Photopolymers in 3D printing applications

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Abstract:

3D printing is an emerging technology with applications in several areas. The flexibility of the 3D printing system to use variety of materials and create any object makes it an attractive technology. Photopolymers are one of the materials used in 3D printing with potential to make products with better properties. Due to numerous applications of photopolymers and 3D printing technologies, this thesis is written to provide information about the various 3D printing technologies with particular focus on photopolymer based systems. The thesis includes extensive literature research on 3D printing and photopolymer systems, which was supported by visit to technology fair and demo experiments. Further, useful information about recent technological advancements in 3D printing and materials was acquired by discussions with companies' representatives at the fair. This analysis method was helpful to see the industrial based 3D printers and how companies are creating digital materials on its own. Finally, the demo experiment was carried out with fusion deposition modeling (FDM) 3D printer at the Arcada lab. Few objects were printed out using polylactic acid (PLA) material.

Keywords:	Photopolymers, 3D printing, Polyjet technology, FDM technology, Photocrosslinking, Stereolithography, Stratasys, Cinnamate group
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Table of content

Figures

Tables

Acronyms and abbreviations

ABS	Acrylonitrile butadiene styrene
AM	Additive manufacturing
UV	Ultraviolet
3D	3- Dimensional
PA	Polyamide
RP	Rapid prototyping
CAD	Computer aided design
COM port	Communication port
T_g	Glass transition temperature
SLS	Selective laser sintering
FDM	Fusion deposition modeling
SLA	Stereolithograph apparatus
$3DP^{TM}$	Three dimensional printing
SLM	Selective laser melting
EBM	Electron beam melting
LOM	Laminated object manufacturing
DMLS	Direct metal laser sintering
Si	Silicon
NMP	N-methyl-2-pyrrolidone
THF	Tetrahydrofuran
PLA	Polylactic Acid
PET	Polyethylene terephthalate
STL (SL)	Stereolithography
.STL	Standard Tessellation Language (file name extension)
PC	Polycarbonate
Z- Corp	Z- Corporation
TMPTA	Trimethylopropane triacrelate
DMAC	Dimethylacetamide

1 INTRODUCTION

1.1 Background

Photopolymers are light sensitive polymeric materials, which changes their physical or chemical properties when exposed to the light sources. The main source of light is UV, which initiates a reaction and changes the properties of photopolymers. These polymers have been used in several printing technologies, such as inkjet printing to recently popular 3D jetted printing. It has a strong demand in printing business as it gives better results.

There are several kinds of 3D printing technologies which are categorized based on their applications. While some products are made with ceramics and metallic materials, most of the products are made with high strength plastics such as acrylonitrile butadiene styrene (ABS) and polycarbonate (PC).
The literature review of photopolymers and 3D printing are mostly dealt in separate topics.

1.1.1 Photopolymers

Photopolymers are light sensitive polymer materials which change their properties when exposed to UV light. They can change their state from water like liquid substance to solid plastic like substance. Only the area exposed to UV-light hardens, whereas unexposed parts will still remain like liquid.

Usually photopolymers are kept in a liquid state for general use. They also exist in the form of sheets. There are other polymers which can change their properties (or cured) under radiation condition such as heat and microwave. But, photopolymers are only curable with light sources (UV laser, lamp, sunlight etc.). The light from these sources initiate chemical reactions which changes their structure and modifies their chemical and mechanical properties. These materials are eco-friendly and therefore popular in recent history since they can work without any volatile solvent in most of the industrial process.

These polymers are quite common in our daily lives and can be visible in different sort of coatings in metal, paper, plastics and wood materials. People even have them in their mouth if they have undergone teeth bonding. Some of the common polymer bases for photopolymers are polyvinyl cinnamate, polyamide (PA), polyisoprene, polyimides, epoxies, acrylics etc. Usually monomers, oligomers and additives are used along with these polymers. [1-2]

1.1.2 3D Printing

3D printing is an additive manufacturing process, as opposed to a subtractive manufacturing process which involves milling or cutting of pieces in order to build the right shape. In additive manufacturing, the material added in layers until it takes the shape of the desired product. Different 3D printers use different materials, for example photopolymer liquids are used in jetted 3D printer and ABS material is used in fusion deposition modeling (FDM) printer. Several 3D printing companies produce their own materials suitable for respective printers.

Besides using polymers, 3D printers are also capable of using other materials like ceramics, metals, glasses etc. This technology is being available in many sectors; for instance schools, labs and industries. Moreover, the development and large scale manufacturing has brought down the cost of 3D printers, thereby making it available for personal use as well. This also shows that there is a strong possibility of having a 3D printer in each household, as technologists believes. New technologies are going through door to door and people are getting more curious about 3D printing and their products. This is the one reason that Arcada University of Applied Sciences has at least one 3D printer which is based on FDM technology that produces parts with different polymers such as ABS, PLA, PC and PA etc. in order to print the several FDM objects. The history behind 3D printing is not very long. The first machine was introduced in the 1980's and cost more than hundred thousand dollars. However, recent developments in such technology have reduced costs significantly (Makerbot's printer cost $ 2000) [3-5].

1.2 Objectives

The main objective of this thesis work is to provide a description of photopolymers and their applications in 3D printing technologies. In order to achieve this, the mechanisms and composition of photopolymers are described. It is also supported by a study trip to plastic fair, descriptive research of 3D printing technologies and comparison of FDM 3D printings with photopolymer based 3D technology (Polyjet printing).

Another part of the thesis includes the demo experiments to print 3D objects using minifactory 3D printer and analyses of the results.

1.3 Scopes and limitation

This thesis is mainly focused on additive manufacturing technologies (AM) based on light sensitive materials, also known as photopolymers. These polymers have high importance in printing industries as many 3D printing technologies have been using photopolymers. Applications in traditional inkjet technology, coating and adhesives technologies still use such materials.

In general, these are easy to handle with and apply in wide area as adhesives, paintings, coatings etc. However, due to the wide area application of the material Polyjet technology and Stereolithography are chosen to be studied literally excluding other non-additive manufactur ing technologies. Besides, FDM based 3D printing experiment will be carried out which will provide the real objects in the hand.

2 LITERATURE REVIEW

This literature survey is categorized in two different parts where first one explains the detail overview of photopolymers and its mechanism to synthesis processes. While the rest provides general knowledge of different AM techniques with information of material usage.

2.1 Materials used in 3D printing

Most of the 3D printers use plastic materials since they are cheaper. There are soft materials like elastomers, silicone and rubber- like materials which are relatively more elastic in addition to the light sensitive materials for (Stereolithography) SL. Developments such as printing on metallic surfaces have created more application areas too. [6] P.81

Nevertheless, materials used in 3D printing depend on the type of printers. For instance, photopolymers are used in Polyjet and Stereolithography technology, while other technologies use a variety of materials. Companies also supply the compatible materials along with the 3D printers. Generally used 3D printing materials in industries are listed below.

- Plastics
- Glass
- Ceramics
- Rubber
- Paper
- Titanium & Metals

The minifactory FDM 3D printer available at Arcada uses polylactic acid (PLA) to print the variety of products. It can also use other materials like ABS however, the objects created for the thesis purpose was made by polylactic acid (PLA).

2.1.1 PLA material

PLA is a shiny, hard and biodegradable substance which is a stronger and flexible material for 3D printer. Chemically PLA contains lactic acid and lactides. This has a low melting temperature of 173-178 °C and tensile strength 2.7-16 GPa with several application areas including medical implantations and compostable packaging material.

PLA is basically derived from corn starch and therefore eco friendly. Mechanically PLA has similar properties with PET except the use of high continuous temperature in case of PET. In the makerbot's experience [80], printing at high temperature using PLA can affect the gear drive and restricts the extruder to operate smoothly because of its low melting point. [11] [78]

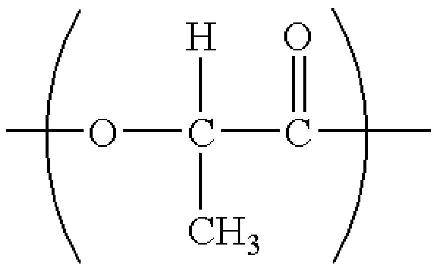


Figure 1 *PLA chain structure [81]*

2.2 Photopolymers in general

The use of light source in the preparation of polymers was quite popular in 19^{th} century. Vinylchloroacetate was converted to polyvinylchloroacetate to produce glass bottles in presence of sunlight. Photopolymers are hugely applied in imaging and electronics.

In 3D printing technologies such as Stereolithography, objects are printed for stamps, medical, military and electronics industries. Stereolithography is a major 3D technique which uses photopolymers. Metal plates can also be coated with photopolymers and is possible to print multiple designs. These polymers are also useful for letterpress which is easier to design than metal once. Furthermore, printing newspapers and boxes also use photopolymers. They are also useful in film, orthopedic, optical devices, biocompatible, filling materials, dentistry, bone replacing material, 3D processing and hologram applications. Here are some popular examples of commercial photopolymer plates and films:

- Toyobo printight plates
- Imago film
- Solar plates
- Z*Acryl Photopolymer Film etc. [7-8]

There are three basic constituents which run the photopolymers processes and are explained below.

2.2.1 Composition of photopolymers

Photopolymers are soluble, light sensitive material which undergoes polymerization with light (UV) reaction. There are many types of photopolymers, which exist in different forms: some are liquid, while some are in the form of sheet. The commonly used photopolymer, ester of cinnamic acid ($C_9H_8O_2$) is produced by reacting cinnamic acid with alcohol in the presence of light [9].

In general, photopolymers may contain several components including binders, photoinitiators, additives, chemical agents, plasticizers and colorants. However, the three main components which build the photopolymers are binders, monomers and photoinitiators. [10], [2]

2.2.1.1 Binders or oligomers

Binders are molecules of reactive intermediate molecular weight consisting of few monomer units, usually dimers (two units), trimers (three units) and tetramers (four units). They are normally liquid in room temperature and are used as ink, adhesives and coating purposes. Typical photopolymers consists of 50- 80% of such binders/oligomers and some of them are listed as follows: [11-12]

- Styrene family: Oligomer Of Styrene-Tetramer-Alpha Cumyl End Group, A-Methyl Styrene-Dimer (1), A-Methyl Styrene-Tetramer etc.
- Methacrylate family: Acrylic Acid Oligomers, Methyl Methacrylate Oligomers, Methyl Methacrylate Tetramer etc.
- Vinylalcohol family: Vinyl Alcohol Trimer, Vinylacetate Trimer, Vinylacetate Oligomer.
- Olefine family: Poly Isobutylene
- Glycerol family: Triglycerol
- Polypropylene Glycol Family: Poly Propylene Glycol (Dihydroxy Terminated) etc. [13]

2.2.1.2 Monomers

Monomers are chemically bonded small molecules which joins with other monomers, oligomers or polymers in a repeated fashion to form new polymers. Mostly, photopolymers consists of monomers based on acrylates or methacrylate ranging from 10-40 %. In the process of polymerization, two types of monomers can be used: multifunctional monomers and monofunctional monomers. Multifunctional monomers can act as both diluents and cross linkers, whereas monofunctional monomers can be either diluents or cross linkers.

Some of examples of monofunctional and multifunctional monomers are given below. [10]

Table 1 *Monofunctional and multifunctional monomers*

Monofunctional monomers	**Multifunctional monomers**
Acrylic acid	Trimethylopropane triacrelate (TMPTA)
Methacrylic acid	Ethoxylated TMPTA
Isodecyl acrylate	Trimethylepropane trimethacrylate
N-vinyl pyrrolidone	Hexanediol diacrylate

2.2.1.3 Photoinitiators

Photoinitiators convert light energy into chemical energy by forming free radicals or cations upon UV exposure. They can break into two or more particles with UV reaction and at least one of the particles will react with monomers or oligomers and binds them together. They exist naturally or can be chemically synthesized and are sensitive to specific wavelengths of light. Cationic photoinitiators forms Lewis acids which lead them into cationic polymerization. The rapid development of photoinitiators took place in between 1960-70 by companies such as BASF, AKZOCIBA GEIGY etc. Photoinitiators form only a small component of photopolymers [14], [2] & [15] P. 5.

Some examples of free radical and cationic photoinitiators listed:

Table 2 *Examples of photoinitiators*

Free radical photoinitiators	Cationic photoinitiators
Isopropylthioxanthone	Diaryliodonium salts
Benzophenone	Triarylsulfonium salts
2,2-azobisisobutyronitrile	

In free radical photopolymerisation, radicals or ions break off the initiators when UV reacts and ions will start reacting with monomers to initiate polymerization. While in cationic reaction strong acid will be released from initiator and it starts a bonding process. One of the examples of cationic photopolymerisation is release of UV curable silicon coatings for label. Diaryliodonium and Triarylsulfonium salts are stable crystalline compounds which can be prepared by synthetic method and are available in the market for commercial purpose. In the other hand, free radical photopolymers are quite popular in the dentistry as an adhesive and in coatings. [10], [15] P. 9-12.

2.2.2 Photopolymer classification system

Photopolymers can be classified into three groups on the basis of their feature, application and concept. They are as follows:

2.2.2.1 Classical photopolymers

They are compounds like acrylic and epoxy polymers which are used in adhesives, coatings and imaging industries. Polymerization of such material gives the product photosensitivity and better handling properties. Below is the pictures attached of components with certain mixtures used for Stereolithography technique.

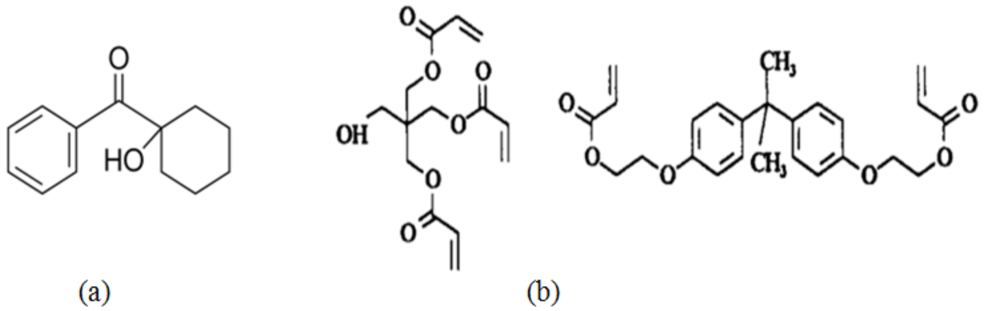


Figure 2 *Hydroxycyclohexylphenyl ketone and acrylates [18]*

Fig 2 (a) Shows the Hydroxycyclohexylphenyl ketone which is an UV curing agent that produces radicals upon UV exposure while Fig 2 (b) is acrylates. The UV curing agent (a) acts in photopolymerisation process of unsaturated acrylate system (b).

2.2.2.2 Combination system

The combination system has been developed in order to overcome the problems associated with single initiator/monomers such as low viscosity in pure epoxy resins. This system enhances the performance when there is interaction between monomers, photoinitiators and prepolymer. It also helps in the manufacturing processes of microelectronic devices such as polyimides material which can tolerate high temperatures needed for circuitries.

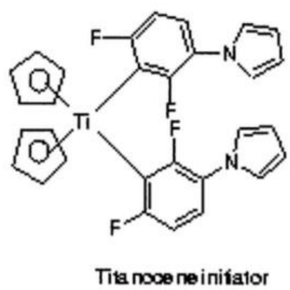


Figure 3 *Titanocene photoinitiator [16] P. 274*

In addition, photopolymerisation and photoinitiator systems are quite sensitive to visible light of wavelength ranging 400-700 nm. Visible spectrum of titanocene photoinitiators (Fig. 3) is convenient for technological development because of its long wavelength i.e. 500 nm and bleaching capability which allows photo imaging of polymer layers of >100 µm thick for acrylate photopolymerisation. This type of photoinitiator is also used in dentistry application in combination with epoxide resin. [17-18], [16] p.274

2.2.2.3 New photopolymers

These polymers participate in assembling of all necessary components in certain proportion in order to build a single macromolecular structure. For example, given polyimide structure is an auto-photosensitive and soluble which is because of some water miscible solvents like N-methyl-2-pyrrolidone (NMP), tetrahydrofuran (THF) etc. in it.

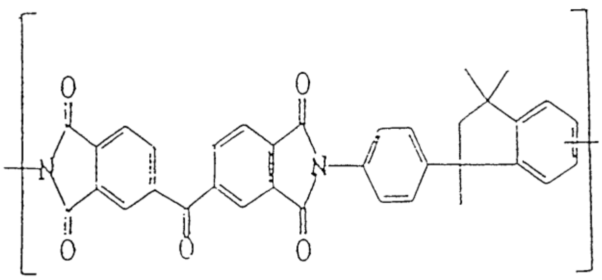


Figure 4 *Auto-sensitive, soluble and fully imidized polyimide [18]*

The structure consists of benzophenone portions, polyimide backbone and alkyl substituents which works as light absorbing chromophore, provides better thermal stability and adjusts the solubility and glass transition temperature (T_g) respectively. [18]

2.2.3 Mechanism of photopolymers reaction

Photopolymers are type of materials which changes their chemical and physical properties in reaction to light. Some are low molecular weight (mol. wt.) monomers and multifunctional, while some photopolymers go into coupling or dimerization on irradiation. Furthermore, some photopolymer go into cross linking polymerization in presence of photoinitiators while some into cleavage reaction by photolysis.
Light initiated reactions used in photopolymer technology are divided into 5 categories based on physical and chemical process utilized. They are as follows: [19], [15] P. 4

2.2.3.1 Photopolymerisation

The formation of bigger sized macromolecules through the addition of monomers is called polymerization and is usually carried out in the presence of several stimuli such as light, laser, electron beam, X-rays, microwaves and thermal processes. The polymerization that occurs in the presence of light is called photopolymerisation in which the lights with proper wavelengths collide on the monomer/oligomers and the reaction takes place. [20] P.4-5

In another word,

$$\text{Monomers/Oligomers mixtures} \xrightarrow{hv} \text{polymers (Photopolymerisation process)}$$

Most commonly used reactive monomers are unsaturated methacrylate or acrylate monomers with low molecular weight which are cross-linked with the help of radical generating photoinitiator. Moreover, monomer is a small molecule with one or more reactive functional groups such as acrylates, while oligomers have larger chain structure and controls the final chemical and physical properties of the cured coatings. Common example of such oligomer is polyurethane.

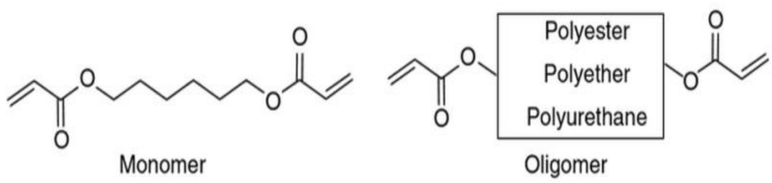


Figure 5 *Polyurethane oligomer [20] P. 4*

Typical photopolymer formulations contain photoinitiators or photoinitiating system, monomer/oligomer matrix and other additives such as inhibitors, plasticizers, light stabilizers etc. depending upon type of application.

There are several application fields of photopolymerisation reaction such as microelectronics, printing plates, coatings, adhesives, dentistry, contact lenses and so on. Furthermore, there are several photosensitive materials such as light sensitive polymer matrix or oligomer/monomers are known as photoresist in microelectronics application, while organic matrix is called as photopolymer in imaging technology. Photopolymerisation are applied in many chain processes such as free radical, cationic, anionic, hybrid sol gel polymerization and step growth polycondensation. Some of them are shortly described below: [19-21], [20] P.5

2.2.3.1.1 Free radical photopolymerisation

In this process, light sensitive photoinitiator molecules like acrylates and methacrylate present in liquid monomers reacts with photon particles of light to produce highly reactive free radicals. These free radicals attack the double bond monomers to make it polymers in order to begin the polymerization process. Commercially, free radical photopolymerisation technology apply combination of multi and monofunctional monomers or only multifunctional monomers in order to build the polymers with insoluble, infusible and cross linked characters. [22], [15] P. 8

Among all other chain processes, free radical photopolymerisation has wider application areas than others because of its usefulness in formulation based unsaturated polyester, acrylates, methacrylate, polyurethanes etc. Furthermore, photoinitiators for such process is available in huge range of wavelengths and less purity demand [21]. Free radical photopolymers have uniquely succeeded in dental application as a photo curable adhesives and protective coating because of easiness in handling, reliability and safety. Other medical applications include surgical masks, hearing aids, syringe barrels etc. [15] P. 8-9

2.2.3.1.2 Cationic photopolymerisation

In contrast to the free radical photopolymerisation, cationic is comparatively less developed but are better in photopolymerisation without oxygen inhibition, low shrinkage, low volatility and toxicity. This can even occur in monomers containing vinyl ethers or epoxides. Moreover, minimum shrinkage occurs in epoxide monomers in a ring opening mechanism. [23-24]

Photoinitiators used in such system is called as onium salts such as phenyl diazonium, diphenyliodonium and triphenyl sulfonium. They are able to polymerize epoxy, vinyl and propylene ether. These salts go into decomposition upon irradiation to support Lewis acids which initiate the cationic polymerization. In addition, cationic photoinitiator salts are responsible for photo absorption and propagation. The concept of hybrid photoinitiators have been developed which improves not only cationic, but also the free radical photopolymerisation. This also helps to develop the final product with better physical and chemical properties because of wider selection possibilities of monomers. [24-25]

2.2.3.1.3 Anionic photopolymerisation

Very limited amount of research have been carried out with anionic polymerization. However, Eishun and his colleagues did such polymerization of epoxides by using catalyst titanium tetraisopropoxide and phenol or its derivatives which were suitable for anionic photopolymerisation of cyclohexene oxide.

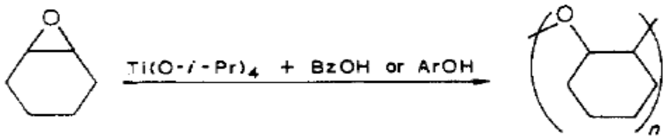


Figure 6 *Anionic photopolymerisation of cyclohexene oxide [26]*

In the given figure, phenolic derivatives works as a prerequisite to control the electronic state of the titanium center for epoxide coordination. In addition, photocontrolled living anionic ring opening polymerization of silicon/phosphorus bridge ferrocenophanes was reported. [26], [20] P.55

2.2.3.2 Photocrosslinking

This is a process which needs light absorption either in the form of laser or sunlight in order to crosslink the polymers. Functional group existing in the polymers, oligomers or monomer chains absorbs light source to create three dimensional network structures. This process can be carried out in several ways such as addition of photosensitizers, photoinitiators, using photocrosslinkable materials etc. [27] P. 5155

In addition, this process develops covalent bond between two macromolecules or two separate parts of a single macromolecule. Crosslinking of monomers, oligomers and polymers have different applications in coatings, imaging, adhesives, wires and cables. Photocrosslinkable polymers are quite popular in the polymer world due to its insensitivity to oxygen unlike free radical photopolymers. These polymers are used to produce photoresist (a light sensitive material) for macro and microlithography which are applied in chemical resistant coatings and nonlinear optical materials. This process takes place by radiation sensitive cross linking agent or monomers or by the polymers with photocrosslinkable groups attached in a chain. In addition, it works by radiation induced crosslinking of polymer chain where high energy source such as gamma rays with greater penetration capacity are applied in order to complete the function. [28], [29] P. 71-75

Moreover, commercial products with this process are based on reactions of unsaturated components with organic polymers. Photocrosslinking reaction of light sensitive polymers may occur either in reversible or intramolecular cyclization process (converting normal hydrocarbon chain into cyclo form within a single molecule). Here are some groups which are formed through the similar cross-linked process and are applicable for commercial purposes;

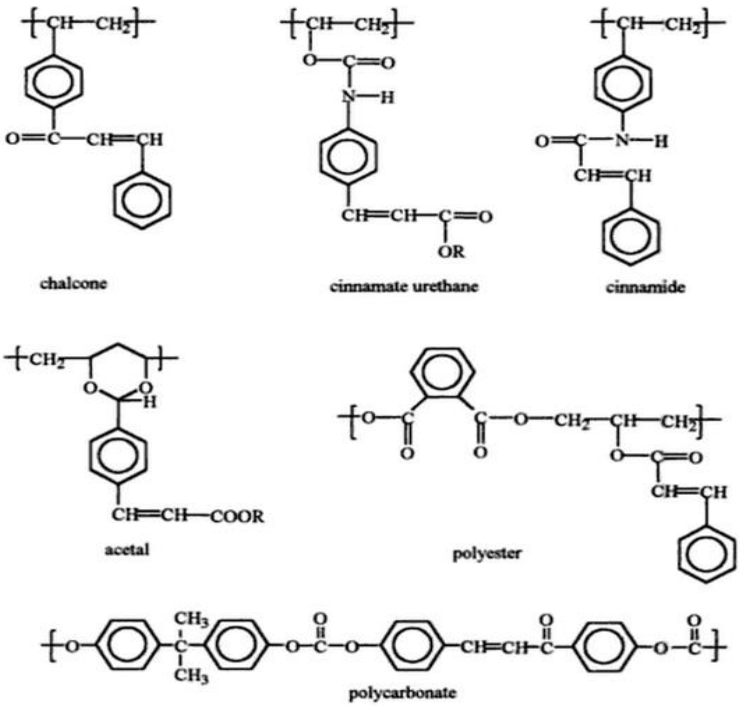


Figure 7 *Photosensitive polymers with similar photocrosslinkable group [30] P. 526*

Cinnamate group are well known photosensitive compounds which undergoes cyclodimerization to form a cyclobutane ring in between the chains of the group. They are used as photocrosslinkable polymers because of the high resistance to UV radiation and chemical resistance properties. In contrast to the cinnamate, chalcones group which existed since 1959 has higher photosensitivity and includes macro molecules with Chalcones type groups in side chain, main chain or epoxy resins. Here are some cinnamate polymer groups which does photocrosslinking reaction upon irradiation condition. They are:

- Cinnamylidenes
- Chalcones
- Coumarins

- Stilbazoliums
- 1, 2diphenylcyclopropene-3-carboxylate (Kodak's recent product) etc.

Photocrosslinking based reactions increases the photosensitivity in photo imaging system with photosensitizer applications. Aromatic nitro and keto based sensitizers are considered to be effective in those fields. Furthermore, 2-benzoylmethylene-1-methyl-β-naphthothiozoline and triphenyl pryrylium salt derivatives are better sensitizers for photocrosslinkable system. Moreover, there are several other photocrosslinkable polymers with different applications for instance Quinone containing poly (methyl methacrylate) is available in holographic recordings. [25], [31], [19] P.3

2.2.3.2.1 Synthesis example

Photocrosslinking is a good way of improving chemical and mechanical properties of polymers. Weiwei et.al and others have carried out a crosslinking experiment by synthesizing fluorinated poly (arylene ether) consisting of chalcones group. The reason behind choosing fluorinated poly (arylene ether) is because of better thermal stability, transparency and solubility.

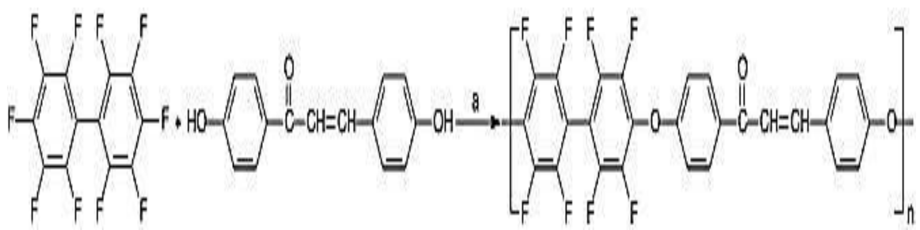


Figure 8 *Synthesis route of PSFPAE (fluorinated poly (arylene ether) group). Reagents and conditions: (a) K 2 CO 3, DMAC, 80 °C [32]*

The above picture is the synthesis diagram of such PSFPAE where compounds like decafluorobiphenyl (DFBP) and 4, 4′-dihydroxychalcone (4DHC) were mixed in N, N-dimethylacetamide (DMAC) solution just before adding some potassium carbonate in order to produce the white polymers by a complete synthesis. Such research has produced better chemical resistant and improved mechanical properties of polymer film by induced photocrosslinking processes. [32] P.1381-1383

2.2.3.2.2 Reaction mechanism

Photosensitizers are substances that determine the crosslinking rates in the reaction process and it works by first absorbing light and then transferring energy to other molecules. Azide is one of the photosensitive groups where crosslinking occurs in condition of irradiation in a proper wavelength condition. Upon decomposition they give rise to nitrene group and nitrogen. Below is the example given which shows the reaction mechanism of acetals formation reacting vinyl alcohol with azide groups,

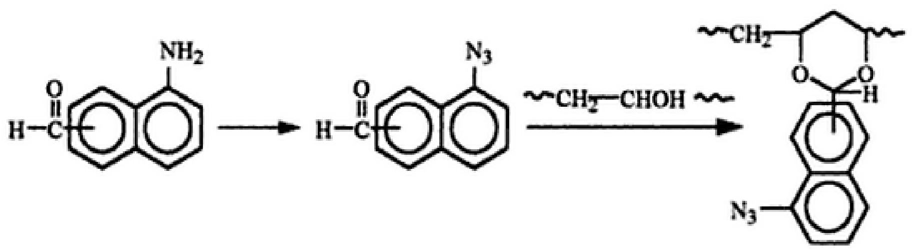


Figure 9 *Formyl 1- napththylazide + polyvinyl alcohol producing acetals [30] p. 527*

There are other compounds such as pendant furan groups which are more photosensitive (in comparison polyvinyl cinnamate) with similar crosslinking mechanism. Furthermore, certain functional groups of the compound can be used to make photocrosslinking such as styrene, alkyne, thymine etc. These groups create bonds and rings with other groups at different positions in order to build the crosslinking. [30] P. 526- 530

2.2.3.2.3 Merits and demerits of photocrosslinking

Advantages or disadvantages are completely dependent on the type of products being made and the materials used. UV-curing is under high level of development due to its wide application and large demand.

Some of the advantages are:

- Crosslinking can be done in normal room temperature to make different coatings.
- Equipment accessories are easily available.
- Most of the organic solvents used are environment friendly.
- Consumption of energy is comparatively less than other techniques.

Some of the demerits are:

- Photocrosslinking is not possible for all photopolymer materials.

- It may have difficulty in dealing with pigmented layers which absorb light. [27] P. 1040

2.2.3.2.4 Application areas of photocrosslinkable materials

The use of photopolymerisation and photocrosslinkable materials in polymer and biomedical engineering are well studied. There are some materials which becomes photocrosslinkable in addition with photoinitiators. For instance, chitosan transforms into insoluble and soft rubber like material within a minute. UV-radiation produces free radical molecules by dissociating photoinitiators in the reaction process. Here are some application areas of photocrosslinkable materials given.

- Dyes and pigment
- Resin
- Glass
- Paintings
- Nano composites
- Adhesives etc. [31] P.10 & P.30

2.2.3.3 Photo/Thermal reaction

This sort of photopolymer reaction is based on physical changes rather than chemical changes in a polymer matrix. Photothermal reaction results in thermal bond breaking of polymers when the electronic excitation is thermalized in a fraction of a second. Laser ablation is a technology based on highly dominated photo thermal or photochemical processes. [19], [34] P. 544. Industrially, laser ablation application for polymers can be categorized into two parts: first application is the production of structure in polymer for instance nozzle production in inkjet printer, production of optical devices and microfluidic channels. In the second application, ablation products are of specific interest, for example polymers work as fuel in micro laser plasma thruster, pulse lase deposition of polymers can be used in deposition of thin films. [34] P. 542

Availability of high energy level of lasers creates more application areas which are based on photo thermal reaction. There are popular non-destructive photothermal measuring technologies based on thermal waves such as laser beams, optical beams and IR radiometry are applicable in coatings and thin films characterization. [35] P. 1461-1465

2.2.3.4 Photomolecular reactions

This mechanism depends on the reaction of light activated small organic molecules in order to improve the polymer based matrix. Other organic materials have also been used to improve the plasticization of a polymer medium, which regulates the adhesion properties and to initiate color changes in presence of light. For instance, light sensitive compound o-quinonediazide derivatives are microresist material and by isomerization of azobenzene derivatives in optical storage devices such as CDs and optical discs. [19], [21]

2.2.3.5 Photodegradation

Most of the polymers get degraded under UV condition. The photopolymer reactions are based on light induced degradation where light sensitive linkages in a chain of polymer breaks when exposed to the UV. Another way of fragmenting polymers is to use light absorbing ingredients such as a l-(plienyl or pyridyl)-3- pyridyl-1, 3-propanedione, which are stable in UV condition. These ingredients may produce some active species such as acids which fragment the polymers. An indication of polymer degradation is the change in solubility of materials from higher to lower molecular weight. Polymer photodegradation can be lowered by adding stabilizers [37]. There are very limited number of commercial products made by using such photopolymer reactions. [19]), [21], [36]

2.3 Overview of 3D printing

Recent improvements in 3D printing allow people to print almost any desired product in a short time. Starting from shoes to bigger machining tools can be printed out quickly which ultimately saves both time and money. In addition to fashion, engineering and laboratory products, 3D printing has also brought unique benefits to the animal world. An Eagle’s beak was replaced by a 3D printed object which helped the bird to survive. [38]

Moreover, it is easier to acquire 3D printing skills compared to traditional injection or extrusion molding machines. This shows that highly skilled people and engineers are not required to operate the printers. However, these molding machines cost comparatively higher and designing the products are even more challenging. Furthermore, it produces less waste in manufacturing process, thereby causing less damage to the environment. [6] P.20

3D printers work in co-operation with 3D modeling software such as CAD which builds the model of the desired object. 3D printers only accept .stl file, which is a machine readable format of the design. This form (.stl) is a file format, also called as Standard Tessellation Language which was derived from Stereolithography. The process of building the complete object is based on layer by layer printing.

2.3.1 History of 3D printing

3D printing was born in 1984 when Charles Hull started playing with printing material instead of ink. Later, he discovered a technique called Stereolithography (SL) which was used to create a 3D printed object. In 1992, the first Stereolithography apparatus (SLA) machine was developed by Hull to make another step of development despite having other technologies in the field such as fusion deposition modeling (FDM) and selective laser sintering (SLS). FDM was established by Scott Crump, founder of Stratasys. In the 1990s, companies such as Stratasys, Z Corp and 3D system gained popularity. These companies started producing 3D printers based on either SL or FDM technology. In addition, development in organ transplant in late 1990s carried out in Wake forest institute for regenerative medicine have opened several doors to engineering 3D printing. During that time, cheaper priced 3D printers came to the market.

In 2002 December, a working 3D printed kidney was created. In the next few years, discoveries in resolution and software capabilities were focused and therefore in 2005, printer Z510, a high definition color printer made a breakthrough in the industry. Then quickly after a year, open source printing project started which is also known as “Reprap” was founded by Dr. Adrian in University of Bath in England which was able to print different plastic parts. Similarly, some 3D companies built printers which could print multiple materials such as plastics and elastomers. Darwin (a self-replicating printer) was a first version or Reprap project which was released in 2008 and later Mendel was released in 2009. In the same year (2009) a hardware company for 3D printers known as Makerbot’s industries started selling out DIY kits which allowed people to build a printing machine and print products at home. Besides, 3D

printed car was developed in 2011 which is believed to be fuel efficient and inexpensive. Likewise, 3D printed robotic aircraft and jewelry were also built in the same year.
Moreover, latest (2012) versions have been experimenting with wires and open beams instead of belts used in previous product. By 2013, companies have successfully launched the mini 3D printers in the market costing less than 1000 € “the guardian wrote on its newsletter”. [39-43]

2.3.2 Families of 3D printers

3D printing can be divided into two families on the basis of working principles.

- ❖ First one works by deposition system, also known selective deposition printer. This kind of printer is mostly used in home-office appliances and works by depositing raw materials layer by layer to create a 3D object. In addition, the printer uses nozzles to spread out the raw materials with different methods such as spraying or squeezing from either paste, solid or liquid form. For instance, Polyjet printing and laser engineered net shaping (LENS) are based on deposition system. [6] P.68
- ❖ The second types of 3D printers are based on fusing or binding of raw materials in order to print the object. They are also called as selective binding printers because it fuses materials layer by layer using light or UV source to solidify the powder or photo polymeric forms of raw materials. These printers started commercially in the early phase of 3D Printing. Techniques such as SL (Stereolithography) and Laser sintering still occupy a big portion in 3D industry. [6] P.73

2.3.3 Methods used in 3D printing technologies

3D printing is also known as desktop fabrication or additive manufacturing and has various methods of product manufacturing. Some methods listed below are based on either lasers, printing or extrusion technology. The first three methods are the most widely used techniques in 3D industries. Stereolithography and Polyjet techniques specifically use photopolymers in order to manufacture the products, while rest of the printing uses metals, powder, ceramics, composites and polymers.

1. Stereolithography (SL)
2. Polyjet photopolymer or Jetted photopolymer (J-P)

3. Selective laser sintering (SLS)
4. 3DP™ - Three dimensional printing
5. Fused deposition modeling (FDM)/ Fused filament fabrication (FFF)
6. Syringe extrusion
7. Selective laser melting (SLM)
8. Direct metal laser sintering (DMLS)
9. Electron beam melting (EBM)
10. Cladding or laser powder forming or Laser deposition technology (LDT)
11. Laminated object manufacturing (LOM)
12. Laser engineered Net shaping etc. [44-46]

2.3.3.1 Stereolithography (SL)

In this technology, the machine called stereolithograph apparatus (SLA) converts liquid plastics into solid materials by UV laser. This technique is the oldest technology in 3D printing developed by Hull in 1984. It works with UV beam or laser by hardening the liquid photopolymer on the surface of filled vat. The major principle of working in all 3D printers are similar since almost all of the technology need 3D design (e.g. CAD) at first, which is a digital representation of an object. Next, the drawn file must change into another printer readable system called Standard Tessellation language (STL), which converts 3D design to the printer readable form. The addition of layers on the top of a liquid occurs by laser beam which is controlled by a computer system. SLA uses liquid photopolymers as a raw material and once it is exposed above perforated platform, UV laser hits the platform which paints the object being printed. In another words, laser beams draw each layer of the object being printed and hardens the photopolymers. [47]

Historically, resins used in Stereolithography techniques were low molecular weight based polymers such as polyacrylate or epoxy macromers, which forms glassy chains with photo initiated polymerization. Nowadays polymers with epoxy based and hybrid systems are preferred rather than the acrylates because of their higher temperature resistance, lower moisture absorption and shrinkage than previously available acrylate based materials. [48] 6121-6130
Here are some commercially available Stereolithography resins with their properties:

Table 3 *Commercially available SL resin*

Somos® 10122 - WaterClear®	Low viscosity, fast, general purpose resin, good temperature resistant and ABS like properties
Somos® 14120 – White	Low viscosity liquid photopolymer and produces water resistant parts
Somos® Nanotool™	Produces strong, stiff and temperature resistant composite parts
SL-100 DMX™	Durable, tough and complex parts can be made with high accuracy

[49]

Application areas:

- Electronics
- Medical and health care
- Sports and leisure
- Packaging
- Military hardware
- Automotive etc. [50]

Manufacturers of SLA given in different parts of the world:

- Envision technologies gmbh, Germany
- Laser solutions, Japan
- Objet geometries, Israel
- 3D system, USA etc. [51]

2.3.3.2 Polyjet photopolymer or jetted photopolymer (J-P)

This is an additive fabrication (manufacturing) process which uses liquid photopolymers in order to create a solid object. The printer consists of jetting heads which moves back and forth in X-axis and draws the sketch of single layer of photopolymer over the build platform. Among the jetting heads one is meant for desired product and the other head is for supporting materials. In this case, liquid photopolymers is cured instantly in each layer by UV-source within the 3D printer, thereby creating a precise model. Once the parts are ready, water jet removes supporting material easily and products can be used instantly which does not necessarily need post curing process. [52-53]

Objet developed the Polyjet photopolymer/ Polyjet technology. In 2012 December, Objet and Stratasys merged and therefore formed a new company consisting of market value approximately $ 3.0 billion and patent of this technology is taken by Stratasys. [54]

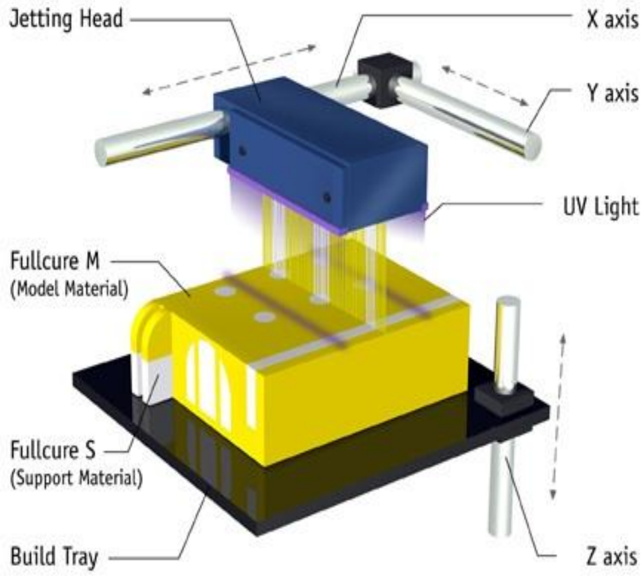


Figure 10 *Objet Polyjet 3D printing [55]*

This technique has the ability to spray the liquid photopolymers in very thin layers as 16 microns, which is even smaller than a human red blood cell. Such technology can play valuable role in critical medical applications. Moreover, photopolymers used in such processes are mostly in liquid form. Although they cost comparatively higher, they are better than the usually available brittle and fragile (easily broken) photopolymers. Technically, Polyjet printers are making big progress in printing, since they can use several materials at the same time. This printer contains several print heads and place for multiple materials in order to produce variety of products at a single time which consequently increases the production volume. [6] P.70

Advantages of Polyjet technology:

- This technology has outstanding surface features with 16 microns per layer i.e. fine layer thickness with accuracy as high as 0.1 mm for complex geometries and smooth surfaces.
- Smooth, clean and no post curing needed.
- Supports the variety of materials with different properties.
- The thin layer technology of this printer is able to print complex parts with the fine details. [56], [53]

2.3.3.2.1 Digital materials made by Polyjet technology (Stratasys)

These days, companies like Stratasys and others make their own materials for their machines in order to build complete parts. There are several types of material used in Polyjet technology and most of them are categorized into tango and Vero based. Some pictures of products made by digital materials are listed in results and discussion where the author had an opportunity to gain some experience in such technology. Some digital materials are listed as follows:

- Polyjet digital material

Digital materials are the combination of different kinds of photopolymers in certain proportions in order to enhance the properties. Examples of such materials are rigid opaque, rubber like material, VeroWhitePlus RGD835, High Temperature RGD525, TangoBlackPlus FLX980 etc.

- Digital ABS

This kind of material is designed to stimulate ABS grade engineering materials in order to develop high impact resistance and shock absorption by combining high temperature resistance to high toughness. For instance, RGD5160-DM is built by combining RGD 155 and RGD 535. Digital ABS is suitable for electrical parts, phone casings, engine parts cover etc.

- High temperature

High temperature materials are useful for testing hot water flow in pipes. Furthermore, tap and other household appliances, post processing of gluing, painting etc. This type of material improves the functional performances of material by stimulating high temperature parts.

- Transparent

Transparent materials in Polyjet 3d printing technology are used for artistic modeling, eye glasses, color dyeing and medical applications. 3D printers can produce varieties of artistic patterns: transparent shades can be created by combining this material with other materials such as black material. Some examples of such materials are VeroBlackPlus RGD875, TangoBlack FLX973 and TangoPlus FLX930.

- Rigid opaque

This sort of material gives perfect visualization and can be found in varieties or colors such as blue, white, black and grey and each have their own applications. Blue is meant for silicon molding, while white is for painting and dyeing. Rigid opaque materials are strong and durable and hence 3d printers can produce accurate products even for movable parts. Moreover, it can create a product with shades if combined with rigid opaque white and rubber like material. It has some family material which has different properties but still belongs in the rigid opaque group. Some of them are:

- Rigid opaque grey (VeroGray RGD850)
- Rigid opaque white(VeroWhitePlus RGD835)
- Rigid opaque black(VeroBlackPlus RGD875)
- Rigid opaque blue (VeroBlue RGD840) [55]

- Polypropylene like

These materials stimulate polypropylene with better thermal resistance. This material is suitable for various applications which need toughness, flexibility, appearance and strength. For instance loud speaker, lab equipment, automotive parts etc. Most common name of polypropylene like material is DurusWhite RGD430. Besides, there exists VeroWhitePlus RGD835, VeroBlackPlus RGD875, and VeroClear RGD810. In fact, it is possible to stimulate polypropylene by combining different types of digital Polyjet materials.

- ➢ Rubber like

Rubbers like material shows elastomer like characters and are applicable in various fields such as gaskets, seats, footwear, models of exhibition and communication, molding etc. This material consists of following members,

- Rubber like grey
- TangoBlack FLX973
- TangoBlackPlus FLX980

It is also possible create the better digital material by combining above mentioned rubber like materials with rigid opaque material.

- ➢ Bio compatible

Biocompatible material is designed for specific functions within the living organisms. [57] This rapid prototyping material features colorless transparency and great dimensional stability. This sort of material is applicable for 3d printing of surgical guides, dental, mouth surgical guidance by parts, implants and other medical applications. All Biocompatible have received medical certification and can be used on Objet Connex 3D printers and Objet Eden. In addition, Objet biocompatible material MED 610 which is applicable in above mentioned areas. [52-53]

- ➢ Dental material

These materials are designed for digital dentistry and similar applications. For a rapidly growing dental industry, 3d printing has brought new era with digital dentistry which can produce crowns, stone modules, bridges etc. with perfect accuracy, economical, fine details and resolution. Here are three dental materials given produced by Stratasys;

- Biocompatible (MED 610)
- VeroDentPlus (MED 690)
- VeroDent (MED 670)

These two provides 16µ thin layers with good strength

Here are some Polyjet 3D printers given based on Stratasys manufacturing including compatible materials and application areas:

Table 4 *Stratasys Polyjet 3D printers and their features*

3D Printers	Materials used	Features
Objet 24	Photopolymer rigid white opaque material(VeroWhitePlus)	Suitable for any product designer or normal users, high resolution, affordable.
Objet Eden 350/350V	Durus white, tango family, Vero clear, rigid opaque material etc.	Wide range of materials, ultra-thin layer, smooth surfaces, complex geometry
Objet 260 Connex	PP like, rigid opaque, rubber like, transparent material etc.	Small, easy to insert material, can print several materials in a single print
Objet 1000	ABS stimulating materials plus other 100 more materials can be used.	For ultra large models, wide and complex details. Suitable for household, industrial, aerospace, automotive industries etc.

[53]

2.3.3.3 Fused deposition modeling (FDM)/ Fused filament fabrication (FFF)

FDM is a rapid prototyping technology developed by Scott Crump, founder of Stratasys nearly two decades ago. This is also a Stratasys- patented technology in 3D printing. FDM 3D printing technology constructs 3D objects from CAD software where temperature controlled head extrudes the thermoplastic material layer by layer. In this process, the material property changes from a solid to a semi liquid state during the extrusion process and follow the path of computer controlled system. A support structure is required which is based on the position of parts in order to complete the product design. [53], [54] [58]

The common materials used in FDM process are ABS, PC, PC-ABS blend, ABSI etc. [59]. In addition, FDM works better in amorphous than with crystalline material. Amorphous material will soften easily and polymers which are extruded from a highly viscous material work better than with lower viscous material. [60] P. 160

Application areas of FDM technology are automotive, medical, industrial, food and beverages etc. Normal households and educational institutions also use FDM 3D printers.

2.3.3.4 Selective laser sintering (SLS)

This is a powder based additive manufacturing technology developed by Carl Deckard in 1986 at the University of Texas. Like other 3D technologies, SLS also begins with 3D designed (CAD) files converted to STL file (machine understandable) and then to the computer processing. In this process, a layer of powder spreads over the machine base area and is rolled uniformly. Computer controlled laser system heats the plastic powder and draws a cross section of a product. This rapid prototyping technology uses CO_2 laser, which provides a high power that heats the powder close to its melting point in order to make them into a solid product. Indeed, laser beam selectively fuses the powdered material and scans the cross section of 3D file obtained in STL format. Once the process is complete, unsintered powders will be removed for reuse-recycle purpose. [52], [62], [61] P. 691-695

SLS has been in use for a long time and some stuff like bricks and jewelleries were made with this technique several years ago. There is another name for metal parts production with the similar process as SLS which is called as DMLAS (direct metal laser sintering). This uses titanium, cobalt stainless steel etc. to manufacture components in layer form. SLS process is comparatively faster and can build smaller features. In addition, this process doesn't need any other support structures like in other methods such as FDM and SLA, since the SLS system uses excess powder in the build piston. [63]

Most commonly used materials for SLS technology are based on polyamides, some are glass filled and some of them are carbon filled. Few examples of materials along with their application areas are given in the table:

Table 5 *Materials used in SLS and applications*

Plastic materials used in SLS	**Application areas**
Duraform materials	Rubber hoses, gaskets, medicals, motor parts, sporting
Nylon 11	Medical, sporting goods
Windfoam LX 2.0	Packaging, driver cockpit kits
PA 615 GS (glass filled nylon)	Housings, motor sports, rapid manufacturing
Flex	Athletic footwear, complex parts production etc.

[64]

2.3.3.5 Three dimensional printing (3DP™)

This technology was born in Massachusetts Institute of Technology (MIT), Cambridge, UAS in 1993. It was commercialized by Z-corporation (Z-corp) which was also developed at MIT. This system also uses the powder material like in SLS, but unlike in SLS, the material is glued by a binder in the platform. It can produce products with different shapes and geometries. Like other 3D systems, it needs 3D object from CAD design. Then the print head of the 3D printer moves to the bed of a powder and draws the sketch of a product by layer basis. This process requires the powder to be spread uniformly over the surface of a build platform. Next, a binding material joins each particle to make the final object. Spreading of powder is done by the help of feed piston and platform which gradually moves upward once the layer completes. Gradually, layer by layer process completes the whole product manufacturing. Unnecessary powders will then clear up by heat treatment or some newer printers can even remove the powder itself upon process completion.

The technology has already made a mark in the rapid prototyping industry and became the first to fabricate ceramic products. Z corp 3DP technology uses these materials:

- Polymer
- Composites
- Metals can be used to create different product. [46], [54], [64], [65]

Here is a table showing the products and their manufacturers:

Table 6 *Companies and applications of 3DP™*

Companies	**Application areas(products)**
Extrude Hone	Engineering components, construction, Mining
Soligen	Housing, sports, aerospace
TDK global	Sensors, ceramic capacitors, wireless charging etc.
Z corporation	3D printers, software etc.

[65]

2.3.3.6 Syringe extrusion

This system works with syringe extruders. Materials like ceramics, clay, Si etc. are used to produce different products. Viscous material such as chocolates can also be produced with this system, where syringe extruders are assembled with 3D printers to create the object. In this process, heating of extruders depends upon type of material used. [44], [67]

2.3.3.7 Selective laser melting (SLM)

This is also one of the additive manufacturing processes which produce three dimensional objects with fine metallic powder. This process uses CAD file to create the object which is later sliced into microlayers. Next, a high power laser beam melts the deposited metal particles in each layer and then gradually forms a bulk object layer by layer. In this technology, the laser completely melts the metal powder in order to create an object. Materials such as titanium, aluminum and cobalt are applied in aerospace, oil and gas and medical application areas. [54], [68]

This process is applicable for low volume productions and saves the cost by optimizing material usage. Complicated shapes can also be made with such technology and with great accuracy.

2.3.3.8 Direct metal laser sintering (DMLS)

This process is closely related to SLM and was developed by EOM Germany. DMLS machine also accepts the CAD drawing and uses high power laser beam to melt the metal powder into solid objects on a layer basis. The process works by fusing many layers of metal powder with laser beam reaction.

This process is applicable in dental, automotive, motor racing and high temperature applications. In addition, materials used in such technology are steel, cobalt, titanium etc. [54], [69]

2.3.3.9 Electron beam melting (EBM)

EBM, a powder based additive manufacturing technology uses metallic powders in order to create 3D products. The technology is patented by Arcam ab, a Swedish additive manufacturing company. Process of EBM includes designing of CAD model, slicing of 3D to 2D design and building the object part layer by layer by using high power electron beam. Electron beam melting takes place in a vacuum and high temperature condition and is controlled by electromagnetic coil.

Materials used in this process are Cobalt chrome (CoCr), Titanium Ti6Al4V, Titanium grade 2 etc. Moreover, some areas of application with EBM are medical, automotive and aerospace. This has been popular in turbine blade repairing and manufacturing because of the technological ability to produce void free parts. [70-72]

2.3.3.10 Cladding or laser powder forming or Laser deposition technology (LDT)

This additive manufacturing process takes place in a controlled environment chamber with <10ppm oxygen. High power laser delivers the metal powder in the melt pool and laser creates a product layer by layer based on the 3D drawing.
Application of such technology is in repairment of damaged components. This method is also used for producing complex and small objects. Materials used in such process are metals, metal powder, polymers and ceramics. [73-75]

2.3.3.11 Laminated object manufacturing (LOM)

LOM is a rapid prototyping system which uses continuous sheet of paper, plastics and metal to create a 3D model. During the operation, materials are usually coated with adhesives and heated roller is pressed over its surface to melt the adhesives with the object. Then laser slices the material into the required pattern.

Raw materials for this technology are easily available and economical. It is useful for production of large parts although the accuracy of the product is comparatively less than SLS or SL technology. Application areas of such technology are in largely build envelop, comparatively cheaper product manufacturing etc. [47], [76]

2.3.3.12 Laser engineered Net Shaping (LENS)

This technology uses metal powders to create a 3D model which is designed in CAD software in the form of stl file. In order to make the layers of product, high power-focused laser beam hits the surface of metal powder and creates the product based on the design. This technology uses titanium and stainless steel to make airplane and automotive parts, since the time when other 3D printing technologies were only using plastic materials. These days' materials like nickel based alloys, titanium based alloys and other specialty materials are in use for LENS system.

This technology is applied in turbine blade making process, which uses hard metals such as titanium alloys. [77], [6] P.71

3 METHOD

3.1 FDM experiment

FDM uses thermoplastics materials in order to print the products with high mechanical and chemical strength which work on layer by layer basis by heating the materials.
Arcada University of Applied Sciences has bought FDM 3D printer which was manufactured in a company called **miniFactory Oy Ltd**. based on Finland. This demonstration experiment was carried out in a composite lab of the school where some simple objects were printed out in the technical guidance of Björn Wiberg. A short description of the printing details is explained below.

3.1.1 Experimental details

The printer used for the demo experiment was miniFactory® 3 Education Edition which is comparatively smaller in size but has great value. The material used in this experiment was PLA. Technical information of the printer based on homepage of the manufacturer is given below: [78]

Table 7 *Technical details of minifactory 3D printer*

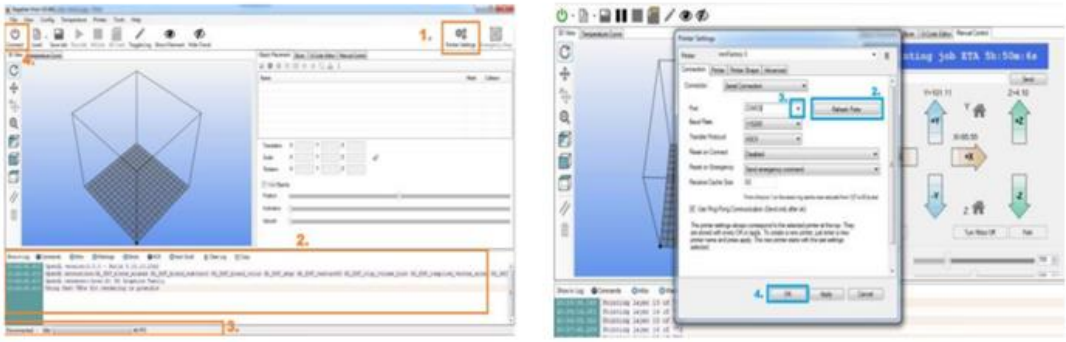
Action motion	80 mm/s
Layer thickness	Max. 100 microns (0,1 mm)
Largest possible size	150 mm * 150 mm * 150 mm
Printing tape thickness	1,75 mm
Nozzle diameter	0,4 mm
Whole printer dimension	43,5 cm * 34 cm * 30 cm
Weight	11 kg

At first the .stl version of product design was downloaded from the web source and imported into the software system. In the case of FDM 3D printing using PLA, glass plate of the printer should always be washed very well and completely dried before use. Technical details were set on the basis of the printer's capacity and technician recommendations. Some of them are listed here:

Table 8 *Technical settings of a 3D printer for demo experiment*

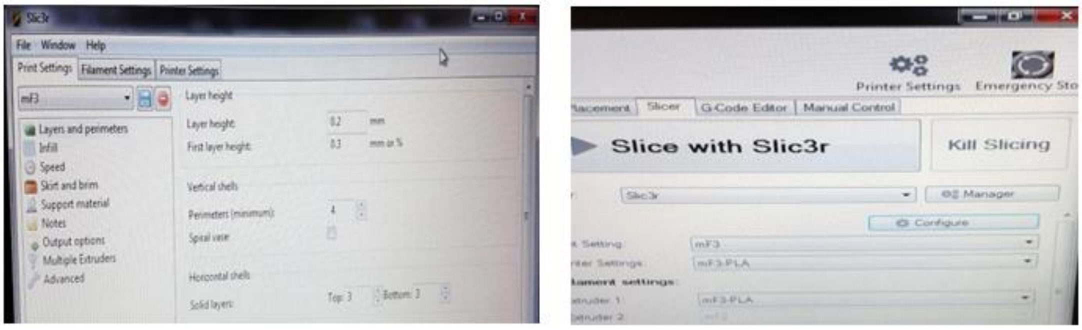
Extruder temperature	200 °C
Bed temperature	70 °C
External perimeter speed	40 mm/s
Layer height	0,2 mm
Travel speed	60 mm/s
First layer height	0,3 mm
Fill pattern	honey comb
Extruder clearance height	30 mm
Extruder clearance radius	40 mm
Extrusion width	0,42 mm
Fill density	0,2
Fill angle	45°

Furthermore, knowledge of some key functions is needed in order to run the printer smoothly. Connection settings of printer can be done through **printer setting**. Another option **log** shows the communication in between printer and computer system. Likewise, there is **status bar** icon to show the status of the device. To turn on and off the computer system, there is **connect** which connects the printer and computer in first click and disconnect in the second click on the same button. Click on the printer setting opens a page (fig.11) where COM Port can be chosen right after pressing the button **refresh**. One click on **ok** makes the device ready. The button, **connect** makes connection between the printer and the computer, which the display shows **connected** and **idle** in status bar.



(a) Setting tools for 3D printer [78]   (b) Connect setting tools of 3D printer

Figure 11 *FDM 3D printer setting tools [78]*



(c) Different setting options in a printer   (d) Configure tool setting

Figure 12 *Setting tools in FDM minifactory 3D printer [photo taken by: Ramji Pandey]*

The printer and material setting can be changed by clicking on **configure** button in the page **slicer** .This leads to the page of slic3r where, different setting tools can be found as can be seen in fig. 12. The changes of different setting can be made through that page.

Below is the fig. 13 given which was downloaded in .stl form from **thingiverse** and was intended to print in the institution lab.

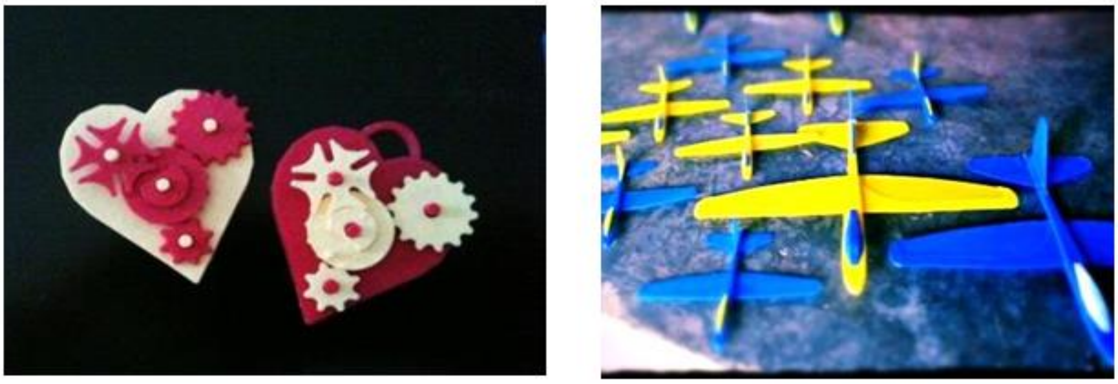


Figure 13 *Valentine's kit and monarch glider [79]*

However, because of some complexities, only certain parts from the above objects were printed in the lab which is attached below:

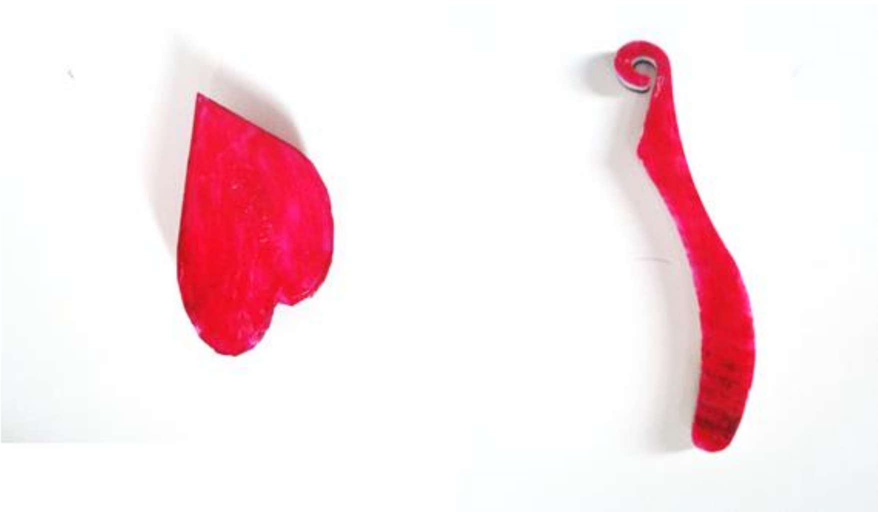


Figure 14 *Colored images of the printed products [Photo by: Ramji Pandey]*

The image of given pictures (fig. 13) consists of several parts and have complex geometries. In order to print those objects in the institution lab needs advance 3D printer. Therefore, only possible parts of such products are taken into the printing system. The material used to print such products in the lab was polylactic acid (PLA). The roll of PLA material which was mass of 1 kg attached in top side of the 3D printer.

Figure 15 *PLA roll available at Arcada [photo taken by- Ramji Pandey]*

Furthermore, technical settings of PLA material for the experiement are listed here:

Table 9 *PLA setting for 3D printing experiment*

Bed temperature	70 ˚C
Bridge fan speed	100 mm/s
First layer temperature	200 ˚C
Maximum/minimum fan speed	100 mm/s
Minimum print speed	20 mm/s
Extruder temperature	200 ˚C

The material used in lab was in the form of filament which was white in color and 1,75mm diameter. Besides PLA material , this 3D printer can also use other materials such as ABS and nylon.

3.2 Study visit to plastic fair

K-Fair is a worldwide event organized by plastic and rubber industries in Dusseldorf Germany in each 3 years period. K-Fair is also a platform for plastic and rubber industries to show different technologies and products. The fair exhibited a variety of 3D technologies and photopolymers. A week period trip was organized by polymer engineering technology (PET) club in the month of October, 2013. During the observation period, the author had some useful conversation with relevant people.

The majority of the companies at the fair represented sales and manufacturing of plastics and rubber products. However, in order to support this thesis work, visit to companies exhibiting 3D printing technologies was the priority including companies representing photopolymer applications in plating systems. Some companies were already world famous (e.g. Stratasys) in the plastics parts printing, while some were specialized in metals and ceramics parts. Some discussions were made during the visit to companies' stall which raised motivation in the field of 3D printing.

3.2.1 Stratasys for 3D world

This giant company is well renowned in 3D business, which has its headquarters based in US and branches in different parts of world. Stratasys is hugely popular in FDM and Polyjet based technology in 3D printing and it was not a surprise to see them in the fair. There were some discussions related to the technologies and future challenges of the industries. The fig. 16 shows the FDM machine (objet connex 500) and Polyjet products. The cost of the Objet 500 connex according to the personnel was estimated at €181,688. Furthermore, this printer is one of the biggest in Polyjet printing.

Objet 500 connex 3D printer *Polyjet products*

Figure 16 *Stratasys products at K-fair, Germany [photo taken by: Ramji Pandey]*

3.3 Comparison between FDM 3D printing and Polyjet technology

New research shows that the market of 3D printing is growing fast and this is because of increasing number of application areas and development of such technologies in other geographical areas outside the dominant North America. The market value of 3D printing technologies such as FDM, Polyjet, SLS and SLA was $ 2,200 million in 2012 and is anticipated to rise close to $ 7,240 million in 2019.

Currently, Stratasys is popular in both FDM and Polyjet 3D printing technologies. The products from these systems have applications in several fields such as medical, automotive, education, aerospace, jewelry etc. Below is the table attached of comparison between FDM and Polyjet technologies:

Table 10 *Comparison between FDM and Polyjet 3D printing technology*

	FDM technology	**Polyjet technology**
Mechanism	This is an extrusion based technology where thermoplastics are heated and deposits in a base plate to create a product layer by layer basis.	It uses two or more jetting heads which create the initial sketch of product by spraying the liquid materials layer by layer basis. More jetting heads are applied in either model or support material applications.
Materials used	Few thermoplastics materials are used such as ABS, PC, PC-ABS blends etc.	Liquid photopolymers are mostly used. There are over 450 types of materials with different properties.
Advantages & Disadvantages	Lower cost of the machine. Produce durable parts. The most commonly used materials are durable thermoplastics. No possibility of multimaterial printing. Printing process is slower.	Can produce similar property type objects with ABS- like material which is also used by FDM. However, this produces high resolution and better surface finish. Can use flexible rubber like and transparent materials. Ability to print multiple materials at the same time. Process of printing is faster.
Surface finish	Further post processing needed to remove the visible line which is the result of extrusion process.	Product comes with better surface finish. No need of post curing.

Although the applications of Polyjet and FDM technologies are different, they have some similar features. For instance, both can use bio compatible materials, they are easy to use and can build similar sized products. [82-84]

4 RESULTS AND DISCUSSIONS

4.1 FDM printing

Operating of the minifactory fusion deposition modeling printer was initially challenging. There were mainly two factors affecting the printing process. At first, bigger file size of the product (.stl file) could not operate the printer especially in the case of monarch glider. Therefore, only a single part of the glider was chosen to print. It has the similar case for valentine’s kit which initially contained complex parts and therefore became impossible to print a complete product. This could be because of the lower capacity of the machine and may need advancement in technology. Secondly, the glass plate of the printer should be cleaned very well in the case of PLA filament. The presence of dust particles which is usually from the composite materials present in the lab may stick to the glass plate and static electricity may affect in the deposition of initial PLA layer. Furthermore, surface quality of the valentine’s kit did not come as good as it should have printed. Printing process of valentine’s kit was just started right after the glider’s part (first one) and hence there was a less time to clean up the glass plate. There could be some unseen leftover residues from the first product that could have affected the printing of the second object.

There were two products printed out within 2.5 hours of experiment each taking more than half an hour and rest of the time for settings and cleaning of equipment. This seemed somehow that FDM is time consuming process in reality. Moreover, PLA also showed variation in character, sometimes it had problem in attaching the very first layer on the glass plate which subsequently affected other layers. Besides, it often turned very hard or brittle on the glass plate and can be dangerous while removing it from the surface [78]. Furthermore, it was also found that minifactory 3D printer was unable to print out more complex designs since the printer could not adjust the file in its system for complex shapes during experiment. This could be because of the very small object boundaries of the machine.

Some of the experimenting pictures were taken during the printing time which is listed below. Fig.17 shows the printer and computer system connection including how the attachment of PLA filament to the extrusion holes.

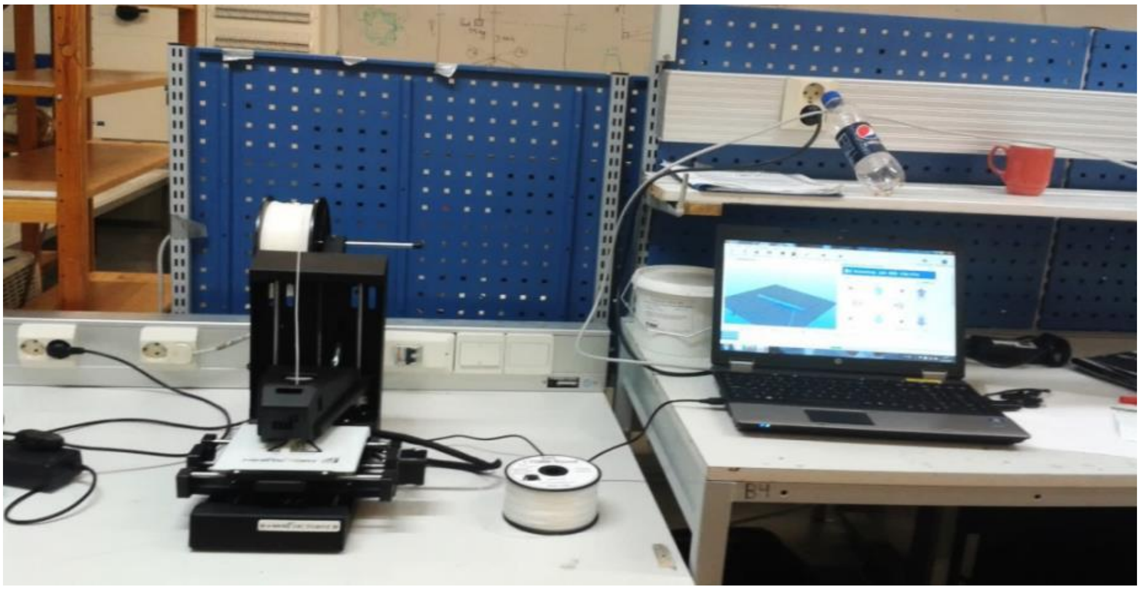
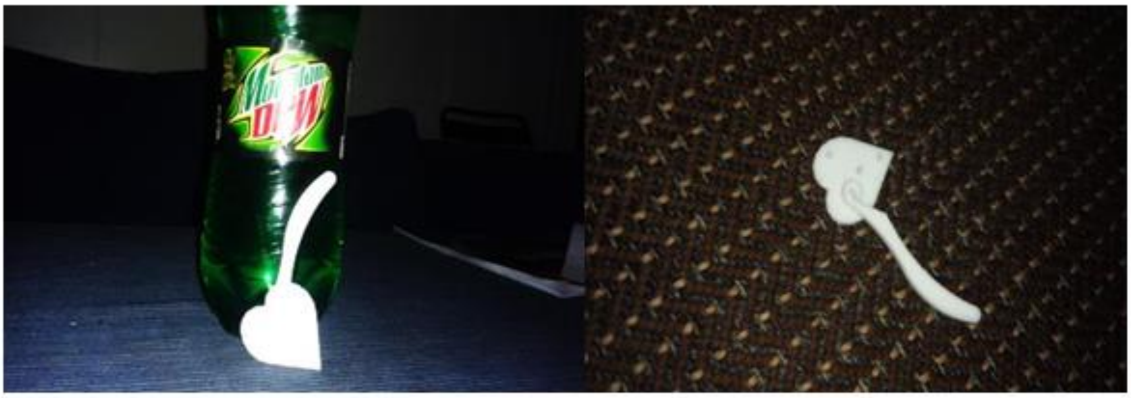


Figure 17 *FDM 3D printer at Arcada lab [photo taken by- Ramji Pandey]*

Below is fig.18, which shows the different products being printed. The various images were taken during the experiment. Some pictures show the desktop image while, some show the printing steps. The final objects are placed together.

(a) Desktop image of valentine's kit being printed *(b) Product being printed*

(b) Desktop image of glider's part being printed *(d) Product being printed*



(c) Final products combination (front and back view)

Figure 18 *Different stages of 3D printing at Arcada lab [photo taken- Ramji Pandey]*

4.2 K-Fair

Plastic and rubber industries world trade fair also known as K-fair was useful in the context of the visual inspection and discussions. K-Fair was not only applicable to see and feel the incredible 3D printers but also became useful in terms of discussions and seeing of live production of interesting objects. Some pictures were taken during the stall visit of Stratasys;

Stratasys product of Polyjet 3D printing

Photopolymers product by polyjet 3D printing technology

Figure 19 *Stratasys Polyjet 3D printing products [photo taken- Ramji Pandey]*

The first picture of the fig. 19 is a wonderful product made by Polyjet 3D printing technology with photopolymer materials while, another image shows the product with digital materials created by the company. These materials can be for instance, PP-like, rubber like, ABS like material etc. This also shows how several products can be made by multiple materials by a newly developed 3D printer.

In short meetings with representatives, some issues related to competitive markets and traditional molding technologies were discussed. They believed that 3D printing technology will grow gradually instead of leaping to overcome other traditional injection and extrusion technologies. They also added prices for machines will become much cheaper. However, some bigger machines such as Connex 500 (Polyjet) cost $ 250,000 which was launched just before Connex 1000.

In addition, it was also explained how the digital materials are developed in industry in order to create different products. To create the new materials, two standard photopolymers are combined in a certain proportions inside the printer in order to develop the properties of desired product. They even explained how the different products (fig.19) can be produced with single 3D printer using different materials at the same time.

Besides, **Marabu** was another company which came to K- fair which manufactures digital, screen and pad printing inks. For example, a unique looking bottle opener was a product of ink printing. In a material perspective, they use resins and polymer additives as an ink material.

There was also a company for laser sintering system called **EOS, e-manufacturing** solution for metal part productions with 3D printing.

Furthermore, the company **moss srl** was the one which were using photopolymers of 0.83mm thick on steel plate. These plates appeared thin and shiny. No pictures were taken since cameras were not allowed.

5 CONCLUSION

To make a greater impact on technology, photopolymers have been playing a vital role since a long history. These soluble and light sensitive materials were already applied in non 3D printing technologies such as coatings, ink and adhesives. In 3D printing technology such as SL, photopolymers continue to make a great achievement. In order to compete with other technologies, Polyjet have developed several digital materials to create the complex shapes from micro objects level to macro products. Moreover, the improvements in the application of photopolymers such as development of photocrosslinkable materials have helped in making products with better chemical and mechanical properties. From the development of classical photopolymers such as epoxy and acrylics into combination system of photopolymers, new photopolymers with different properties in terms of auto photo sensitivity and solubility have been developed.

In recent times, the FDM and Polyjet technologies have gained popularity in 3D printing business. FDM 3D printers are used to produce high performance products, whereas Polyjet printers are useful for creating products with multiple materials with better surface finish. Since FDM technology is affordable, it is widely used in offices and educational institutions. However, their applications are limited compared to Polyjet technology. With rapid advancement in research and development, technologies such as Polyjet could become more cost-effective and eventually have a much bigger market.

Minifactory 3D printer has a capability of printing small objects with simple design. The bigger file sized product was unsuccessful in the Arcada’s 3D printer. Moreover, making the product surface with **honey comb** printer settings is economic as it consumes less material. It was learned that glass plates of the printer should be very clean and dry just before printing out the material. Sometimes problems in nozzle of the printer may clot or jam and create printing problems. Hence, taking precautions such as cleaning the plate and having the right temperature settings will make a proper first layer as well as the final product. It also prevents issues such as clotting in the printing nozzle.

Study visit to K-Fair was quite useful in terms of learning the existing and future technologies related to 3D printing and photopolymers. Face to face conversations and discussions about photopolymers with company representatives provided lively information, from inks applications to 3D printing technology. Stratasys had the latest Polyjet 3D printers and products made from newly developed materials.

Development of photopolymers with desirable properties such as chemical composition, mechanical strengths, and bio compatible material will be useful in creating complex products and thereby increase the application areas. Rapid development in 3D printing technology brings the possibility of applying photopolymers from the existing two systems (SL and Polyjet) to several other technologies.

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