 2017).

Nowadays, development of 3D printing technology or known as additive manufacturing become fast. This technique produces a 3D product by using layer-by-layer printing. Some of these technologies have move forward to utilise the UV curing technique to fabricate 3D printed product due to the fast production rate, dimension precise and solvent-free (Quan et al., 2020). One of the most common 3D UV curing technique is called the stereolithography (SLA) technique.

For SLA 3D printing, it involved selective curing of pre-deposited photopolymer using some type of light energy such as UV or laser beam. Two primary

configurations, namely vector scanning based and mask projection-based styles have been commonly used in practice. The vector scanning based system has relatively high precision (Lin et al., 2015). However, there is limitation when using SLA method such as polymer with long chains of conjugated π bonds causing intense absorption in the UV and visible region, and their complex redox chemistries, which may be incompatible with the reactive species formed during some photo-initiator decomposition (Athukorala et al., 2021).

Methyl methacrylate (MMA) is a colourless liquid which having methacrylic acid as carboxylic acid component and methanol as alcohol component. Various approach can be done to synthesis MMA such as acetone cyanohydrin (ACH) approach, AVENEER process, BASF process, etc (Fabrizio, 2010). MMA usually used for the production of polymethyl methacrylate (PMMA) which widely used in dentistry, biomedical application, optical application, etc.

MMA was widely used to produce methacrylic resins and plastics, impregnation of concrete to make it water-repellent, and also has uses in the fields of medicine and dentistry to make prosthetic devices and as a ceramic filler or cement. Besides, MMA also can be polymerized to PMMA which also has a vast of applications in wide range of field.

PMMA is widely used in different range of field due to the high clarity and lightweight properties. This makes PMMA suitable to be used for aircraft windows, indicator light covers, etc. Besides, PMMA also can be found in biomedical application, optical application, dentistry and other prosthodontic applications.

Irgacure 819 is an example of photo-initiator used to promote radical polymerization upon exposure to UV light. It is suitable to be used in white pigmented formulations, curing of glass fiber reinforced polyester or styrene systems. Due to the

photosensitivity of Irgacure 819 at longer wavelengths, it can be used with UV absorbers such as TINUVIN 400. Therefore, weather-resistant UV curable coatings can be achieved. Irgacure 819 also promote thick section curing when expose to UV lights. It also can be used in combination with other photo-initiators to reduce the curing time, photopolymerization rate, higher penetration depth (layer thickness).

Graphene oxide (GO) is a sp^2 carbon domain surrounded by sp^3 carbon domains which arranged in honeycomb lattice with oxygen containing functional groups (Bai et al., 2019). It appeared with black powder and is odourless. GO is well-known with its ability to disperse in many solvents. GO can be synthesized by either using Hummer's method or modified Hummer's method.

Due to the unique properties of GO, functionalization of GO has become an interesting topic for researcher. One of the common methods used by many researchers is amine-functionalized GO. Jeyaseelan *et al.* (2021), Caliman et al. (2018) and Yan et al. (2012) utilised diamine to react with GO, producing amine-functionalized GO at high temperature or with the presence of coupling agent.

There are various applications of GO nowadays due its unique mechanical, electrical, thermal, and optical properties (Tsagakias et al., 2017). Due to the hydrophilic properties of GO which allows for easy dispersion process in order to produce transparent conductive films on a substrate. Besides, monolayer of GO increases the transparency of thin films due to the lower concentration of GO in the dispersion and even has the potential to replace indium tin oxide transparent conductors.

Polymer nanocomposites with GO as filler such as polystyrene (PS), PMMA, polyvinyl alcohol (PVA), polypropylene (PP), polyester, polyurethane and polycarbonate, etc. also getting more attention from the researcher. This is because GO

as filler in nanocomposites show improved properties in term of elastic modulus, tensile strength, electrical conductivity and thermal stability at low loading of GO.

There are various methods to synthesize PMMA/GO nanocomposites. One of the most common methods used by researchers to synthesize PMMA/GO nanocomposites is via in situ radical polymerization as reported by Tsagkalias and co-workers (2017). The results showed that the presence of GO increased the thermal-stability and mechanical properties of the composites.

1.2 Problem Statement

Nowadays, UV curing of monomer has been applied in many industries such as dentistry, coatings, 3D printing technology and even in microelectronics industry. The viscosity of liquid resin are the key parameters for the successfulness of resin 3D printing technology. However, literature on GO/PMMA reinforced composites for 3D printing technology are still few.

Also, literature on optimum filler loadings and dispersibility of GO and AGO inside PMMA liquid resin are less, hence different loading of GO and AGO are examined to choose the best filler dispersity inside PMMA liquid resin. Markandan & Lai (2020) reported that with addition of graphene at very low concentration in the polymer, the mechanical properties of composites increased. Therefore, by incorporating GO and AGO in the PMMA, the mechanical properties of composite are expected to increase as reported by Wang and co-workers (2012).

For 3D printer using SLA technology, one of the major challenges is the light source is a moving laser beam (Quan et al., 2018). It is difficult to control the moving

laser beam inside the printer which affect its UV intensity and thus the printability of the printer.

1.3 Research Objectives

- i. To synthesize a simple UV-curable PMMA resin using photo-initiator
- ii. To evaluate the dispersibility of GO and AGO in PMMA-based liquid resin for UV curing process.
- iii. To investigate the UV curing process using different UV light source.
- iv. To investigate the mechanical and thermal properties of PMMA at different amount of PMMA and MMA.

1.4 Research Gap

Lin et al. (2015) studied about the GO content in the polymer resin showed better tensile properties with only 0.2% GO and is aligned randomly in the cross section of polymer. In this research, GO and AGO content is varied to evaluate the dispersibility of GO and AGO in PMMA liquid resin which influence the mechanical and thermal properties of the product.

Research done by Tsagkalias et al. (2017) which study the effect of GO on the reaction kinetics of MMA in situ radical polymerization via the bulk or solution technique. In this research, AGO and GO is used to study the mechanical and thermal properties of the PMMA/GO and PMMA/AGO composites.

The viscosity of PMMA-based resin is influenced by the amount of PMMA. According to Hata et al. (2021), PMMA-based resin with more than 50wt% of PMMA

powder is not suitable to be printed using 3D printer due to the high viscosity of the resin. Higher concentrations of PMMA tend to form aggregates in the resin, significantly increasing their viscosity (Hata et al., 2021).

1.5 Thesis Outlines

Chapter 1: Introduce the UV curing mechanism, SLA, methyl methacrylate (MMA), graphene oxide (GO), functionalization of GO, PMMA/GO composites.

Chapter 2: Discusses in details of the literature review of MMA, Irgacure 819, GO, functionalization of GO and photopolymerization mechanisms. The terminology of photo-initiator and photopolymerization mechanisms systems will be explain in this chapter.

Chapter 3: Provides the information about the materials and method used in this study which is suitable methodologies conducted based on certain standard for all conventional testing procedure with description of the sample characterization methods.

Chapter 4: Focus on the experimental result obtained throughout the experiment and discussion as well as the further elaboration on the problems encountering during experiment.

Chapter 5 Summarizes the significant findings in this study. Suggestions for future studies are also recommended.

CHAPTER 2

LITERATURE REVIEW

2.1 Photopolymerization Mechanisms

2.1.1 Radical System

Radical systems include three main steps of radical generation, initiation, and propagation. Radical will be generated under light irradiation, in which a photoinitiator or photoinitiator system is responsible to convert photolytic energy into the reactive species to initiate the photopolymerization. Most of the commercially available photoinitiators undergo Type I α -cleavage reaction and generate radical fragments under light irradiation (Ligon et al., 2017).

The mechanism of radical photopolymerization system involves three main steps which are initiation, propagation and termination. First, initiation start when the photoinitiator with the presence of monomer is irradiated with light source which produced free radicals.

Then, propagation starts at which the reactive initiator containing radicals will react with monomer to form reactive monomer. After that, monomers will continue to add and forming macro-radicals or known as end-active polymer.

Finally, termination step is which the interaction between two active polymer chain ends with an initiator containing radical. There are two possible route of termination which are combination or disproportionation. Combination occurs when two growing polymer chains terminated each other by an initiator fragment and form a single polymer molecule. Disproportionation occurs when hydrogen transfer and form two polymer molecules, one with saturated end and the other with an unsaturated

terminal end (Selimis & Farsari, 2017). Figure 2.1 shows the typical radical photopolymerization mechanism (Selimis & Farsari, 2017)

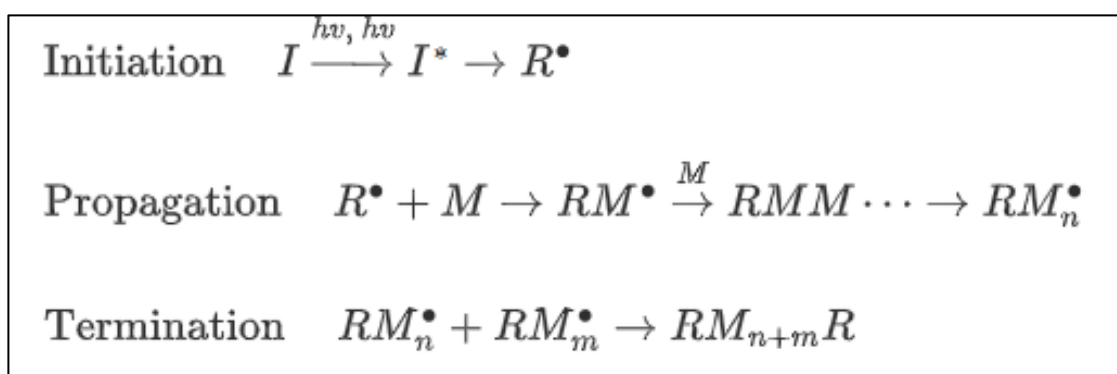


Figure 2.1 Typical radical photopolymerization mechanism (Selimis & Farsari, 2017)

Depending on the chemical structures of the photo-initiators, the incident light required to induce the cleavage differs in wavelength and intensity will be different. According to Bagheri & Jin (2019), methacrylate-based resins are widely used for radical polymerization system in 3D printing. However, they have certain limitations which are the tendency of shrinkage during polymerization, oxygen inhibition and auto-acceleration in the early phase of the free radical polymerization.

Thiol–Ene or Thiol–Yne system can solve the above limitation. This system uses the reactions of thiols with reactive carbon–carbon double bonds, or “enes”, via a radical step-growth polymerization or Michael-addition reactions. However, this system also having some limitations including product with poor shelf-life, bad odor and soft materials with low modulus product (Bagheri & Jin, 2019).

The Addition–Fragmentation Chain Transfer (AFCT) reagents can be incorporated into a methacrylate or thiol–ene systems to regulate the radical network formation. This result in the formation of homogeneous networks and hence provides high toughness networks. Besides, this system also shows less shrinkage stress, high

storage stability and less odor. However, due to inherent mechanism of AFCT-based polymerization, overall curing time proceed with retardation (Bagheri & Jin, 2019).

2.1.2 Cationic system

This system uses cationic photo-initiators of aryl iodonium salts or sulfonium photo-initiators which can decompose under UV light irradiation to produce reactive species. Example of monomer used in cationic photopolymerization systems are shown in Figure 2.2.

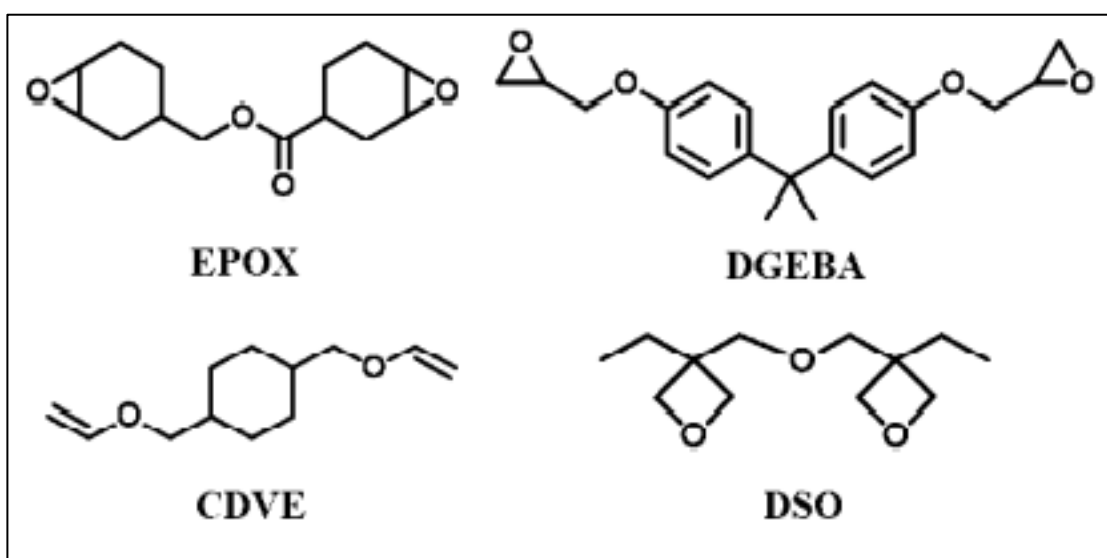


Figure 2.2 Monomers for cationic photopolymerization (Bagheri & Jin, 2019)

For cationic photopolymerization system, the initiator will decompose after irradiate with light source to produce Lewis acid and initiate the cationic photopolymerization process. The strength of the acid is important to ensure the polymerization process done successfully. For weak acid, paired anion has strong nucleophilicity which easily combined with carbon cation center and prevent polymerization (Shi et al., 2021).

According to Shi and co-workers (2021), aryl diazonium tetrafluoroborate, is one type of photoinitiator used in cationic photopolymerization system. When it was

irradiated with UV light source, it produces boron trifluoride (BF₃), nitrogen (N₂) and fluoro aryl group (ArF). BF₃ is Lewis acid which can readily initiate cationic polymerization or can react with water to form protons and initiate cationic polymerization. Figure 2.3 shows the typical cationic photopolymerization mechanism (Shi et al., 2021).

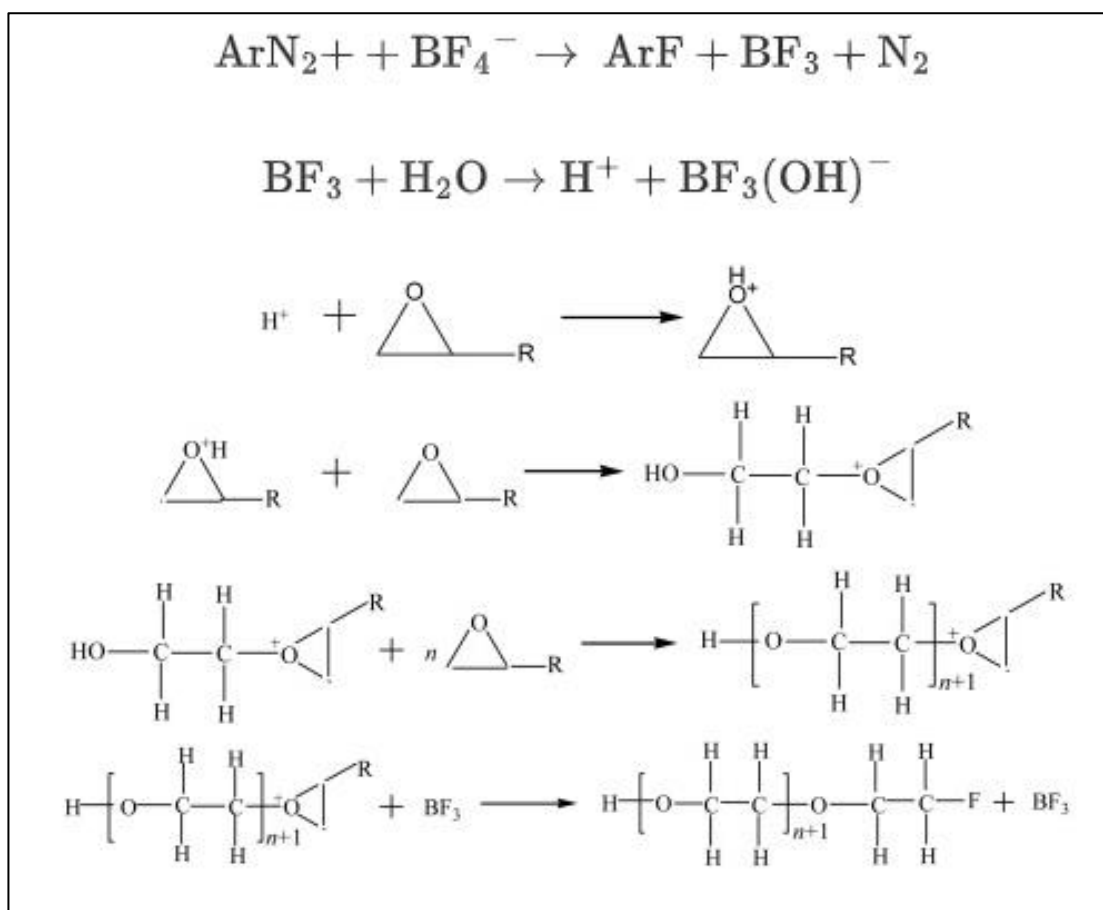


Figure 2.3 Typical cationic photopolymerization mechanism (Shi et al., 2021)

The anion of diazonium salt must have very weak nucleophilicity. This is because strong nucleophilicity such as amines, thiols might cause termination to occur. From the above mechanisms, only one Lewis acid is generated but the polymerization reaction can still progress. Hence, it can be said that the life of the cationic active center is long which the reaction can still be progressed even after the light source is removed.

However, protonic acid may remain in the system after polymerization which might cause damage to the product (Shi et al., 2021)

Ligon and co-workers (2017) reported that cationic initiators can be used in combination with the type I radical initiators, in which radical intermediates generated from radical initiator may react with iodonium or sulfonium cationic reagents to generate radical cations. Cationic curing process proceeds in a chain growth mechanism with high number of cross-linking points along the polymer backbone, resulting in increased brittleness (Bagheri & Jin, 2019).

2.2 Additive manufacturing (AM)

Additive manufacturing (AM) or better known as three-dimensional (3D) printing, rapid prototyping or solid free-form fabrication (Jungst et al., 2016). It is a technique of creating 3D objects or products by addition of material layer by layer from bottom to top through computer-aided design (CAD) and computer-aided manufacturing (CAM) software such as SolidWorks. AM allows direct production of products without the use of costly molds and hence enables design freedom for complex structures and efficient product development (Jungst et al., 2016).

According to Feng et al. (2019), there are various categories in AM which are direct ink writing (DIW), selective laser sintering (SLS), fused deposition modelling (FDM) and stereolithography apparatus (SLA). SLA technique is one of the 3D photopolymerization techniques.

DIW is categorized in extrusion-based additive manufacturing method at which the “ink” which in the liquid phase flowing and passing out through a small nozzle at a stabled and controlled rate. The ink which passed through the nozzle is deposited along the pre-defined path layer by layer and formed 3D structure. Hausmann et al. (2018)

reported that the criteria for the ink materials including high viscoelasticity properties before extruded through nozzle, good shear-thinning effect when passing through the nozzle, then the viscoelasticity should restore after passing through the nozzle to achieve shape fidelity. According to Zhu and co-workers (2020), the material used DIW method is wide, which include polymer, ceramic, metal, composites, etc and the application of DIW is mainly focus in biomedical industry (Guerra et al., 2021). Figure 2.4 shows the typical DIW setup.

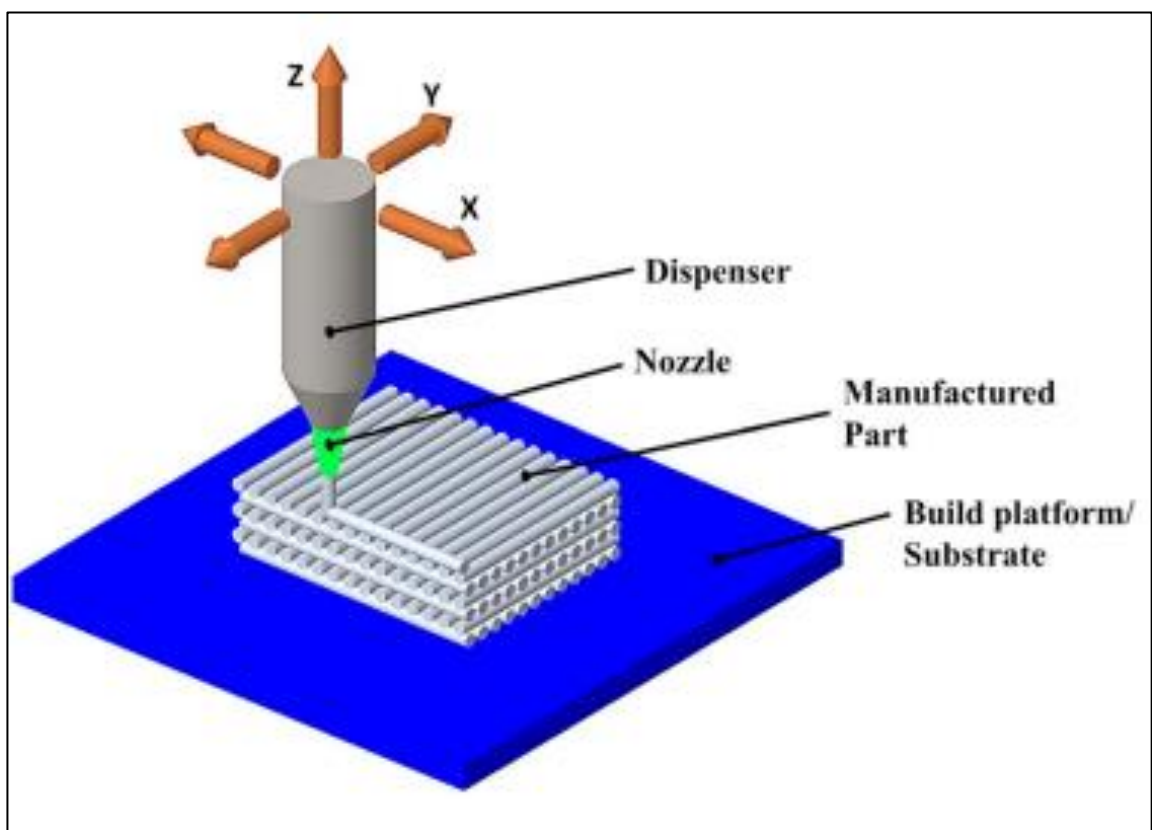


Figure 2.4 Typical DIW setup (Khan & Lazoglu, 2020)

SLS is categorized as a power bed fusion method at which a laser or high power directional heating source is targeted to a bed of powder polymer. This result in a solidified layer of fused powder. Then, stacking of layer by layer and formed a desired 3D printed part (Dizon et al., 2018). According to Gan et al. (2020), the properties of part produced via SLS method is affected by the powder quality. Hence, powder design

and preparation is important to ensure good quality of parts produced. The materials used in SLS technology include metals, polymers and composites and the application of SLS technology includes biomedical, aerospace, bone tissue engineering and drug delivery devices (Dizon et al., 2018). Figure 2.5 shows the typical SLS setup.

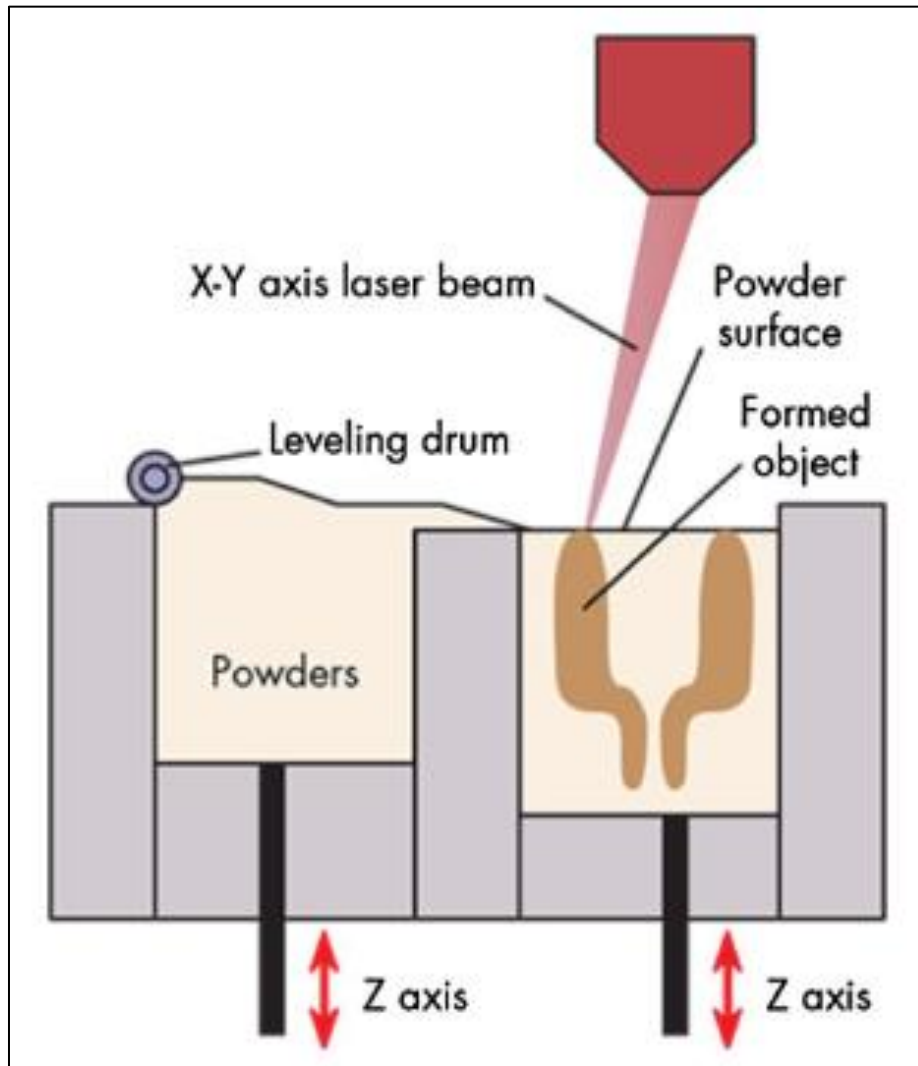


Figure 2.5 Typical SLS setup (Dizon et al., 2018)

FDM technology is another type of extrusion-based additive manufacturing method at which the materials especially thermoplastics filament such as polylactic acid (PLA), acrylonitrile butadiene styrene (ABS), polyethylene terephthalate (PET) was melted and extruded through the nozzle onto the building platform. Then, this layer

instantly solidified and consecutive layers are formed onto previous layer and formed the desired part (Dizon et al., 2018). FDM is one of the most popular and frequently used 3D printing technology due to its versatility, low costing and can create complex parts. The filament for FDM should be in consistent diameter to ensure continuous feeding and melting of filament. The application of FDM is vast, ranging from low-cost functional prototype, architecture model, prosthetics and automotive industry. Figure 2.6 shows the typical FDM setup.

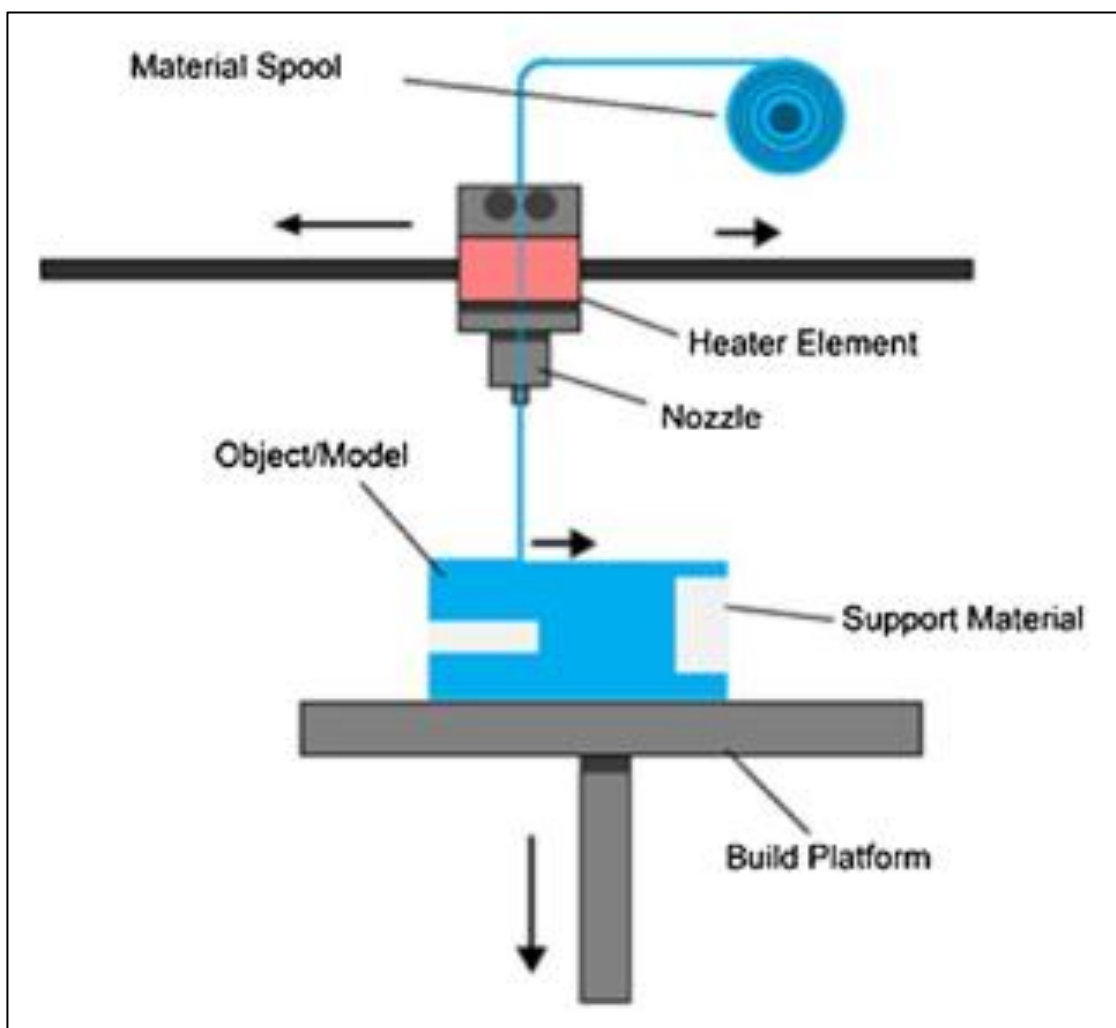


Figure 2.6 Typical FDM setup (Dizon et al., 2018)

As mentioned previously, SLA is categorized as 3D photopolymerization technique which uses light source to cure the materials. The resin used was added with

photoinitiator which then undergo photopolymerization when exposed to specific light wavelength and formed a solid layer. Then, subsequent layers of solid is formed on the previous layer and formed the desired 3D parts. SLA technology is famous with its high resolution printing as compared to other 3D printing technology. However, the cost of the raw materials which is the liquid resin is comparable higher than the raw materials of other 3D printing technology (Dizon et al., 2018). Figure 2.7 shows the typical SLA setup.

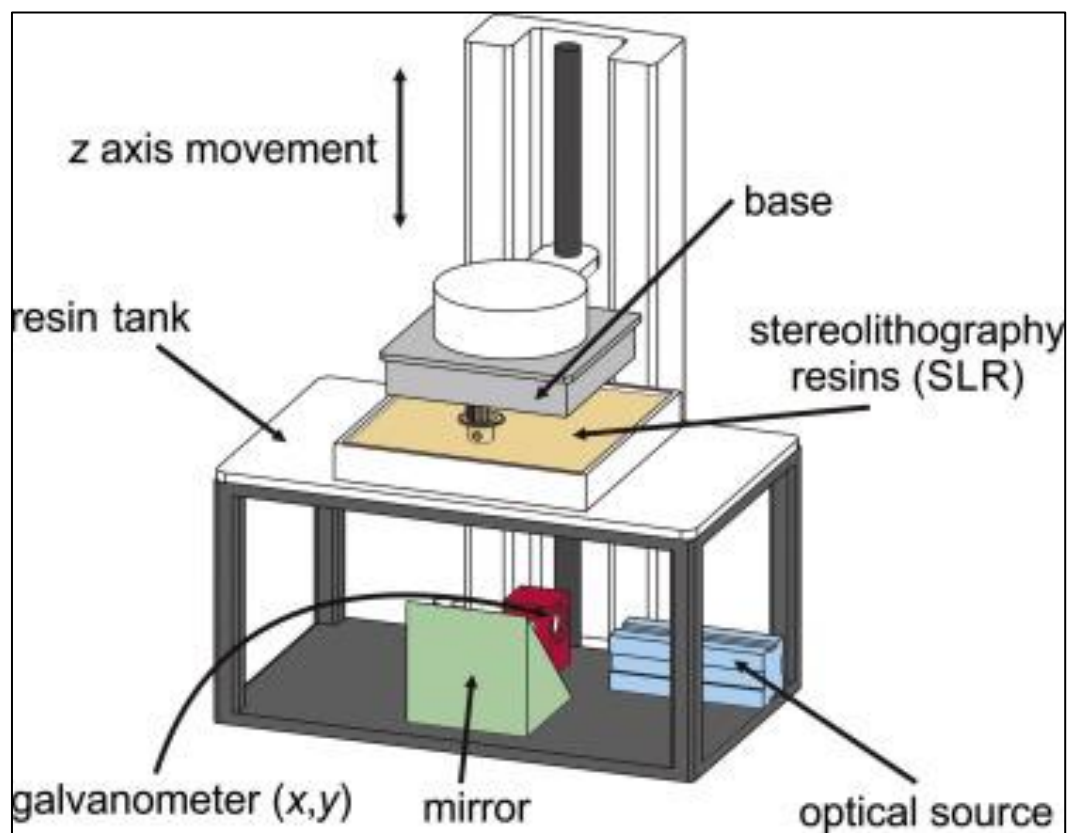


Figure 2.7 Typical SLA setup (Weng et al., 2016)

2.2.1 3D Photopolymerization

3D photopolymerization-based techniques can be divided into SLA, continuous liquid interface production (CLIP) and digital light processing (DLP), as stated by Bagheri and Jin (2019). The difference between these technologies is the source of the

curing device whereas for SLA the curing device is a laser beam but for CLIP and DLP the curing device is a light beamed from a projector.

The CLIP process uses an oxygen-permeable window to inhibit the photopolymerization process by creating a thin layer of uncured liquid between the cured surface and the windows. It is also called an oxygen-containing “dead zone” (Tumbleston et al., 2015). This thin layer of uncured liquid is formed because of the role of oxygen which form a peroxide when interact with the free radical of propagation chain. Besides, oxygen also quench the photoinitiator which in the excited state. Therefore, photopolymerization is inhibited by oxygen. This “dead zone” help in faster printing speeds in a continuous manner (Bagheri & Jin, 2019). Figure 2.8 shows the typical CLIP 3D printer.

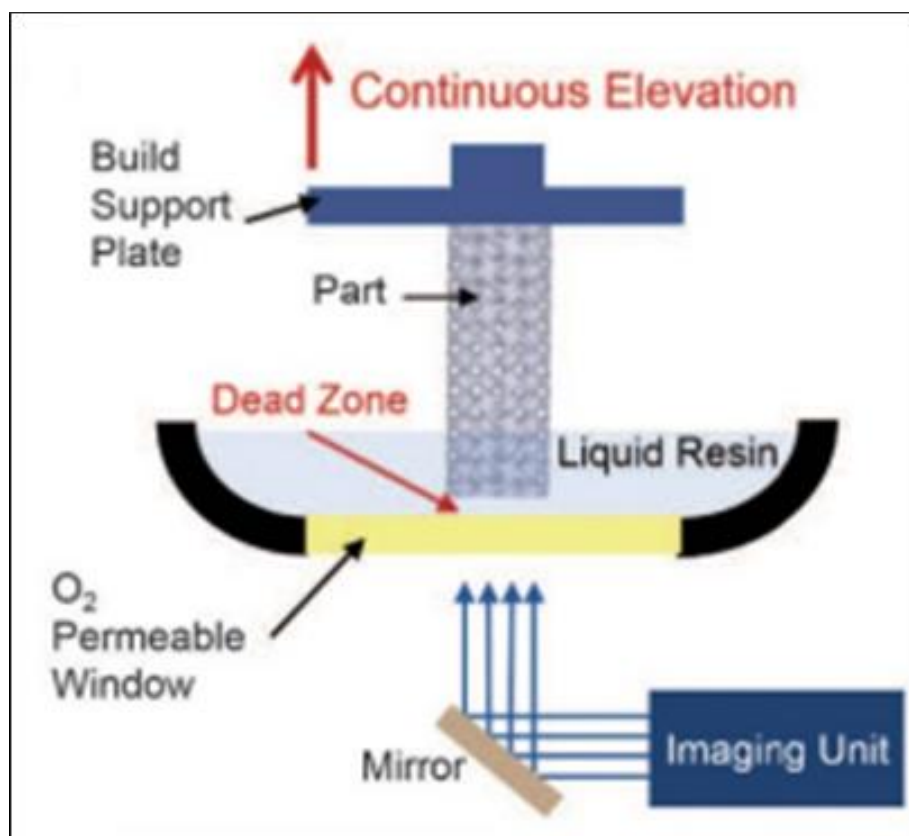


Figure 2.8 Typical CLIP 3D printer (Tumbleston et al., 2015)

For DLP system, the light source irradiated each sliced layer at once as compared to SLA which the exposure of light source is point-by point methods. The build platform is dipped into the liquid resin from above and the light source is irradiated from the bottom. Since the cured layer is not directly in contact with air, hence less oxygen inhibition occurs. DLP method for 3D printing also reduce the printing time and the parts produced also has higher accuracy (Bagheri & Jin, 2019). Figure 2.9 shows the typical DLP 3D printer.

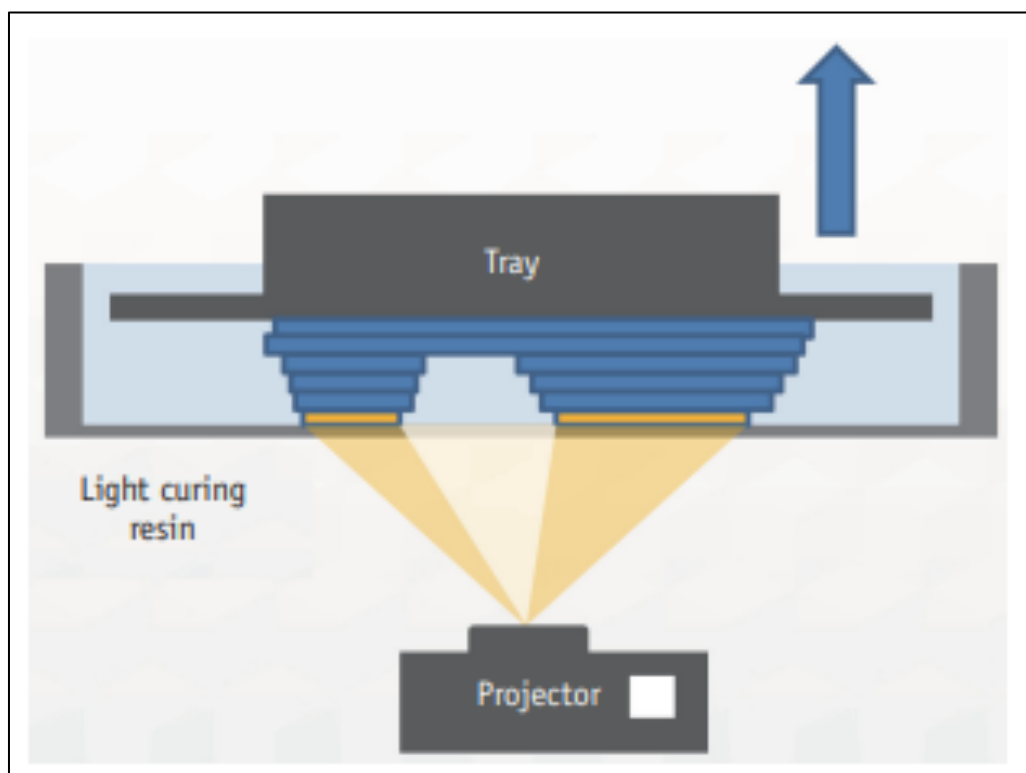


Figure 2.9 Typical DLP 3D printer (Kim et al., 2016)

For SLA method, it used a movable light source, typically UV light to initiate the photopolymerization process of the liquid resin. As compared to CLIP and DLP which use projector as light source, SLA use a laser beam as light source for the initiation of photopolymerization process. The irradiation process is done point-by-point as compared to DLP which irradiation is done at the entire layer.

3D photopolymerization technique uses liquid monomers or oligomers resin which can be polymerized upon exposure to a specific wavelength light source. A photo-initiator or photo-initiator system (more than one type of photo-initiator) is added to the liquid monomer resin to convert photolytic energy into the reactive species, either radical or cationic (Lalevée et al., 2013). Then, chain growth occurs via either radical or cationic mechanism. The mechanisms will be explained in more detail later in Chapter 2.5.

There are various light sources available for photopolymerization such as xenon lamps, mercury arc lamps, LEDs, etc. The wavelengths of a light source can be within UV (190–400 nm), visible (400–700 nm), or IR range (700–1000 nm) (Bagheri & Jin, 2019). Also, there are various types of photoinitiators commercially available in the market. The choice of photoinitiators is based on the wavelength of the photon source used.

For the past few years, 3D photopolymerization techniques have developed rapidly due to their potential for fast and simple production with specific properties. This technique can be found in various fields for different applications such as drug delivery, biomedical devices, soft robotics, dentistry, etc.

2.2.2 Stereolithography Apparatus (SLA)

As mentioned previously, SLA involve selective curing of photopolymer by light energy such as UV or laser beam. Two primary configurations, namely vector scanning based and mask projection-based styles have been commonly used in practice. The vector scanning based system has relatively high precision (Lin et al., 2015). However, there is limitation when using SLA method such as polymer with long chains of conjugated π bonds which cause absorption in the UV and visible region. Their

complex redox chemistries, which may be incompatible with the reactive species formed during some photoinitiator decomposition (Athukorala et al., 2021).

2.3 Acrylic polymers

Acrylic polymers or better known as acrylics, are the long chain of methacrylic acid and esters of acrylic (acrylate). The esters can contain any methyl, butyl, hydroxyl, amino, etc. Example of multifunctional group of acrylate can be trimethylol propane triacrylate or butylene glycol diacrylate. The common formula of acrylics is shown in Figure 2.10.

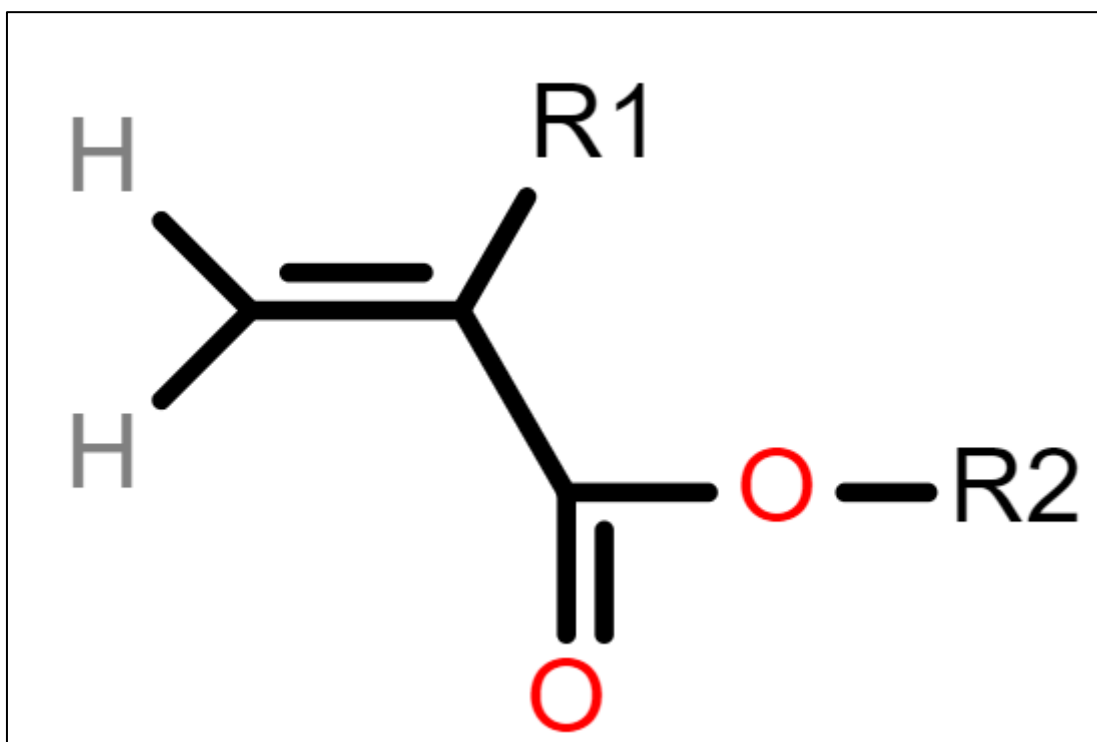


Figure 2.10 Common formula of acrylics

Example of simple formula of acrylates is when $R = H$ (acrylate) and when $R = CH_3$ (methacrylates). R_1 and R_2 groups are important because it determines the properties of monomers and polymers (Jalal Uddin, 2010).

2.3.1 Types of acrylic polymers

There are various types of acrylic polymers such as polymethyl methacrylate (PMMA) and polyvinyl acetate.

PMMA, a transparent polymeric material which usually used in application which required high transparency, dentures, bone repair materials, etc. The properties of PMMA including high transparency, excellent resistance to chemical corrosion, low toxicity (Manoukian et al., 2018). It also is widely used as an alternative to glass and polycarbonate at which high strength is not a consideration.

Polyvinyl acetate is a nontoxic water-dispersed adhesives which used as glue. Besides, it is also widely used to improve stress and antishrink properties for glass fiber-reinforced plastics (Kaboarani & Riedl, 2015). It also formed emulsion in water of vinyl acetate and due to its resistance to micro-organisms attack and low cost, the adhesive is widely used in manufacture of furniture (Conner, 2017).

2.3.2 Synthesis route of acrylic polymers (PMMA)

PMMA is synthesized from methyl methacrylate (MMA) via free radical polymerization mechanisms which is a chain polymerization reaction across the double bond of the monomers. The radicals generated from initiator can be by heat, radiation or chemical agents. The polymerization can be done by bulk, solution, suspension or emulsion polymerization. During polymerization, oxygen must be removed to ensure successful polymerization reaction can be done. This is due to oxygen which act as radical scavenger which will terminate the free radical polymerizations (Rasmussen, 2001). Figure 2.11 shows the chain polymerization of acrylate system.

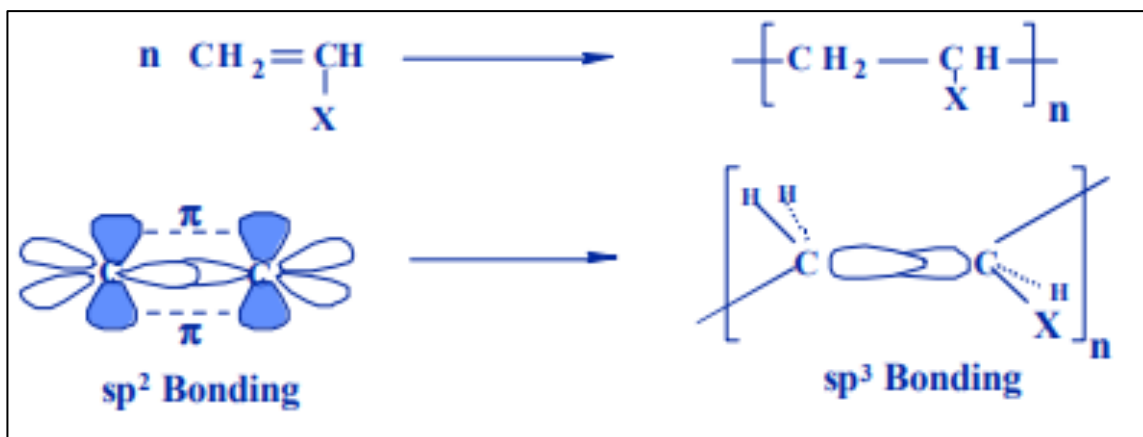


Figure 2.11 Chain polymerization of acrylate system (Rasmussen, 2001)

Besides, PMMA also can be obtained by anionic polymerization of MMA. However, this method is not used famous and not widely used because polymerization must be performed at very low temperatures and MMA used must be very pure (Rasmussen, 2001).

2.3.3 UV-curable Acrylic Polymers (PMMA)

PMMA also can be generated using UV-curable MMA. The photoinitiation of MMA must be done with UV light source. This type of photopolymerization of MMA are usually done by bulk polymerizations.

Photopolymerization is one of the most efficient techniques to produce good characteristics of cross-linked polymeric materials. Also, photopolymerization is usually the chosen method for rapid, assembly style, through-put polymerizations.

2.4 Methyl Methacrylate (MMA) Monomer

Methyl methacrylate (MMA) is an enoate ester which having methacrylic acid and methanol as carboxylic acid and alcohol component respectively. It is a colourless

liquid with fruity odor. The chemical formula of MMA is $\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_3$. MMA usually used for the production of polymethyl methacrylate (PMMA). It is widely used in dentistry, biomedical application, optical application, etc.

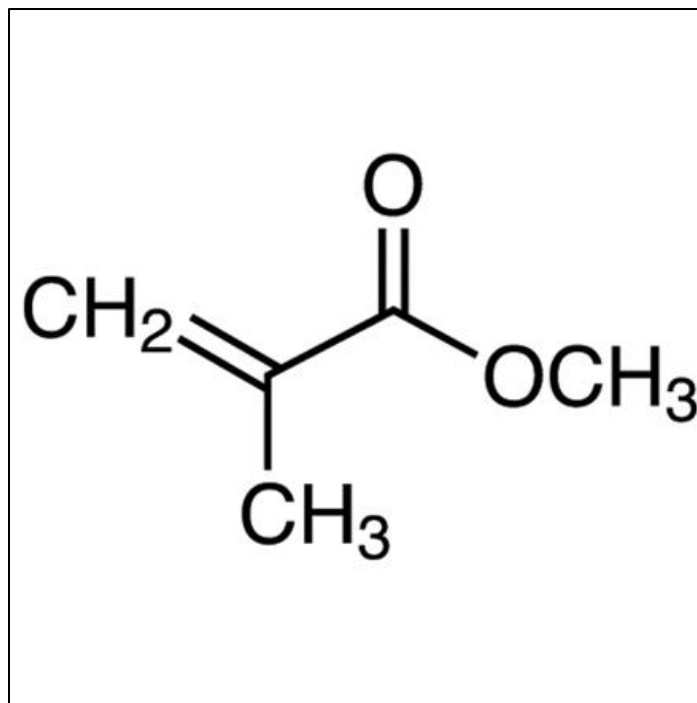


Figure 2.12 Structure of MMA

2.4.1 Chemical and physical properties of MMA

The chemical and physical properties of MMA were shown in Table 2.1.

Table 2.1 Properties of MMA

Properties	
Molecular formula	C ₅ H ₈ O ₂
Molar Mass	100.12 g/mol
Appearance	Colourless liquid
Density	0.94 g/cm ³
Melting point	-48°C (225K)

Boiling point	101°C (374K)
Solubility in water	1.5g/100ml (25°C)
Viscosity	0.6 cP at 20°C

2.4.2 Synthesis of MMA

There are many routes to synthesis MMA such as acetone cyanohydrin (ACH) approach (Figure 2.13), AVENEER process (Figure 2.14), BASF process (Figure 2.15).

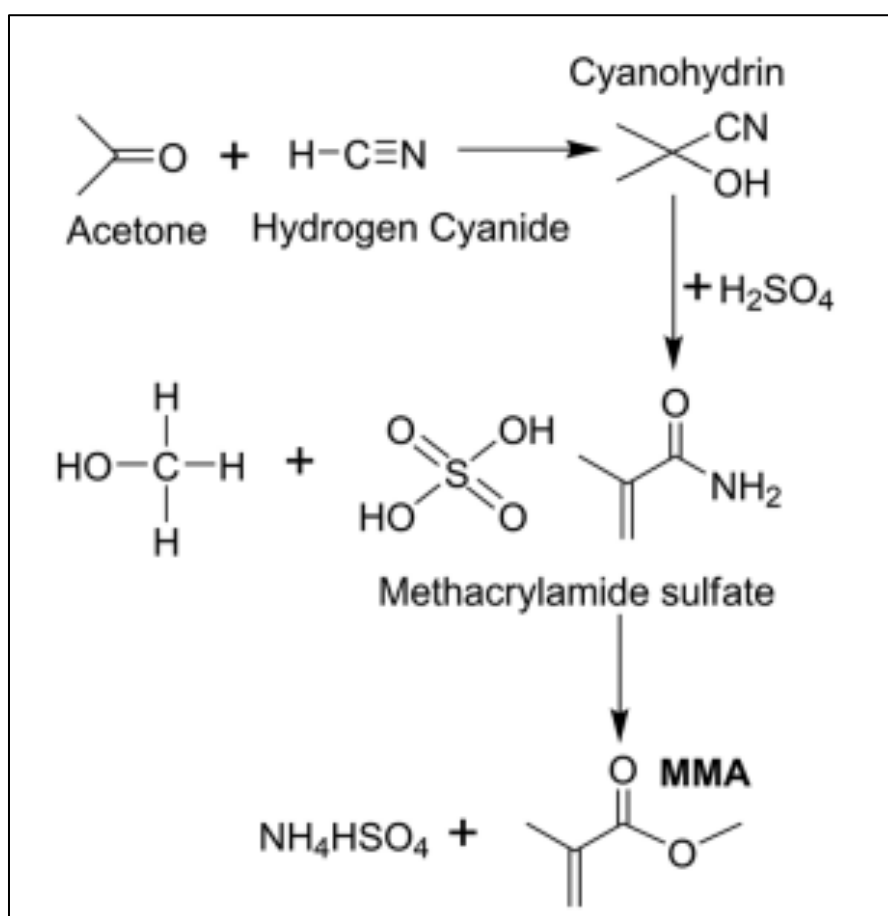


Figure 2.13 ACH approach to produce MMA (Fabrizio, 2010)

In ACH approach, acetone and hydrogen cyanide react to form acetone cyanohydrin intermediate. Then the intermediate reacts with excess concentrated sulfuric acid to form methacrylamide sulfate. It is then treated with excess aqueous

methanol which hydrolysed and esterified the amide to form the mixture of MMA and NH_4HSO_4 (Darabi et al., 2018).

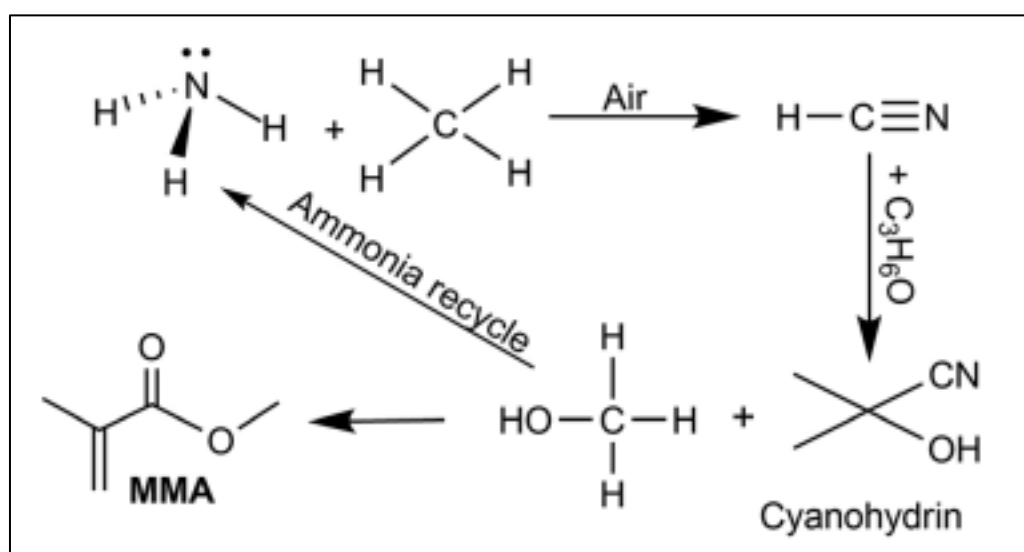


Figure 2.14 AVENEER approach to produce MMA (Darabi et al., 2018)

For AVENEER approach, ammonia, methane, acetone and methanol are the feedstocks. Ammonia is first react with methane in air to produce HCN. Then, HCN and acetone react to form cyanohydrin (ACH). Esterification process is then done to produce MMA.

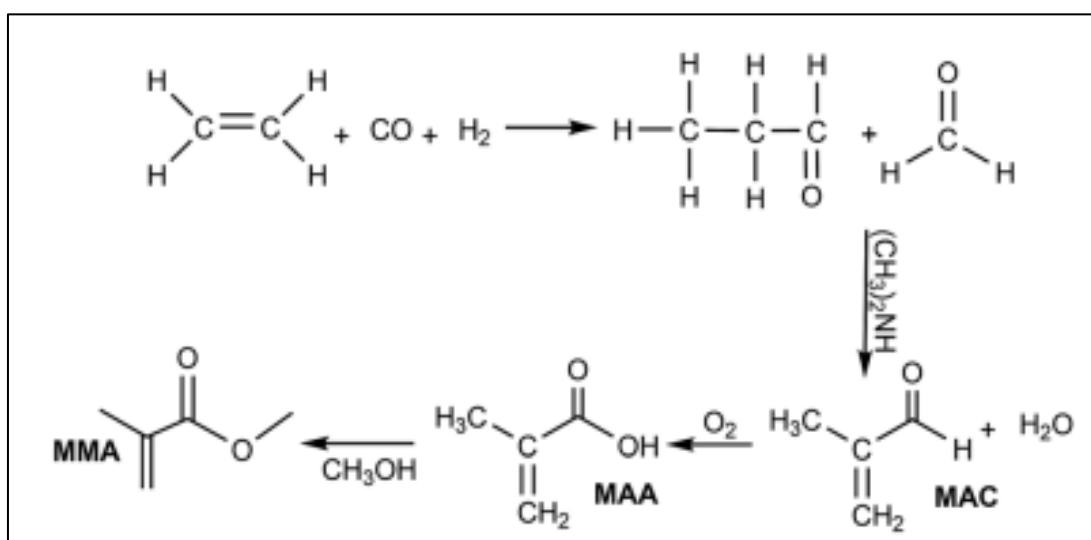


Figure 2.15 BASF approach to produce MMA (Darabi et al., 2018)