Photopolymerization Materials

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Lecture No 6

Photopolymerization Materials

Photopolymerization Materials (UV Curable Photopolymers)

- Photopolymers were developed in the late 1960s.
- Various types of radiation may be used to cure commercial photopolymers:
  - Gamma Rays
  - X-rays
  - Electron Beams
  - UV, and
  - in some cases Visible light
- In SL systems, UV radiation is used exclusively although, in principle, other types could be used. 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 (Neodymium-doped yttrium orthovanadate).
- In mask projection DMD-based systems, UV and visible-light radiation are used.

UV Curable Photopolymers

- Thermoplastic polymers that are typically injection molded have a linear or branched molecular structure that allows them to melt and solidify repeatedly.
- SL photopolymers are cross-linked and, as a result, do not melt and exhibit much less creep and stress relaxation.

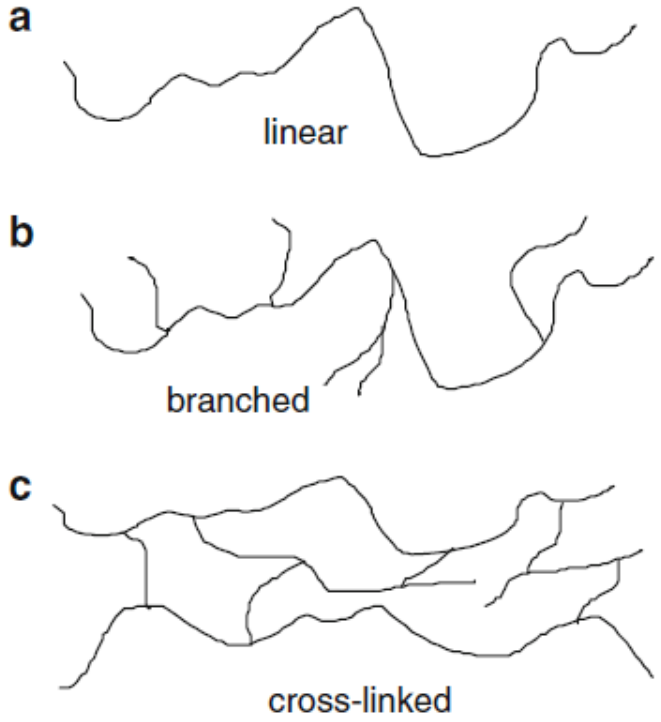


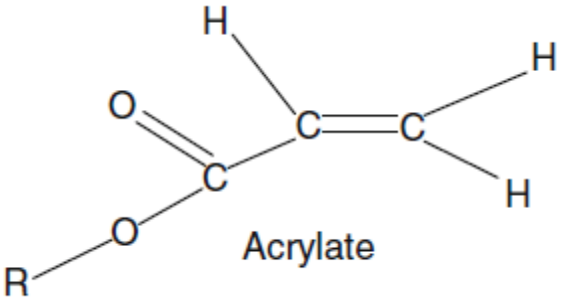
Fig. Schematics of polymer types

Photopolymer Chemistry

- SL photopolymers are composed of several types of ingredients:
  1. Photoinitiators,
  2. Reactive diluents,
  3. Flexibilizers,
  4. Stabilizers, and
  5. Liquid Monomers
- 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.

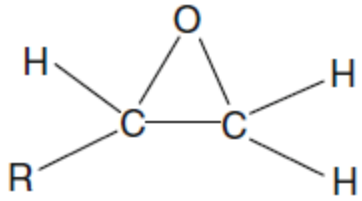
Photopolymer Chemistry

- Polymerization is the term used to describe the process of linking small molecules (monomers) into larger molecules (polymers) composed of many monomer units.

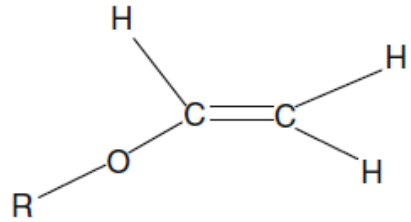


Acrylate

- Two main types of photopolymer chemistry are commercially evident:
  1. Free-radical photopolymerization – Acrylate
  2. Cationic photopolymerization – Epoxy and Vinyl ether



Epoxy



Vinylether

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Photopolymer Chemistry

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- Free-radical photopolymerization was the first type that was commercially developed. Such SL resins were acrylates.
- 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.
- The most common cationic photopolymers are epoxies, although vinyl ethers are also commercially available.

Photopolymer Chemistry

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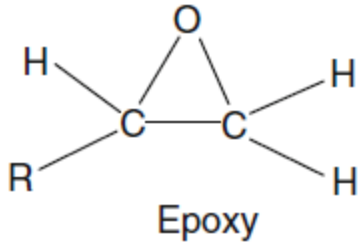
- Epoxy monomers have rings, when reacted, these rings open, resulting in sites for other chemical bonds.
- Ringopening is known to impart minimal volume change on reaction, because the number and types of chemical bonds are essentially identical before and after reaction.
- Epoxy SL resins have much smaller shrinkages, and much less tendency to warp and curl.
- Almost all commercially available SL resins have significant amounts of epoxies.



Epoxy

Photopolymer Chemistry - Free-Radical Photopolymerization

- Polymerization of SL monomers is an exothermic reaction, with heats of reaction around 85 kJ/mol for acrylate monomer.
- Despite high heats of reaction, a catalyst is necessary to initiate the reaction. photoinitiator acts as the catalyst.
- On average, for every two photons (from the laser), one radical will be produced.
- One 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.

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

Photopolymer Chemistry - Free-Radical Photopolymerization

- Polymerization terminates from one of three causes: Recombination, Disproportionation, or Occlusion.
- 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. These occluded sites will most certainly react eventually, but not with another polymer chain or monomer. Instead, they will react with oxygen or another reactive species that diffuses into the occluded region.

Photopolymer Chemistry - Cationic Photopolymerization

- 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.
- A typical catalyst for a cationic polymerization is a Lewis Acid.
- 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.
- The ringopening reaction mechanism of epoxy monomers is similar to radical propagation in acrylates.