Rapid Manufacturing

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Lecture – 18
Polymerization processes (Part 1 of 2)

So, welcome to the next lecture in the course of Rapid Manufacturing which is focused towards rapid prototyping processes. In the concept of rapid manufacturing, rapid prototyping place a very major important role or in the era where rapid manufacturing is going on rapid prototyping is a processes are playing a very very major role and a major share.

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In order to understand rapid prototyping process more in detail, we will first see the science or the principle behind these processes.

So, first we will try to see polymerization that is photopolymerization, then we will see photopolymerization of materials, then we will see reaction rates and then we will start looking into various processes stereo lithography. And we will see a machine in stereo lithography, then what are the different scan patterns, vector scanning, then mask projection photopolymerization process, then at last to be Two-Photon stereo lithography processes.

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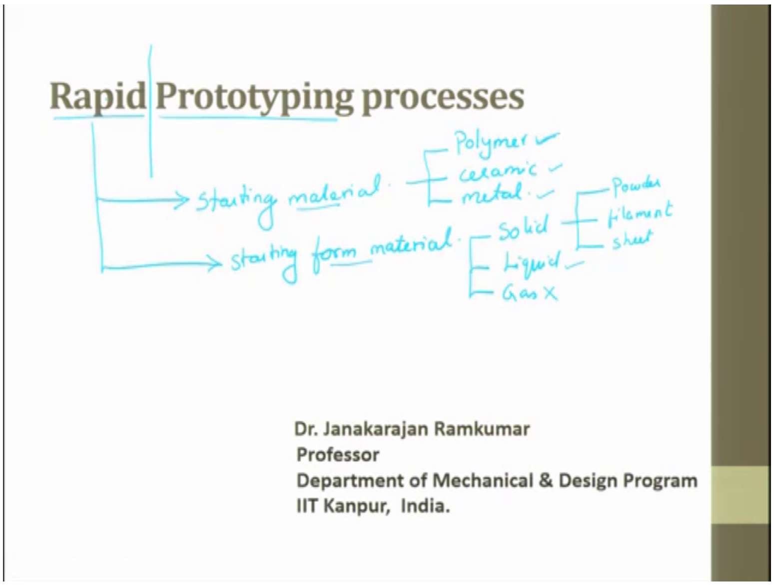

Rapid Prototyping processes

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When we talk about rapid prototyping so, it is very clear that it is rapidly you are suppose to make prototypes. So, when you are rapidly suppose to make prototypes it primarily depends upon what is your starting material and the next thing is, what is your starting form of material. So, what is the starting material, you can have a polymer, you can have a ceramic, you can have a metal and the starting form material can be a solid, can be a liquid, of course, you can also have gas.

But since the thickness whatever you make is going to be very less in gaseous form. So, we do not take this gaseous as a predominant starting form of material to do prototyping. So, now, it is very clear you can have polymer material, ceramic material, metals and they can exist in solid form and liquid form. Again I will try to classify in solid form also 3 things it can be in powder form; it can be in filament form, it can be in sheet form basically 0 D, 1 D, 2 D, liquid form as you know it is it is very easy for processing.

So, now what is happening is when you choose the material correspondingly we have to choose how can I join these materials together such that you can form a prototype. So, basically here what we do is the polymer which exist in liquid form is chosen. And here what happens is when we wanted to convert a liquid into a solid there is a process which happens to convert the liquid into a solid is called as photopolymerization is called as first solid a liquid to solid is polymerization, even if it initiates or activates or happens because of the presence of photo; that means, to say light it is called as photopolymerization.

When you try to take a polymer and a powder form, you can use laser. So, it will be more of selective laser sintering, if you take it as metal which can be selective laser sintering or selective laser melting. When you try to take filament it can be polymer if it is like you take it a visco elastic state allow it to cure or when you take metals also you can try to apply heat and convert this filament into a droplet and droplet is again converted into a 3 D form to give a shape to it. So, depending upon the starting material the rapid prototyping process cost time accuracy depends. So, with this basic fundamental understanding let us keep moving.

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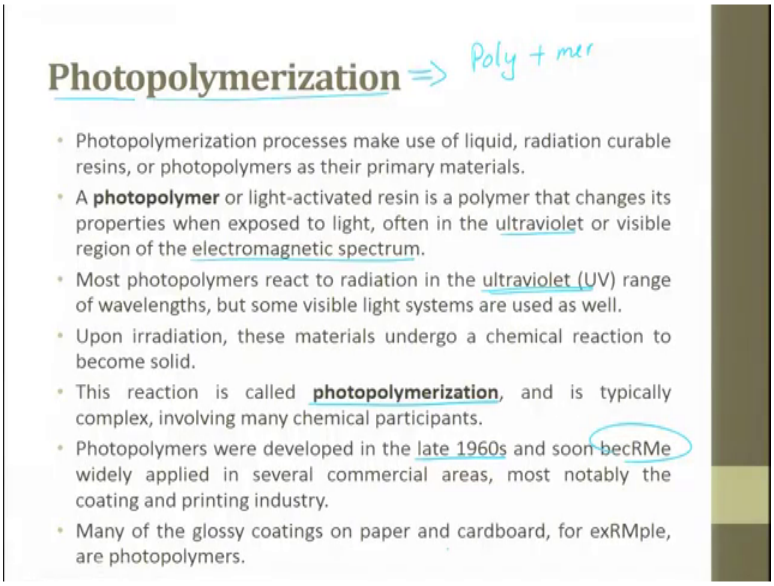

Photopolymerization ⇒ Poly + mer

- Photopolymerization processes make use of liquid, radiation curable resins, or photopolymers as their primary materials.
- A **photopolymer** or light-activated resin is a polymer that changes its properties when exposed to light, often in the ultraviolet or visible region of the electromagnetic spectrum.
- Most photopolymers react to radiation in the ultraviolet (UV) range of wavelengths, but some visible light systems are used as well.
- Upon irradiation, these materials undergo a chemical reaction to become solid.
- This reaction is called **photopolymerization**, and is typically complex, involving many chemical participants.
- Photopolymers were developed in the late 1960s and soon becRMe widely applied in several commercial areas, most notably the coating and printing industry.
- Many of the glossy coatings on paper and cardboard, for exRMple, are photopolymers.

So, as I told you polymerization, polymerization is what is polymer it is poly plus mer. So, it is several of these mers join together to form a polymer. So, the process of joining several of these mers to form a polymer is called as polymerization process. If the polymerization process can be initiated by a presence of light, it is called as photopolymerization. Photopolymerization makes use of a liquid, radiation crucible resin or a photopolymer as their primary material. A photopolymer or a light activated resin is a polymer that changes it is property when exposed to light, often in the presence of UV light or visible region of a electromagnetic spectrum.

Most photopolymers react to radiation in the UV range of wavelengths, but some visible light systems are also used for. So, predominantly it will be UV based so, you take a UV light. So, basically you can take a UV lamp or you can take a UV laser for curing it. We prefer UV laser because you can have fine resolutions in the developed material. Upon irradiation, these materials undergo a chemical reaction to become a solid. This reaction is called as photopolymerization and is typically complex involving many chemical participants.

Photopolymers where in the late 1960s and soon became widely applied in several commercial areas most notably the coatings and printing industry. Many of the glassy coating on paper and cardboard; for example are photopolymerization.

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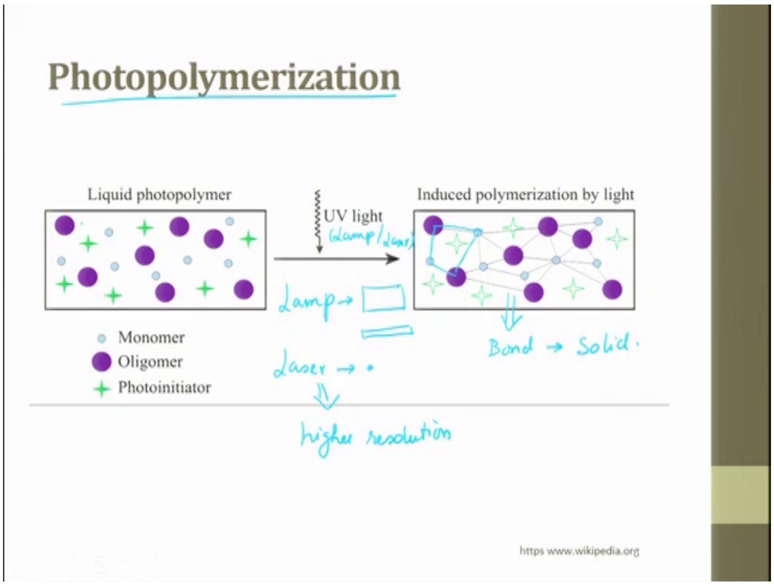

Photopolymerization

https www.wikipedia.org

So, this is a liquid polymer (Refer Time: 07:21) you can see blue small small dots are called as monomers and along with the monomers you have this violet one are called as oligomers and then we have photoinitiators which are green and when the UV light hits on it you can see these mers are trying to form a network with oligomer. They are trying to form a oligomer and the photoinitiator are used to start the reaction and form this bond between them. So, because of the bond forming this is the bond this tries to make it into a solid.

As I told you this UV can be from a lamp or it can be from a laser and when I talk about lamp so you will not your exposure area many a times will be over a large area or it will be along a single line, but when I talk about laser it will always be a spot. So, this has more higher resolution so, I would like to prefer having a UV laser for doing this photopolymerization. So, it is very clear from this diagram the mers and the oligomer joins together by a bond by this process.

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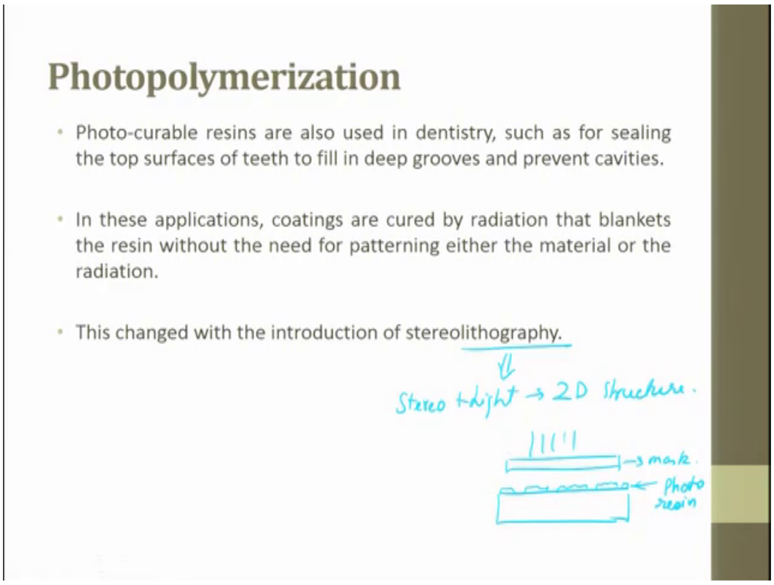

Photopolymerization

- Photo-curable resins are also used in dentistry, such as for sealing the top surfaces of teeth to fill in deep grooves and prevent cavities.
- In these applications, coatings are cured by radiation that blankets the resin without the need for patterning either the material or the radiation.
- This changed with the introduction of stereolithography.

Stereo + Light → 2D Structure.

Photo curable resins are also used in dentistry such as for sealing the top surface of the teeth to fill in deep grooves and prevent cavities. In these applications, coatings are cured by radiation that blankets the resin without the need of patterning either the material or the radiation. This changed with the introduction of stereolithography. Stereolithography is a process it is also interesting if you go back and look at it.

Stereolithography lithography, lithography is lights for making 2 D structures. If I want to make a 3 D structure so, I call this process as stereolithography. Lithography means you have a light where in which this light is exposed on top of a mask. So, light exposed on top of a mask this is a mask and then you have some material this material is getting the mask is getting transferred you have a photopolymer. So, because of the light exposure, you get this photo resin on curing it tries to create this structure.

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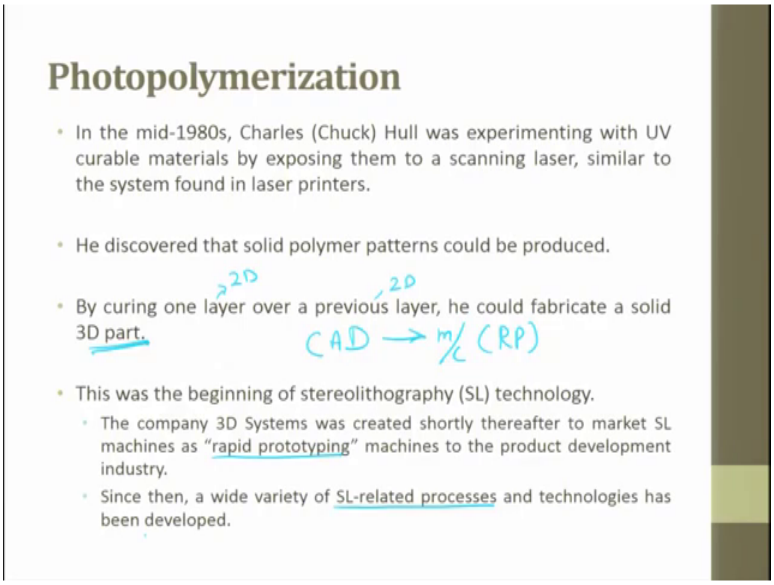

Photopolymerization

- In the mid-1980s, Charles (Chuck) Hull was experimenting with UV curable materials by exposing them to a scanning laser, similar to the system found in laser printers.
- He discovered that solid polymer patterns could be produced.
- By curing one layer over a previous layer, he could fabricate a solid 3D part.
- This was the beginning of stereolithography (SL) technology.
  - The company 3D Systems was created shortly thereafter to market SL machines as "rapid prototyping" machines to the product development industry.
  - Since then, a wide variety of SL-related processes and technologies has been developed.

In the mid 1980s, Charles Hull was experimenting with UV curable material by exposing them to a scanning laser similar to the system found in the laser printer. He discovered that solid polymer patterns could be produced. By curing one layer over a previous layer, he could fabricate a solid 3 D part. So, one layer is nothing, but a 2 D layer. So, by curing one layer over the previous 2 D layer he got a 3 D part made. This was the beginning of stereolithography which is otherwise called as SL technology. The company 3 D systems was created shortly thereafter to market SL machines as “rapid prototyping” machine to the product development industry.

So, you can quickly develop, why quickly you can develop the process starts it from cad, it goes to the machine and these machines are rapid prototyping machines where in which you get the output so, this try to reduce the cycle of product lifecycle. So, since then a wide variety of SL related processes and technologies have been developed.

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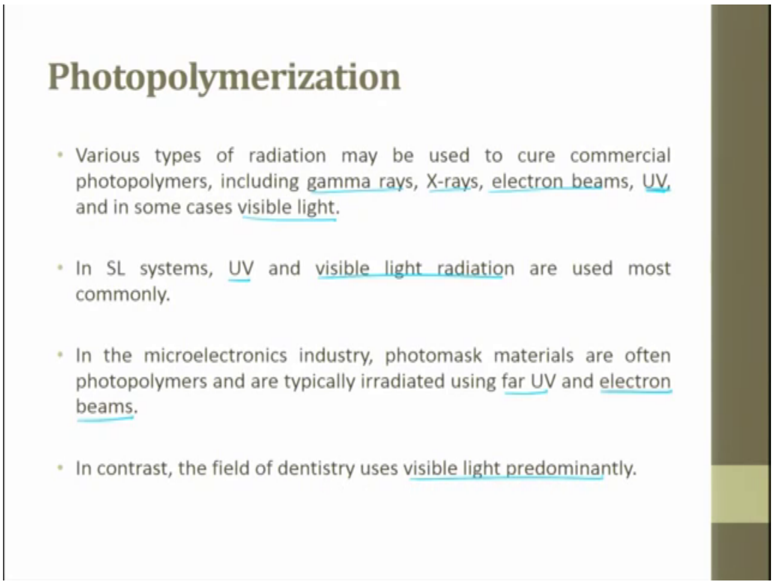

Photopolymerization

- Various types of radiation may be used to cure commercial photopolymers, including gamma rays, X-rays, electron beams, UV, and in some cases visible light.
- In SL systems, UV and visible light radiation are used most commonly.
- In the microelectronics industry, photomask materials are often photopolymers and are typically irradiated using far UV and electron beams.
- In contrast, the field of dentistry uses visible light predominantly.

The various types of radiations maybe used to cure commercial photopolymers including gamma rays, X-ray, electron beam, UV and in some cases visible light. This UV compared to electron beam X- ray, gamma ray; there are lot of advantage. The advantage can be the resolution can be as small as possible, but the disadvantages as it has lot of side effects and controlling the system also becomes very difficult from the source to the workpiece.

So, we always prefer to use UV light. In SL system UV and visible light radiations are used most commonly UV and visible light radiation. In the microelectronic industry photo mask material are often photopolymers and are relatively irradiated using far UV and electron beam. If the resolution or if you want the resolution of the feature which is getting generated on a polymer surface to be as small as possible. For example, you wanted in nanometers, then we go for electron beam which is otherwise called as electron beam lithography. In contrast the field of dentistry uses a visible light predominantly, this is used for curing and making the caps.

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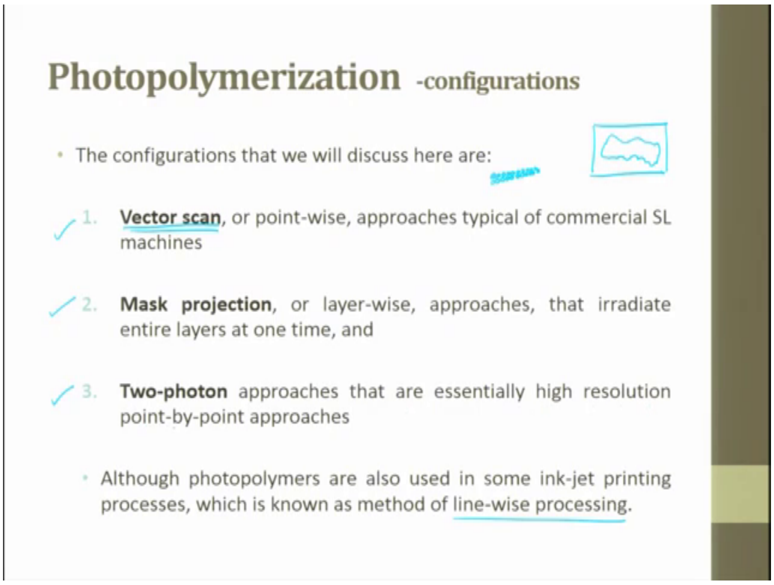

Photopolymerization -configurations

- The configurations that we will discuss here are:
  1. **Vector scan**, or point-wise, approaches typical of commercial SL machines
  2. **Mask projection**, or layer-wise, approaches, that irradiate entire layers at one time, and
  3. **Two-photon** approaches that are essentially high resolution point-by-point approaches
  - Although photopolymers are also used in some ink-jet printing processes, which is known as method of line-wise processing.

The configuration that we will discuss here are vector scan or point wise approaches typically of commercial SL machines, mask projection or layer wise approach that irradiates entire layer at one time. We will see Two-photon approach that are essentially high resolution point by point approach. Although photopolymers are also used in some ink-jet printing processes, which is known as the method of line- wise processing. So, the configuration can be vector scanning can be mask projection and Two- photon.

Predominantly what happens is vector scanning, mask projection is you ah. So, here vector scanning means you have a point several of these points join together to form a line and several of these lines join to form a figure whatever it is right and when I say a mask one layer of entire information is exposed and you get it in one shot. So, that is mask production and two - photon approach that are essentially high resolution point by point approach. So, here instead of a single photon which is used in vector scan here we use two- photons to cure it.

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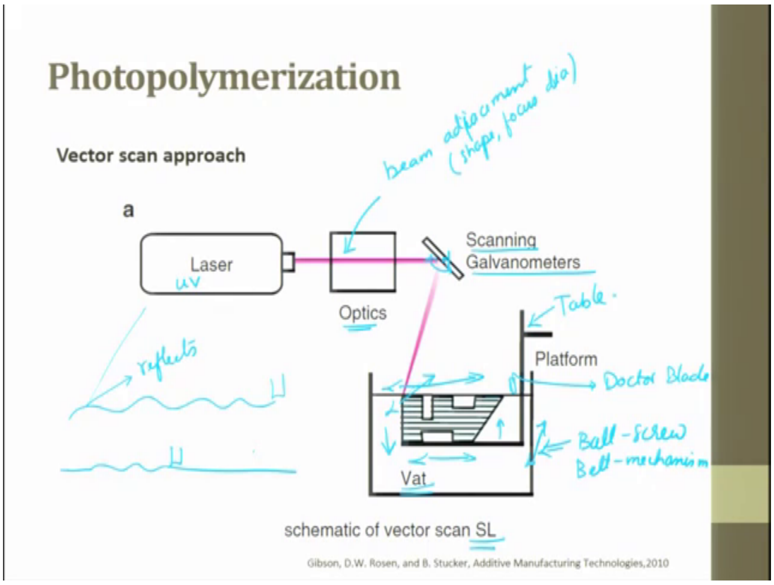

Photopolymerization

Vector scan approach

schematic of vector scan SL

Gibson, D.W. Rosen, and B. Stucker, Additive Manufacturing Technologies,2010

So, this is a typical setup of stereolithography schematic diagram. So, you have a laser this laser predominantly is UV laser. So, that it can go cure the liquid polymer passes through optics so this optics is for beam adjustment in terms of shape, in terms of focus diameter. So, this optics place a very very important role. The thing is when we wanted to make an object which is slightly large and if you want to move this table in a high speed maybe 100 meters per minute or something like that. So, then what happens the ball screw mechanism what is used or the belt drive mechanism what is used, is not of high repeatable or it gives you a poor repeatability.

So, in order to avoid this what we do is, nowadays we try to go for a scanning galvanometer, this galvanometer tries to sweep in one direction; it is pivoted here in one direction. So, it tries to hit at layer of polymer and tries to cure in the x and y plane. So, it hits and moves on the x and y plane of a single layer. So, this once a single layer is cured the table is move down by a required layer thickness or whatever you have assigned layer thickness it sinks down. So, then once the object which is cured sinks down now the fresh photopolymer face on top of it.

Now, again the laser hits on top of it and starts curing it. So, the repetitive curing of layer and sinking down of vat tries to help in building a 3D object that vat is nothing, but a container where a liquid polymer is held this is a table where in which the table sinks and then new layers are getting formed. There is also a doctor's blade which is kept here the it is called as doctor blade doctor blade ok. So, this will make sure that the layer thickness height is uniformly maintained along the surface because in water what happens, you will always have wrinkles so, or you will have wave patterns. So, this has to be nullified by a knife. So, this will be like this when you move the knife ok.

So, the knife is moving so, all the world the wave pattern which is there will be removed and then you have a smooth surface on top it hits why, because if you have a wavy pattern and when the laser tries to hit there is a possibility it reflects ok, if it reflects the efficiency of the process goes down. So, this is a vector scan approach.

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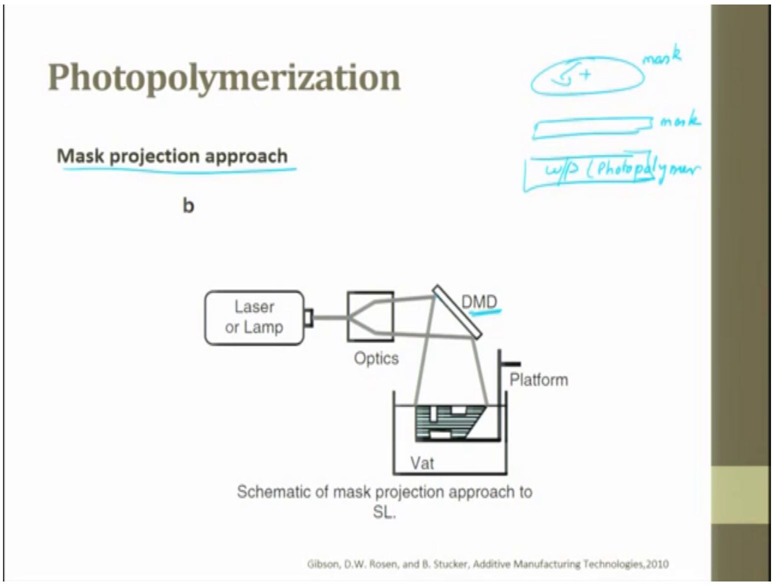

Photopolymerization

Mask projection approach

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Schematic of mask projection approach to SL.

Gibson, D.W. Rosen, and B. Stucker, Additive Manufacturing Technologies,2010

So, next technique for our discussion is mask projection technique, as I told you there will be a mask. So, this mask you can have a static mask static mask which is getting exposed this is a mask which is getting try to export or exposed on a workpiece you can do it and this workpiece is nothing, but a photopolymer.

You can have a static mask or you can have also a disc which is rotating. You can also use this as a mask and start developing the entire detail, but due to the recent developments in the electronics we have DMDs. So, in DMSs what will happen? You will have small small small small mirrors which are placed at the galvo. So, the laser light passes through the optics get itself exposed and this DMD will try to expose the complete layer as though there is a mask on top of it complete layer on top of the photopolymer thin film whatever was there or the liquid whichever is there and it tries to cure it. So, this is called as mask projection approach. In mask projection approach the complete layer of information will be exposed in one shot. So, this process is much faster than the previous process.

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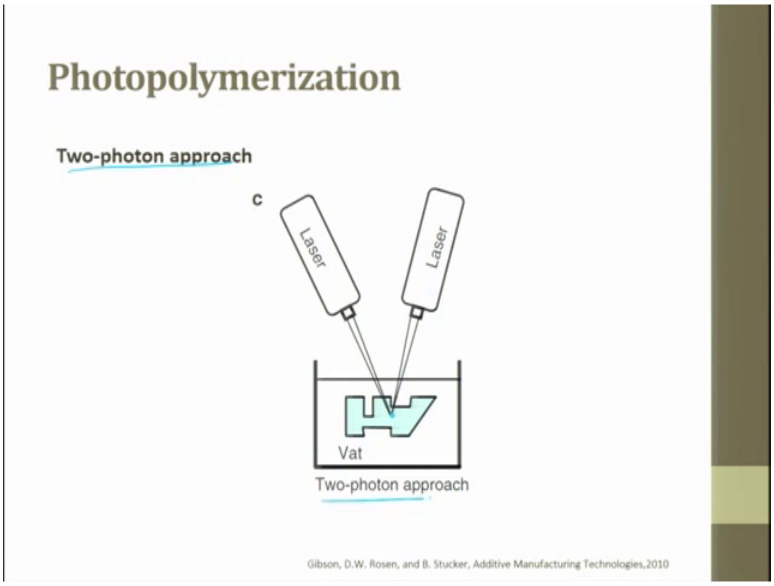

Photopolymerization

Two-photon approach

Two-photon approach

Gibson, D.W. Rosen, and B. Stucker, Additive Manufacturing Technologies,2010

The next process which we are going to discuss is laser photon approach, here in which we use 2 lasers these 2 lasers who hit at the at a single point on the liquid polymer and start curing it so, this is what is Two- photon approach.

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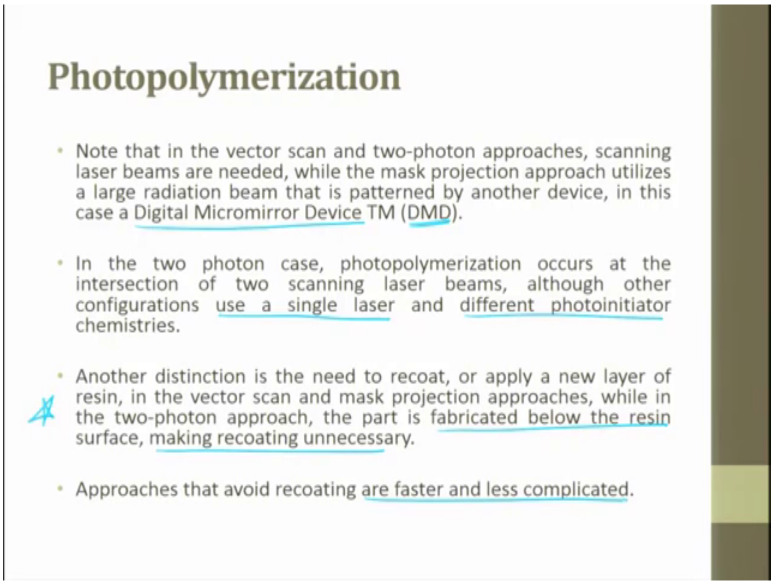

Photopolymerization

- Note that in the vector scan and two-photon approaches, scanning laser beams are needed, while the mask projection approach utilizes a large radiation beam that is patterned by another device, in this case a Digital Micromirror Device TM (DMD).
- In the two photon case, photopolymerization occurs at the intersection of two scanning laser beams, although other configurations use a single laser and different photoinitiator chemistries.
- Another distinction is the need to recoat, or apply a new layer of resin, in the vector scan and mask projection approaches, while in the two-photon approach, the part is fabricated below the resin surface, making recoating unnecessary.
- Approaches that avoid recoating are faster and less complicated.

Noted that in the vector scan and the Two-photon approach, scanning laser beam are needed, while the mask projection approach utilizes a large radiation beam that is patterned by another device, in this case it is a digital micromirror device. Which is nothing, but DMD, DMD stands for digital micromirror device.

In the Two-photon case photopolymerization occurs at the interaction of 2 scanning laser beams, although other configuration uses a single laser at different photoinitiator chemistry. So, although the other configurations uses a single laser both vector and even the mask use a single layer and different photoinitiator chemistries. All another distinction is the need to recoat or apply a new layer of resin in the vector scan and mask projection approach while in the 2 photon approach, the path is fabricated below the resin surface making recoating unnecessary.

This is a very very valid point and important which distinguishes itself from vector and mask projection technique. As I told you the wave pattern which is there on top of the surface of the photopolymer; if it is not made flat, the process efficiency falls down drastically, the curing does not happen properly. So, there is a possibility of defects like shrinkage or warping can happen in due course of time. In order to avoid that in two-photon approach the part is fabricated below the resin surface making recoating unnecessary, the approaches that avoid recoating are faster and less complicated.

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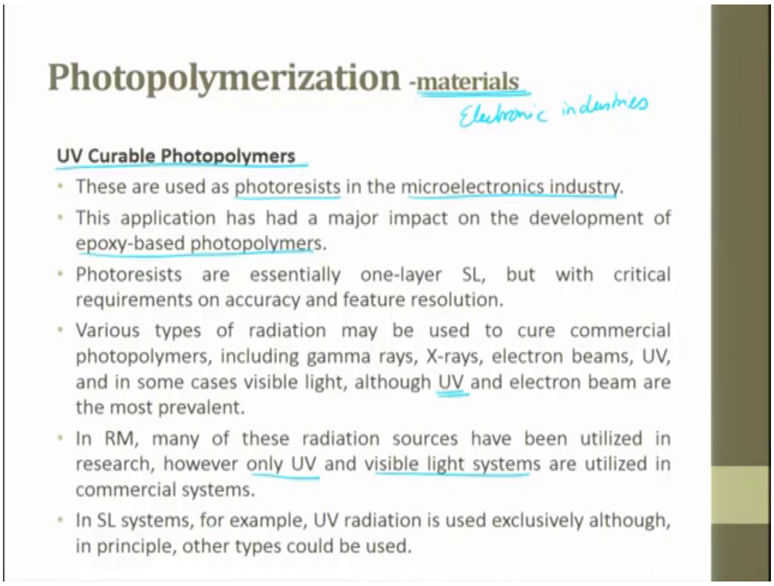

Photopolymerization -materials

Electronic industries

UV Curable Photopolymers

- These are used as photoresists in the microelectronics industry.
- This application has had a major impact on the development of epoxy-based photopolymers.
- Photoresists are essentially one-layer SL, but with critical requirements on accuracy and feature resolution.
- Various types of radiation may be used to cure commercial photopolymers, including gamma rays, X-rays, electron beams, UV, and in some cases visible light, although UV and electron beam are the most prevalent.
- In RM, many of these radiation sources have been utilized in research, however only UV and visible light systems are utilized in commercial systems.
- In SL systems, for example, UV radiation is used exclusively although, in principle, other types could be used.

UV curable photopolymer we have now going talk about materials more. So, UV curable photopolymers these are used as photo resists in the microelectronic industry. So, it see anything which happened you there will be a parallel track as I told you cut and paste technology. So, there were lot of things happening in electronic industry electronic industry, there were lot of advancements happening, lot of miniaturization startened and the transistors have started adding the in IC circuit, lot of transistors were started adding the time the processing time become a critical parameter so, there were lot of innovative things going on there.

So, parallely rapid prototyping also started initiating during that time, rapid prototyping people were looking forward for material which could be used for 3 D making. So, when they looked at electronic industry they saw photoresists exhaustively used. So, initially these resists were been used for rapid prototyping. So, this application has a major impact on the development of epoxy based photopolymers. The photoresists are essentially one layer stereolithography, but with critical requirements on accuracy and feature resolution, feature resolution is how small features you can make.

The various types of radiation maybe used to cure commercial photopolymers include gamma ray which I discussed earlier, X ray, electron beam, UV and in some cases visible light, although UV and electron beam are most commonly used. In rapid manufacturing many of these radiation sources have been utilized in research. However, only UV and visible light systems are effectively used in real time product in SL system for example, UV radiation is used although in principle other types could be also used.

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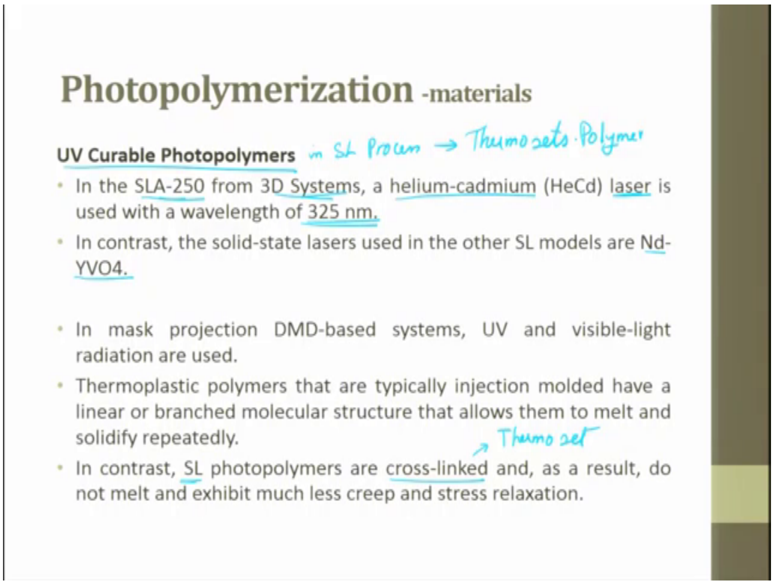

Photopolymerization -materials

UV Curable Photopolymers in SL Process → Thermosets Polymer

- In the SLA-250 from 3D Systems, a helium-cadmium (HeCd) laser is used with a wavelength of 325 nm.
- In contrast, the solid-state lasers used in the other SL models are Nd-YVO4.

- In mask projection DMD-based systems, UV and visible-light radiation are used.
- Thermoplastic polymers that are typically injection molded have a linear or branched molecular structure that allows them to melt and solidify repeatedly.
- In contrast, SL photopolymers are cross-linked and, as a result, do not melt and exhibit much less creep and stress relaxation.

Thermo set

In SLA 250 from 3 D system, this is a machine which is supplied by 3 d system a helium - cadmium laser, helium- cadmium laser with a wavelength of 325 nanometer which is in UV is used. In contrast, solid state laser used in the other SL models are Nd YVO4 laser is also used. In mask projection DMD digital micromirror device based system mask projection system UV and visible light radiations are used. Thermoplastic polymers that are typically injections molded have a linear or a branched molecular structure, that allows them to melts and re solidify repeatedly. In contrast SL photopolymers are cross linked thermo sets, and as a result do not melt and exhibit much less creep and stress relaxation.

So, you should know understand photopolymers used in SL process are predominantly thermosets, in thermosets what happens thermoset polymers thermoset polymers, in thermoset polymer what happens the branches we will see in detail we will see the branches carbon chain these branches when they form a cross link they get so rigidly fixed and they do not give any mobility for the movement of carbon or hydrogen.

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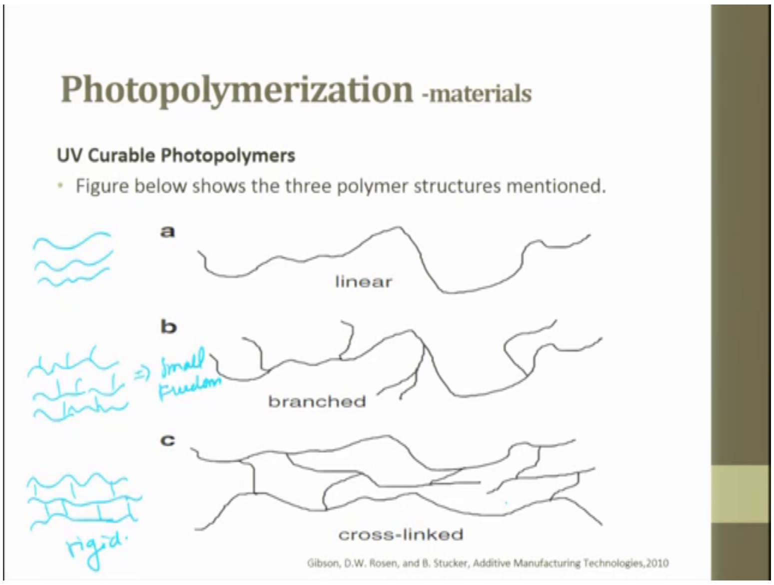

Photopolymerization -materials

UV Curable Photopolymers

- Figure below shows the three polymer structures mentioned.

Gibson, D.W. Rosen, and B. Stucker, Additive Manufacturing Technologies,2010

So, this is a linear structure, this is a branched structure, this is a cross linked structure. So, when you look at a photopolymer you will have linear structure like this branched structure will be something like this and when I talk about cross link. So, if you see crosslink. So, here still you have a small freedom of moving these 2 are not attached you still have small freedom of moving, but here it is rigid completely ok.

So, when the photopolymer is used by the exposure of the UV light when the light hits at this photopolymer what happens is there is a cross link getting formed between the linear chains. This crosslink makes the product rigid and it is also does not have the freedom of a shrinkage ok. So, this is what is the science behind photopolymerization, in photopolymerization liquid polymer is used exposure of UV light converts a linear chain into a cross linked chain or a branched into a cross linked chain. So, the mobility of the chains are arrested so, the strength increases.

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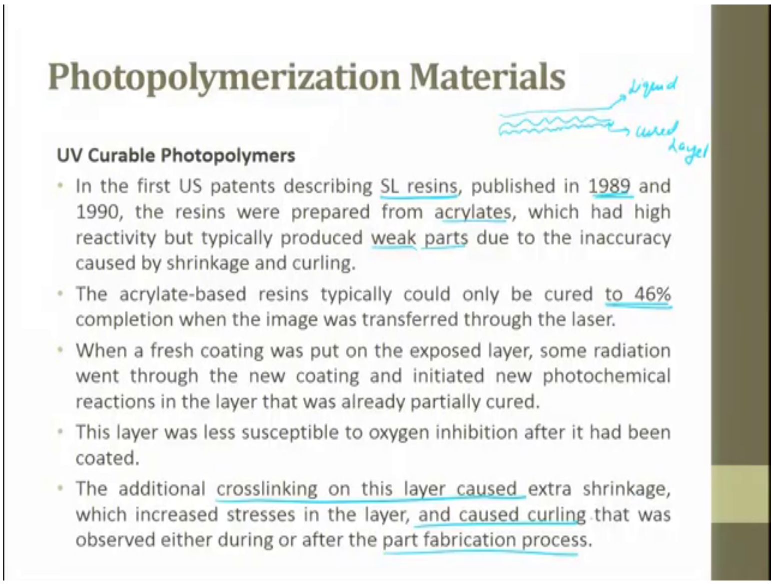

Photopolymerization Materials

UV Curable Photopolymers

- In the first US patents describing SL resins, published in 1989 and 1990, the resins were prepared from acrylates, which had high reactivity but typically produced weak parts due to the inaccuracy caused by shrinkage and curling.
- The acrylate-based resins typically could only be cured to 46% completion when the image was transferred through the laser.
- When a fresh coating was put on the exposed layer, some radiation went through the new coating and initiated new photochemical reactions in the layer that was already partially cured.
- This layer was less susceptible to oxygen inhibition after it had been coated.
- The additional crosslinking on this layer caused extra shrinkage, which increased stresses in the layer, and caused curling that was observed either during or after the part fabrication process.

UV curable photopolymers in the first US patent describing SL resin published in 1989 it is not very far behind 89 now it is 2019. So, when it came into in real time industry, it should have come in 99 or 97 or 96 that would should be the time when could have come in the industry. In the first US patent describing SL resin published in 1989 and 1990. The resin were prepared from acrylates, which had high reactivity but typically produced weak parts due to inaccuracy caused by shrinking and curling. The acrylate based resins typically could only be cured to 46 percent completely when the image was transferred through the laser.

When a fresh coating was put on the exposed layer some radiation went through the new coating and initiated new photochemical reaction in the layer that was already partially cured. So, what we are trying to say you had one layer cured and then on top of it you had a liquid which is there. So, this is a cured layer, this is a liquid on top when the light is exposed it tries to form a shrinkage. This layer was less susceptible to oxygen inhibition after it had been coated, so that this is the coating which is there. So, the layer was less susceptible to oxygen inhibition after it has been coated. The additional crosslink on this layer caused extra shrinkage additional crosslink on this layer extra shrinkage which increases stress in the layer and cost curling.

That was observed either during or after the part fabrication process. So, once it is done and over a period of time the polymer starts curing over a period of time. So, when it starts curing it started creating curling or wrapping and then delamination between the layers. So, please relook into these 2 points this layer was less susceptible, what is this layer the fresh coating was put on the exposed layer some radiation went through the new coating and initiated new photochemical reaction in the layer that was already partially cured right and this layer was less susceptible which layer the bottom layer to oxygen inhibition after it has been coated.

The additional crosslink on this layer caused extra shrinkage, already it has formed the cross linking now you put a one more layer and then expose it light this exposes light once again hits on the layer which is cured. So, there is a extra shrinkage which is happening which increases the stress in the layer and causes curling that was observed either during or after the part fabrication process.

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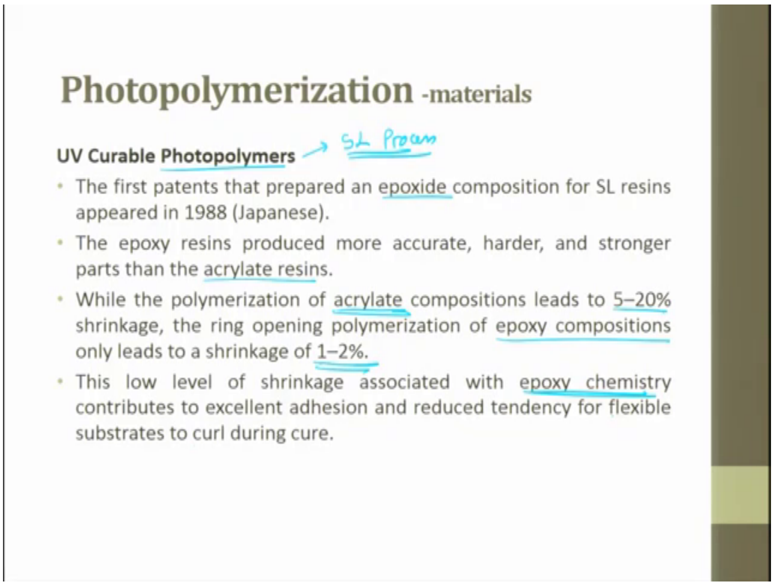

Photopolymerization -materials

UV Curable Photopolymers → SL Process

- The first patents that prepared an epoxide composition for SL resins appeared in 1988 (Japanese).
- The epoxy resins produced more accurate, harder, and stronger parts than the acrylate resins.
- While the polymerization of acrylate compositions leads to 5–20% shrinkage, the ring opening polymerization of epoxy compositions only leads to a shrinkage of 1–2%.
- This low level of shrinkage associated with epoxy chemistry contributes to excellent adhesion and reduced tendency for flexible substrates to curl during cure.

The first pattern that prepared an epoxide composition of SL resin appeared in 1988 in the Japanese patent. The epoxy resin produced more accurate harder and stronger parts than the acrylate parts so poly epoxide composition. While the polymerization of acrylate composition leads to 5 to 20 percent shrinkage, the ring open polymerization of epoxy composition only lead to the shrinkage of 1 to 2 percent then people started getting away from this acrylate based photopolymerization to epoxy composition photopolymerization. This low level of shrinkage associated with epoxy chemistry contributes to excellent adhesion and reduced tendency for flexible substrates to curl during curing.

So, this epoxy chemistry made a big change in photopolymerization which is the principle when used in stereo lithography process. So, from acrylic based we went to epoxy chemistry to which contributes to excellent adhesion and reduce tendency for flexible substrate to curl during curing.

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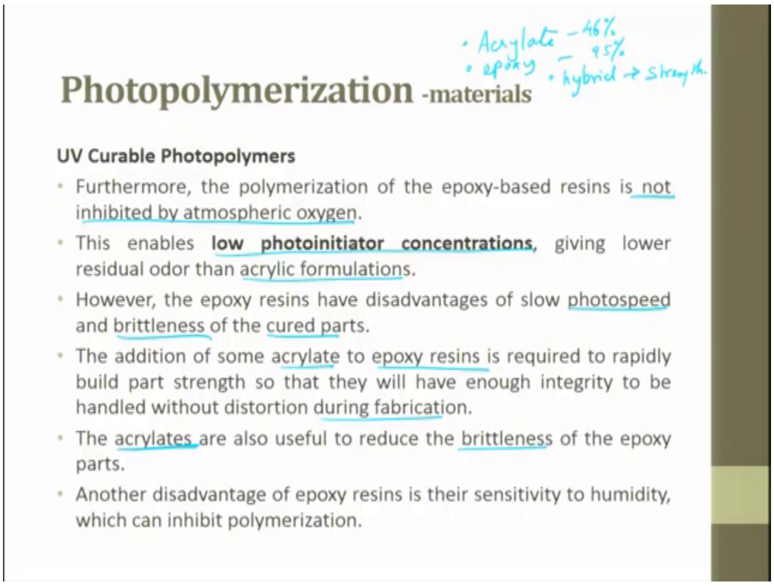

Photopolymerization -materials

- Acrylate – 46%
- epoxy – 95%
- hybrid → Strength.

UV Curable Photopolymers

- Furthermore, the polymerization of the epoxy-based resins is not inhibited by atmospheric oxygen.
- This enables **low photoinitiator concentrations**, giving lower residual odor than acrylic formulations.
- However, the epoxy resins have disadvantages of slow photospeed and brittleness of the cured parts.
- The addition of some acrylate to epoxy resins is required to rapidly build part strength so that they will have enough integrity to be handled without distortion during fabrication.
- The acrylates are also useful to reduce the brittleness of the epoxy parts.
- Another disadvantage of epoxy resins is their sensitivity to humidity, which can inhibit polymerization.

Furthermore the polymerization of the epoxy based resin is not inhibited by atmospheric oxygen. This enables low photoinitiator concentrations giving low residual odor than acrylic formulations ok. So, this is not inhibited by atmospheric or so it does not react with acrylic reacted with atmosphere epoxy did not react with atmospheric oxygen.

This enables low photoinitiator concentrations giving low residual odor than acrylic formulations. However, the epoxy resins have disadvantages of slow photo speeds and brittleness of the cured part because it is thermoset so it will have brittleness of the cured part, The addition of some acrylate to epoxy resin is required to rapidly build part strength so that they will have enough integrity to be handled without distorting during fabrication.

The acrylates are also useful to reduce the brittleness the acrylates so, acrylates you see epoxy some acrylate to epoxy is required to rapidly build part strength so that they will have enough integrity to handle without distorting during fabrication. So, first what we saw was, we saw acrylate acrylate based, then we went to epoxy base, then we have a hybrid of these 2 ok. So, acrylate 46 percent curing, here it is 95 percent or 94 percent curing. So, here when you have a hybrid it has a high strength that is what it is. The acrylates are also useful to reduce the brittleness of the epoxy part. Another disadvantage of epoxy resin is there sensitivity to humidity which can inhibit polymerization.

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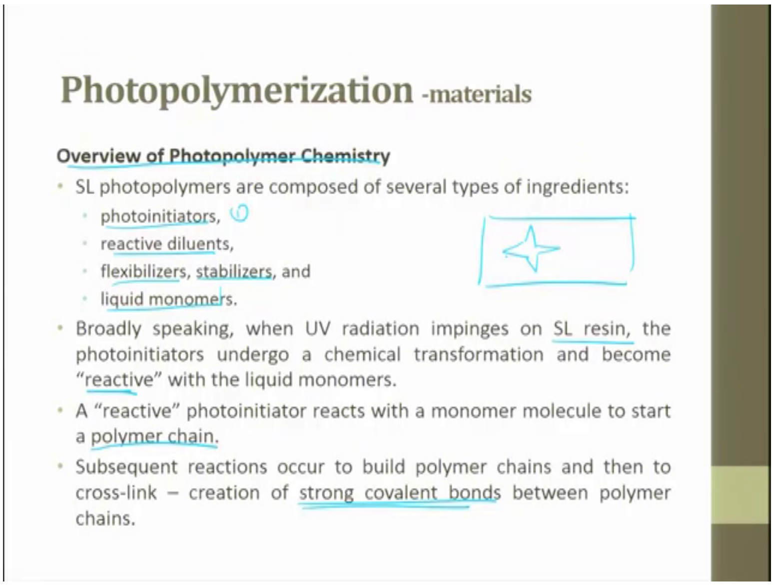

Photopolymerization -materials

Overview of Photopolymer Chemistry

- SL photopolymers are composed of several types of ingredients:
  - photoinitiators,
  - reactive diluents,
  - flexibilizers, stabilizers, and
  - liquid monomers.
- Broadly speaking, when UV radiation impinges on SL resin, the photoinitiators undergo a chemical transformation and become "reactive" with the liquid monomers.
- A "reactive" photoinitiator reacts with a monomer molecule to start a polymer chain.
- Subsequent reactions occur to build polymer chains and then to cross-link – creation of strong covalent bonds between polymer chains.

The overview of photo polymer chemistry the SL stereolithography photopolymer are composed of several types of ingredients, photo initiator, reactive diluents, flexibilizer, stabilizer, liquid monomer. Broadly speaking when UV radiation impinges on SL resin the photoinitiator undergo a chemical transformation and becomes reactive with a liquid monomer. So, this fellow will absorb the UV and start giving energy or start initiating the bond between the different mers. The reactive photoinitiator reacts with the monomer molecules to start a polymer chain. So, if we go back and see the previous diagram where I had beautiful star figures these figures are photoinitiators.

Subsequently reaction occurs to build the polymer chain and then to cross link creation of strong covalent bond between the polymer chains covalent bonds are always strong. So, this photo initiator means starter photo light. So, photoinitiator means a light which initiates. So, how does a slice initiate, somebody should have a liking towards that light so that fellow are called as photoinitiators.

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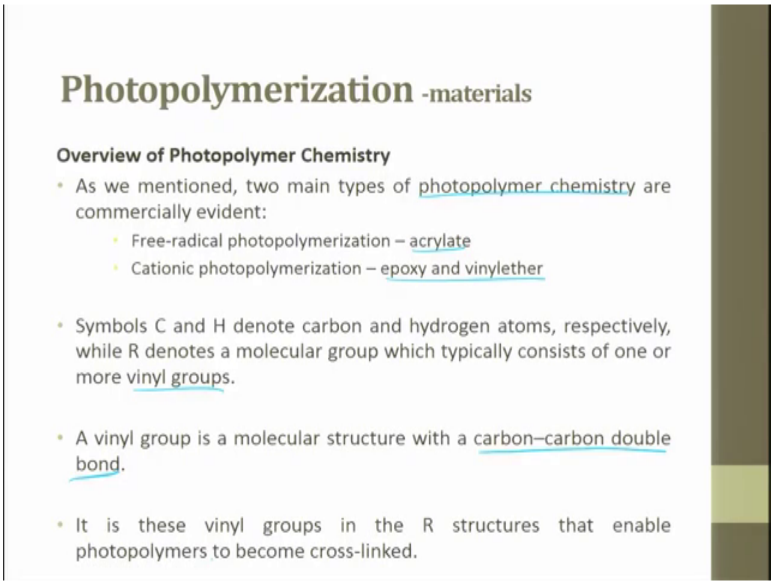

Photopolymerization -materials

Overview of Photopolymer Chemistry

- As we mentioned, two main types of photopolymer chemistry are commercially evident:
  - Free-radical photopolymerization – acrylate
  - Cationic photopolymerization – epoxy and vinylether
- Symbols C and H denote carbon and hydrogen atoms, respectively, while R denotes a molecular group which typically consists of one or more vinyl groups.
- A vinyl group is a molecular structure with a carbon–carbon double bond.
- It is these vinyl groups in the R structures that enable photopolymers to become cross-linked.

Two main types of photopolymer chemistry are commercially evident, free radical photopolymerization which is nothing but an acrylates, cation photopolymerization which is epoxy and vinylether. The symbol C and H denotes carbon and hydrogen atoms respectively, while R denotes a molecular group which typically consists of one or more vinyl groups. A vinyl group is a molecular structure with a carbon - carbon double bond, in this vinyl group in the R structure that enables photopolymers to become cross linked.

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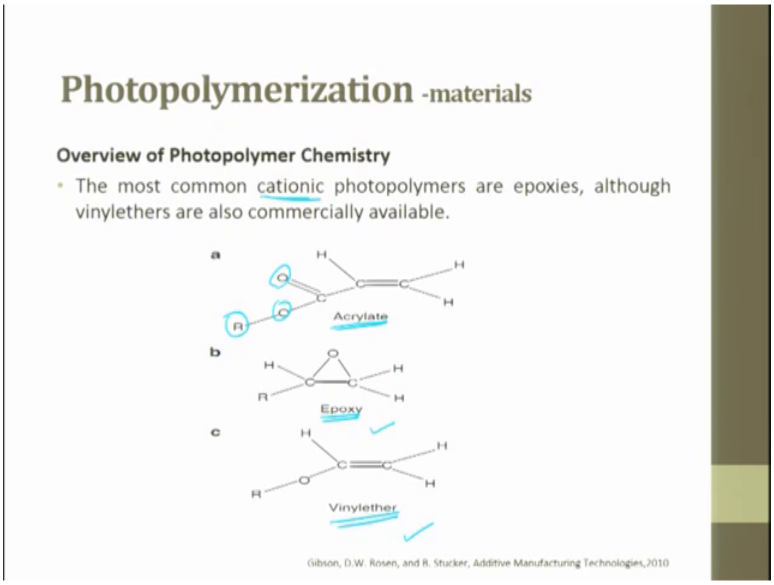

Photopolymerization -materials

Overview of Photopolymer Chemistry

- The most common cationic photopolymers are epoxies, although vinylethers are also commercially available.

Gibson, D.W. Rosen, and B. Stucker, Additive Manufacturing Technologies,2010

So, this is what it is. So, we have talked about all this things where R. So, C double bond H, we have oxygen, we have R structures, these are for acrylates, these are for epoxy, these are for vinylether. So, the over view of photopolymer chemistry the most common cation photopolymer are epoxies, although vinylether are also commercially available. So, these 2 are cation based, the other one is free radical photopolymerization which is acrylate. So, finally, it looks like you have to have a combination of epoxy acrylate for forming a strong curable part.

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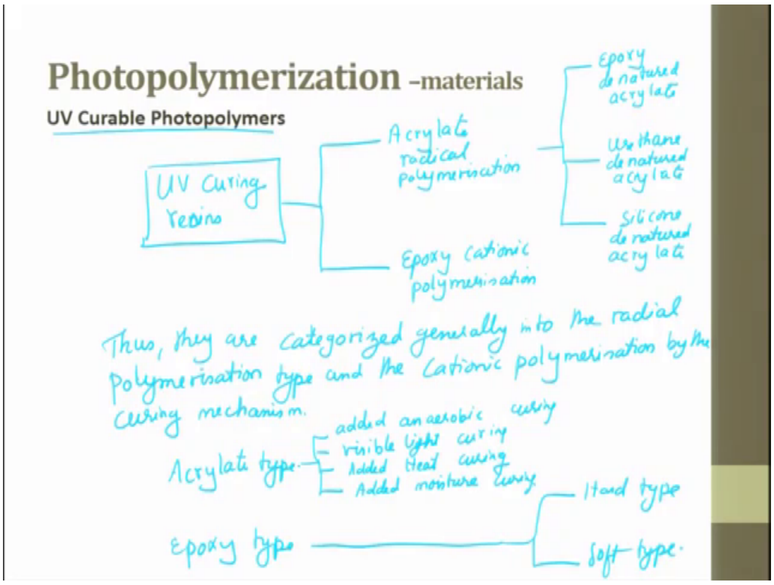

Photopolymerization -materials

UV Curable Photopolymers

Thus, they are categorized generally into the radial polymerisation type and the Cationic polymerisation by the curing mechanism.

So, we will see in a consolidated manner UV curable a photopolymers. So, UV curing resins they are classified into two, one is acrylate radical polymerization, the other one is epoxy cationic polymerization ok. So, here again we have 3 classifications, one is epoxy denatured epoxy denatured acrylate, the other one is urethane urethane denatured acrylate, the last one is silicon denatured acrylate ok.

So, thus they are categorized generally into the radial polymerization type and the cationic polymerization type by the curing mechanism ok. So, the acrylate type and we have epoxy type, epoxy type you have 2 categories, one is hard type, another one is soft type ok. When we talk about acrylate it is added an aerobic curing, then we will have visible light curing, then we have heat added heat curing, then last one we have is added moisture curing. So, this slide in totality talks about UV resin acrylated epoxy and then what are the different kinds of it then 2 types of curing that is acrylate type is adding anaerobic curing visible light curing heat curing and moisture curing. Epoxy type is hard and soft types. So, other than this we also have radial type products whose main material is silicon. So, these are the primary materials which are used in photopolymerization.

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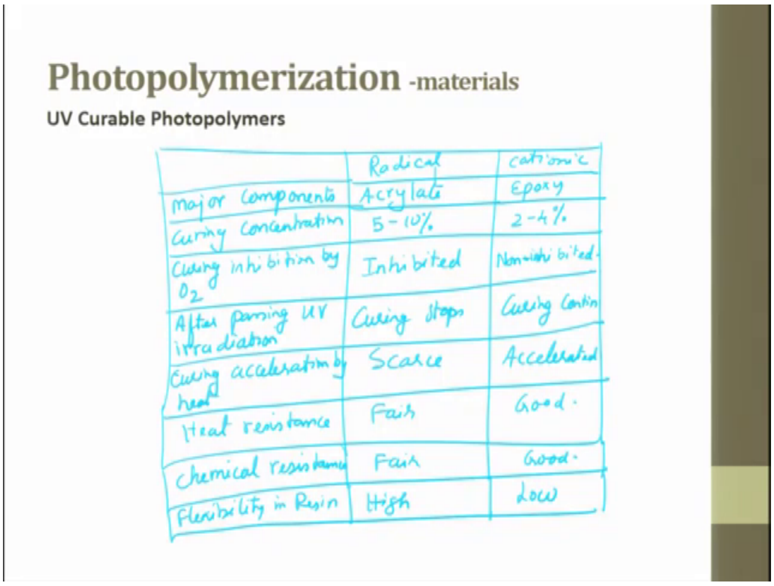

Photopolymerization -materials

UV Curable Photopolymers

	Radical	cationic
major components	Acrylate	Epoxy
Curing concentration	5-10%	2-4%
Curing inhibition by O_2	Inhibited	Non-inhibited
After passing UV irradiation	Curing stops	Curing contin
Curing acceleration by heat	Scarce	Accelerated
Heat resistance	Fair	Good.
chemical resistance	Fair	Good.
Flexibility in Resin	High	Low

So, if we wanted to compare it in terms of a table. So, I will write to put it as radical and cationic, the major components it will be acrylate and then here it will be epoxy.

Then if you try to talk about the curing concentration it is 5 to 10 percent here it is 2 to 4 percent, when we talk about curing inhibition by oxygen it is inhibited and this one is non inhibited. Then after passing UV radiation you we will curing stops curing continues, then we have curing acceleration by heat scarce accelerated, heat resistant this is fair and this is good.

So, if we talked about chemical resistance it is fair; it is good and the last one is flexibility in resin it is high it is low. So, this table clearly states what is the response of different points in terms of radical and cationic you can choose which you want for your stereolithography process.

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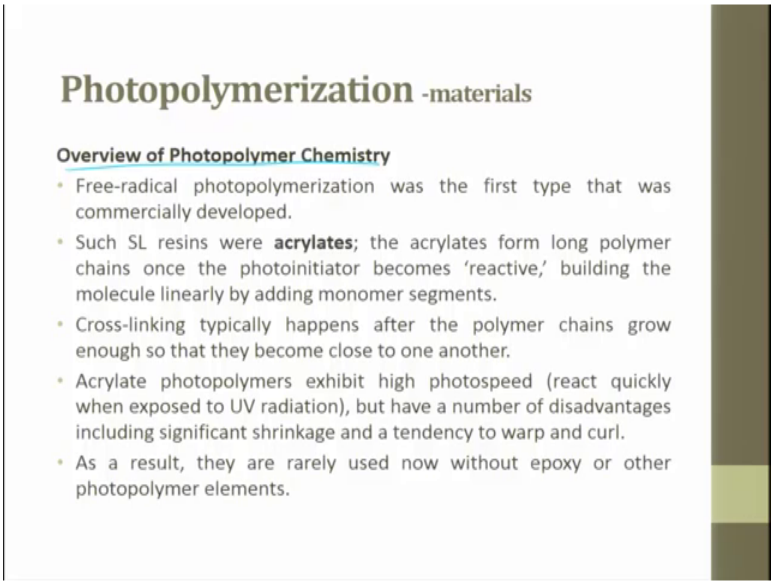

Photopolymerization -materials

Overview of Photopolymer Chemistry

- Free-radical photopolymerization was the first type that was commercially developed.
- Such SL resins were **acrylates**; the acrylates form long polymer chains once the photoinitiator becomes 'reactive,' building the molecule linearly by adding monomer segments.
- Cross-linking typically happens after the polymer chains grow enough so that they become close to one another.
- Acrylate photopolymers exhibit high photospeed (react quickly when exposed to UV radiation), but have a number of disadvantages including significant shrinkage and a tendency to warp and curl.
- As a result, they are rarely used now without epoxy or other photopolymer elements.

The overview of photopolymer chemistry, free - radical photopolymerization was the first type that can be commercially developed. Since SL resins were acrylate the acrylates form long polymer chain once the photoinitiators becomes 'reactive' building the molecular linearly by adding monomer segments. Cross- linking typically happens after the polymer chain grows enough so that they become close to each other. Acrylate photopolymer exhibits high photo speed, but have a number of disadvantages including significant shrinkage and the tendency to warp and curl. As a result they are rarely used now without epoxy or other photopolymer elements.

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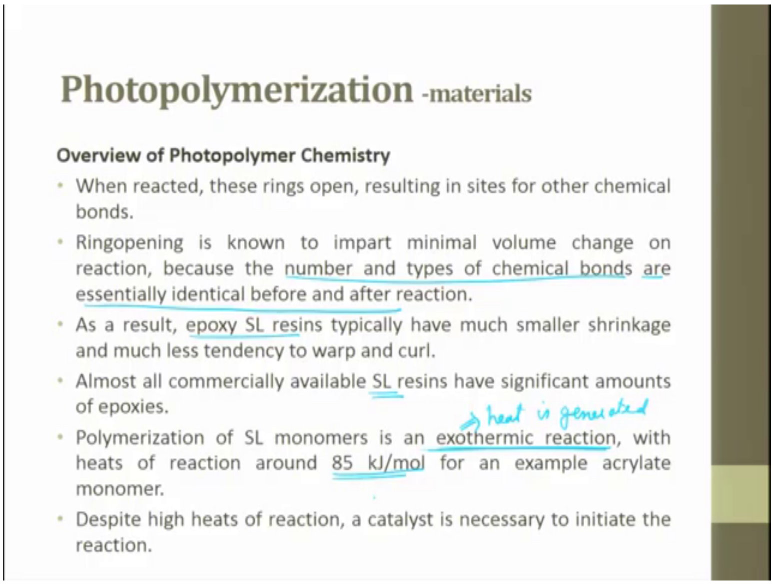

Photopolymerization -materials

Overview of Photopolymer Chemistry

- When reacted, these rings open, resulting in sites for other chemical bonds.
- Ringopening is known to impart minimal volume change on reaction, because the number and types of chemical bonds are essentially identical before and after reaction.
- As a result, epoxy SL resins typically have much smaller shrinkage and much less tendency to warp and curl.
- Almost all commercially available SL resins have significant amounts of epoxies.
- Polymerization of SL monomers is an exothermic reaction, with heats of reaction around 85 kJ/mol for an example acrylate monomer.

  → heat is generated
- Despite high heats of reaction, a catalyst is necessary to initiate the reaction.

When reacted, these rings open resulting in sites for other chemical bonds. Ring opening is known as impart minimal volume change on reaction because the number and the type of chemical bonds are essentially identical before and after reaction. This is a very very important point number and the types of chemical bonds are essentially identical before and after reaction. As a result epoxy SL resins typically have much smaller shrinkage and much less tendency to warp and curl almost all commercial available SL resins have significant amount of epoxies.

Polymerization of SL monomers is an exothermic reaction, please understand exothermic heat is generated during the curing process with heat of reaction around 85 kilo joule mole for an example acrylic monomer does. Despite high heat of reaction a catalyst is necessary to initiate the reaction. So, temperature alone does not initiate we need one more catalyst to initiate such that the epoxy type SL resins get cured and they form a solid object.

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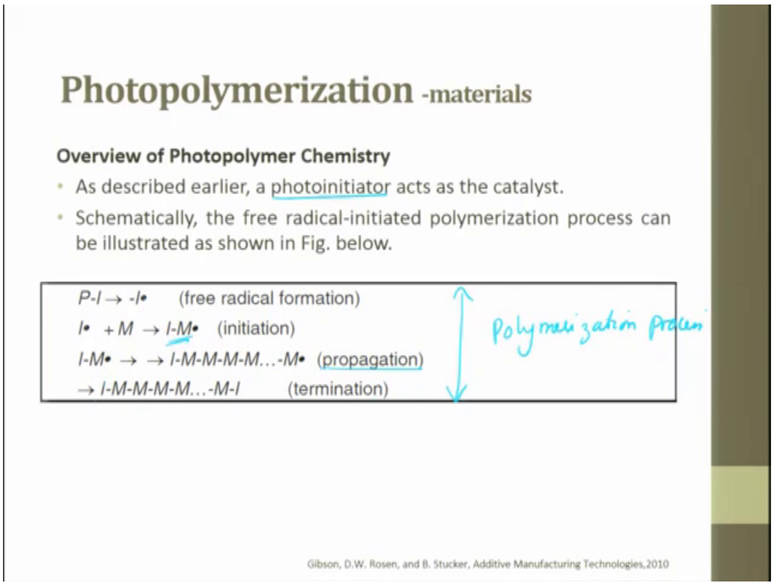

Photopolymerization -materials

Overview of Photopolymer Chemistry

- As described earlier, a photoinitiator acts as the catalyst.
- Schematically, the free radical-initiated polymerization process can be illustrated as shown in Fig. below.

$P\text{-}I \rightarrow \text{-}I\bullet$ (free radical formation)

$I\bullet + M \rightarrow I\text{-}M\bullet$ (initiation)

$I\text{-}M\bullet \rightarrow \rightarrow I\text{-}M\text{-}M\text{-}M\text{-}M\ldots\text{-}M\bullet$ (propagation)

$\rightarrow I\text{-}M\text{-}M\text{-}M\text{-}M\ldots\text{-}M\text{-}I$ (termination)

Polymerization process

Gibson, D.W. Rosen, and B. Stucker, Additive Manufacturing Technologies,2010

The overview of photopolymer chemistry and as described the earlier a photo initiator acts as a catalyst photo initiator. Schematically the free radical initiates photopolymerization process can be illustrated as shown in the figure 1 P bond I is I, I with the free radical. So, free radical formation with M reaction forms are initiator I M dot when it gets bond to several of this monomers forms a propagation and when this I gets to meet with an M and I which is getting there so, it gets terminated.

So, this is the polymerization process polymerization process which is very important you should understand radical initiates.

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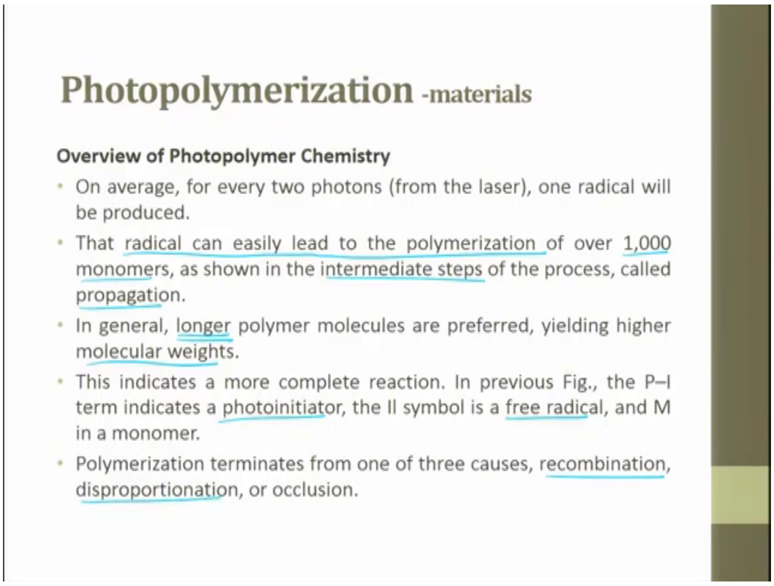

Photopolymerization -materials

Overview of Photopolymer Chemistry

- On average, for every two photons (from the laser), one radical will be produced.
- That radical can easily lead to the polymerization of over 1,000 monomers, as shown in the intermediate steps of the process, called propagation.
- In general, longer polymer molecules are preferred, yielding higher molecular weights.
- This indicates a more complete reaction. In previous Fig., the P–I term indicates a photoinitiator, the II symbol is a free radical, and M in a monomer.
- Polymerization terminates from one of three causes, recombination, disproportionation, or occlusion.

On an average for every 2 photons from the laser one radical will be produced, that radical can easily lead to the photopolymerization of over 1000 monomers as shown in the intermediate steps of the process called propagation. The radial can easily lead to photopolymerization or polymerization of over 1000 monomers as shown in the intermediate steps is called as propagation. In general, long polymer molecules are preferred, yielding higher molecular weight, we do not prefer short we always prefer long polymer or longer polymer molecules.

This initiates a more complete reaction in the previous figure as we show the P I term indicates a photo initiator and double I symbol is a free radical and the M is a monomer. The polymerization process terminates from one of the 3 causes recombination disproportionation or occlusions.

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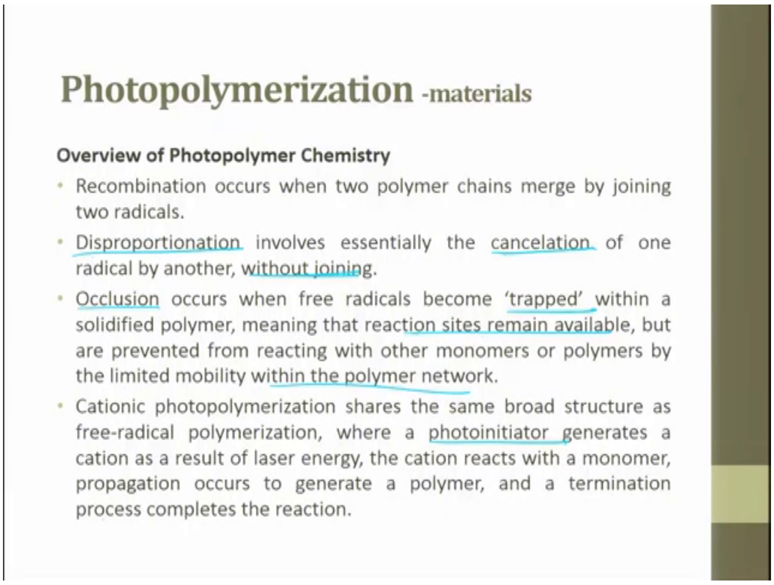

Photopolymerization -materials

Overview of Photopolymer Chemistry

- Recombination occurs when two polymer chains merge by joining two radicals.
- Disproportionation involves essentially the cancelation of one radical by another, without joining.
- Occlusion occurs when free radicals become 'trapped' within a solidified polymer, meaning that reaction sites remain available, but are prevented from reacting with other monomers or polymers by the limited mobility within the polymer network.
- Cationic photopolymerization shares the same broad structure as free-radical polymerization, where a photoinitiator generates a cation as a result of laser energy, the cation reacts with a monomer, propagation occurs to generate a polymer, and a termination process completes the reaction.

Recombination occurs when 2 polymer chains merges to by joining 2 radicals. Disproportionation involves essentially the cancellation of one radical by the other, without joining so, disproportionation. Occlusion occurs when free radicals becomes 'trapped' within a solidified polymer meaning that the radical sites remain unavailable, but are prevented from reacting with the other monomer or polymer by limiting mobility within the polymer network so, this is occlusion.

The cationic photopolymerization shares the same broad structure as free radical polymerization, where a photoinitiator generates a cation as a result of laser energy, the cation reacts with the monomer, propagation occurs to generate a polymer, and the termination process to complete the reaction.

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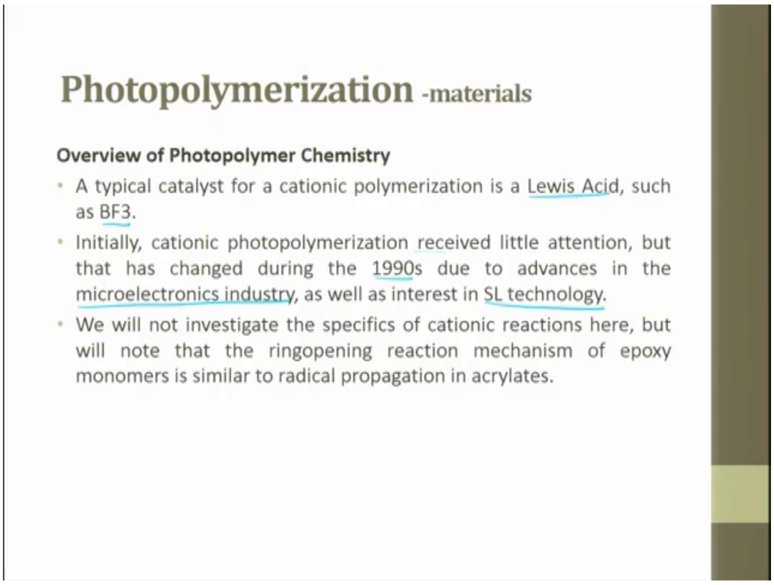

Photopolymerization -materials

Overview of Photopolymer Chemistry

- A typical catalyst for a cationic polymerization is a Lewis Acid, such as BF3.
- Initially, cationic photopolymerization received little attention, but that has changed during the 1990s due to advances in the microelectronics industry, as well as interest in SL technology.
- We will not investigate the specifics of cationic reactions here, but will note that the ringopening reaction mechanism of epoxy monomers is similar to radical propagation in acrylates.

A typical catalyst for a cationic photopolymerization is Lewis Acid such as BF 3. Initially cationic photopolymerization received little attention, but they have changed during the 1990s due to advancement in the microelectronic industry and in SL. We will now investigate the specifics of cationic reaction here, but will note that the ring opening reaction mechanism of epoxy is similar the radical polymerization.

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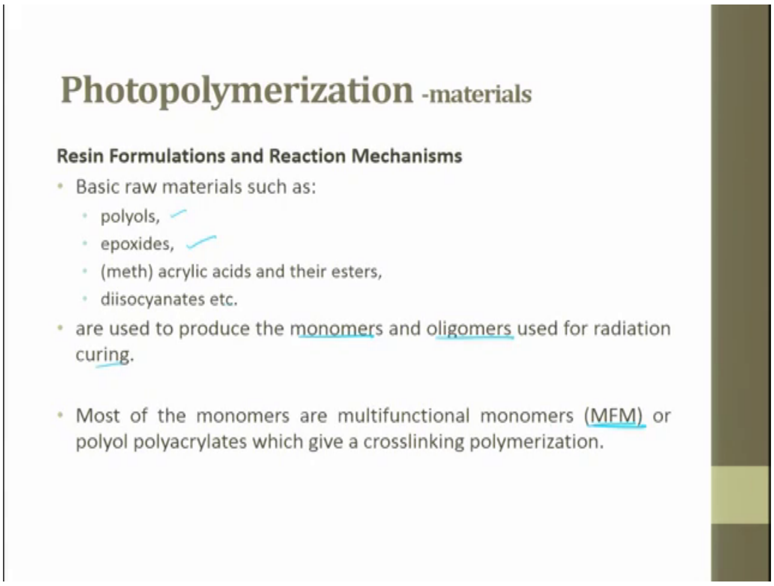

Photopolymerization -materials

Resin Formulations and Reaction Mechanisms

- Basic raw materials such as:
  - polyols,
  - epoxides,
  - (meth) acrylic acids and their esters,
  - diisocyanates etc.
- are used to produce the monomers and oligomers used for radiation curing.
- Most of the monomers are multifunctional monomers (MFM) or polyol polyacrylates which give a crosslinking polymerization.

The resin formulation and reaction mechanism the basic raw material such as polyoxyl, epoxides and acrylic acid and other esters, diisocyanates etcetera are used to produce monomers and oligomers used for the radiation curing. Most of the monomers are multifunctional monomers MFM or polyol poly acrylates which gives a cross linking polymerization.

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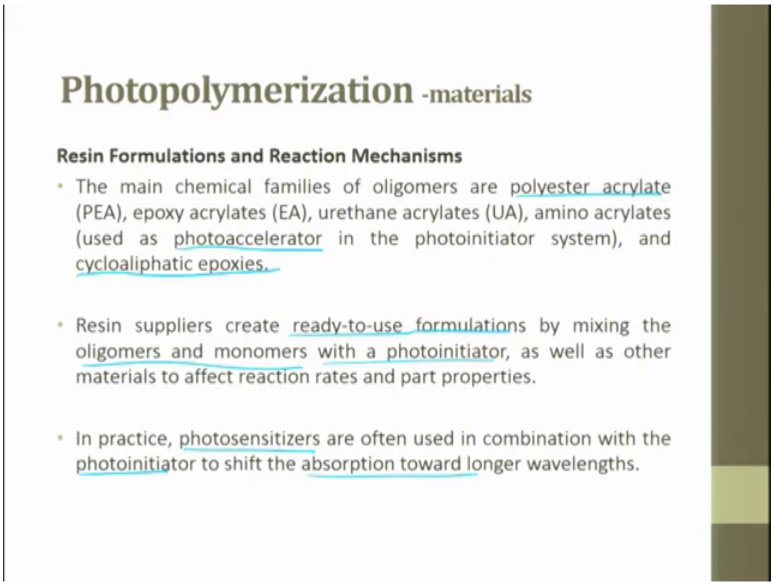

Photopolymerization -materials

Resin Formulations and Reaction Mechanisms

- The main chemical families of oligomers are polyester acrylate (PEA), epoxy acrylates (EA), urethane acrylates (UA), amino acrylates (used as photoaccelerator in the photoinitiator system), and cycloaliphatic epoxies.
- Resin suppliers create ready-to-use formulations by mixing the oligomers and monomers with a photoinitiator, as well as other materials to affect reaction rates and part properties.
- In practice, photosensitizers are often used in combination with the photoinitiator to shift the absorption toward longer wavelengths.

The main chemical families of oligomer are poly ester acrylate PEA, epoxy acrylate EA, urethane acrylates UA and amino acrylates used as photo accelerators in the photo initiator systems and cycloaliphatic epoxies. Resin supplier creates ready to use formulation by mixing the oligomers and monomers with the photoinitiators, as well as the other materials to affect reaction rate and part properties. In practice photosensitizers are often used in the combination with the photoinitiator to shift the absorption towards the longer wavelength. So, we would stop here we will continue in the next class.

Thank you very much.