Introduction to Polymer Science
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Lecture-41
Polymer Additives

Welcome back. In this lecture we will start discussion on polymer additives and blends, and in this particular lecture I will talk about polymer additives.

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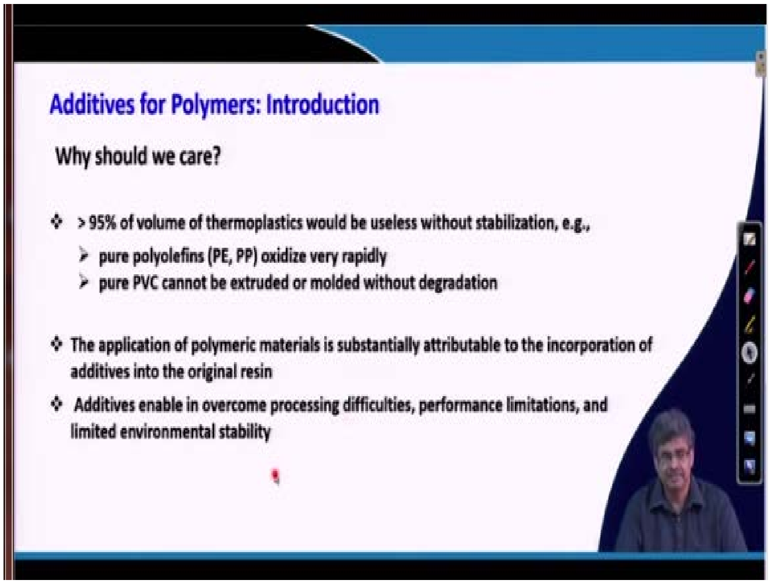

Additives for Polymers: Introduction

Why should we care?

- > 95% of volume of thermoplastics would be useless without stabilization, e.g.,
  - pure polyolefins (PE, PP) oxidize very rapidly
  - pure PVC cannot be extruded or molded without degradation
- The application of polymeric materials is substantially attributable to the incorporation of additives into the original resin
- Additives enable in overcome processing difficulties, performance limitations, and limited environmental stability

Additive of polymers are very important and why should you care about that? Because more than 95% of the volume of thermoplastics would be useless without stabilization, e.g. pure polyolefins like polyethylene and polypropylenes oxidize very rapidly. We require antioxidants to be added in these samples to be useful. Similarly, pure polyvinyl chloride or PVC cannot be extruded or molded because of poor thermal stability. We need to add thermal stabilizer to PVC to have an effective processing. The application of polymeric materials is substantially attributed to the incorporation of additives into the original resin. Additives enable to overcome processing difficulties, performance limitations and poor weatherability. We actually add additive to overcome these limitations as described here and I will describe more about these limitations little later.

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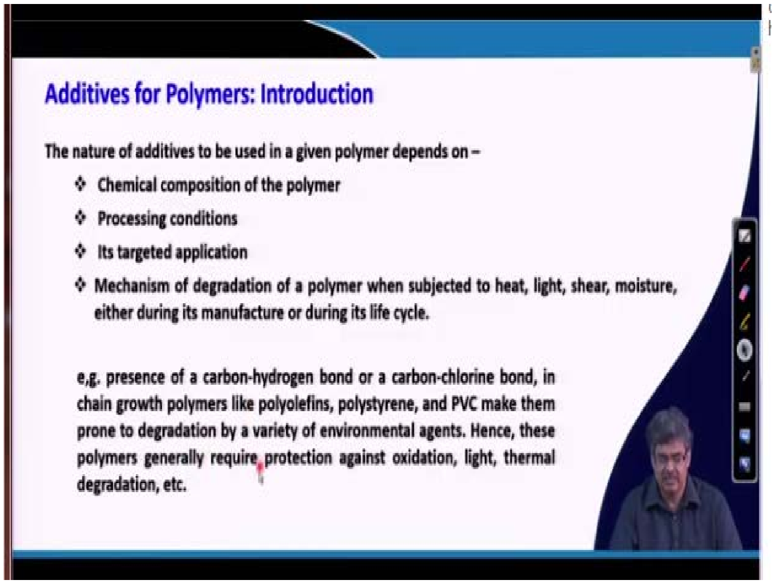

Additives for Polymers: Introduction

The nature of additives to be used in a given polymer depends on –

- Chemical composition of the polymer
- Processing conditions
- Its targeted application
- Mechanism of degradation of a polymer when subjected to heat, light, shear, moisture, either during its manufacture or during its life cycle.

e,g. presence of a carbon-hydrogen bond or a carbon-chlorine bond, in chain growth polymers like polyolefins, polystyrene, and PVC make them prone to degradation by a variety of environmental agents. Hence, these polymers generally require protection against oxidation, light, thermal degradation, etc.

The nature of additives to be used in a given polymer system depends on various factors like chemical composition of the polymer, processing condition and its target application**.** When you talk about stabilizer, the mechanism of degradation of a polymer need to be understood when the polymer is subject to heat, light, shear or moisture during it is manufacturing and entire life cycle. So, we need to understand how polymer degrades during processing or during its use in outdoor application or some other application.

Unless we understand the mechanism of degradation, we will not be able to identify or design additives to prevent this degradation. For example, presence of a carbon hydrogen bond or a carbon chlorine bond in chain growth polymers like polyolefin, polystyrene and polyvinyl chloride make them prone to degradation by variety of environmental agents. Hence, these polymers generally require protection against oxidation, light, thermal degradation etc. as I discussed now.

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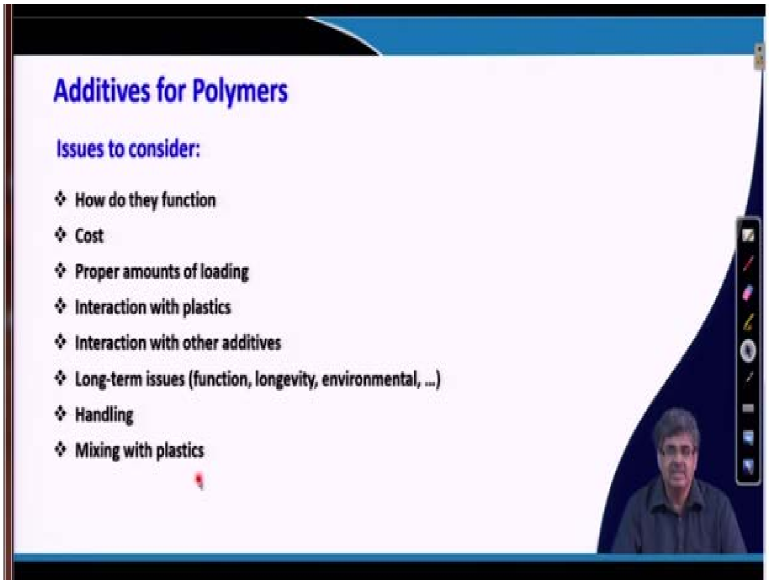

Additives for Polymers

Issues to consider:

- How do they function
- Cost
- Proper amounts of loading
- Interaction with plastics
- Interaction with other additives
- Long-term issues (function, longevity, environmental, …)
- Handling
- Mixing with plastics

There are some issues to be considered when we design or add additives to polymer samples. How do they function? What is the cost of the additives? Proper amount of additives needs to be loaded so that it actually does its function, it does not deteriorate the function of the base polymer. How the additives interact with the base polymer material, that is to be understood. If there are multiple additives, then how the multiple additives interact with each other that needs to be understood as well.

Long term issues, like how the presence of these additives actually affects the base polymer properties in the long run, like its function, longevity, environmental aspect and so on. How can you handle the additives? And how good they mix with the base plastics?

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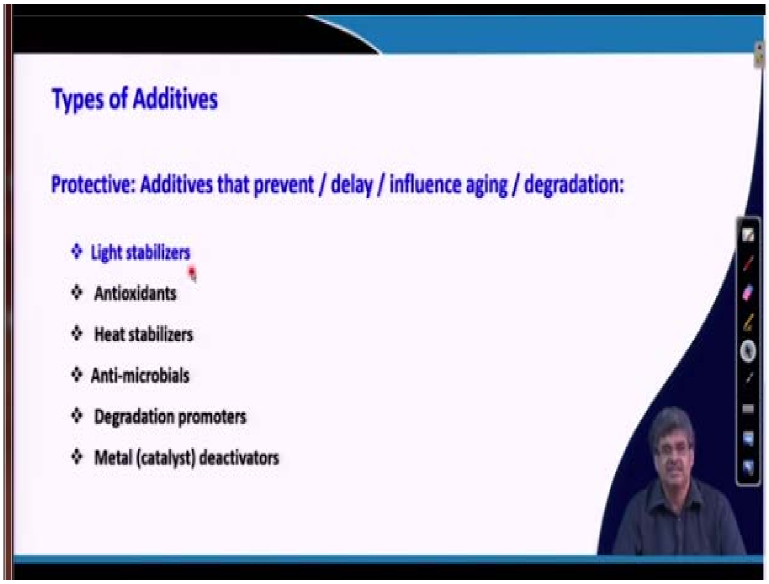

Types of Additives

Protective: Additives that prevent / delay / influence aging / degradation:

- Light stabilizers
- Antioxidants
- Heat stabilizers
- Anti-microbials
- Degradation promoters
- Metal (catalyst) deactivators

There are different types of roles that additives can play, and accordingly we add additives to the base material. For example, protective additives, these additives generally prevent or delay or influence the aging or degradation behavior of the base polymer. Some examples are given. Light stabilizers act against light exposure, antioxidants which prevent oxidative degradation, heat stabilizers which actually prevent or slow down the heat related degradation, especially during processing. Similarly, anti-microbials which basically protect polymer from microbial attack and so on.

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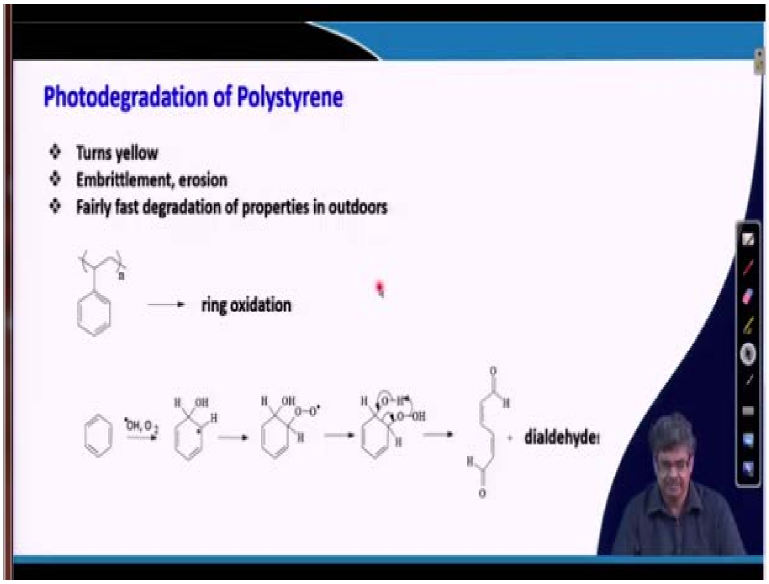

Photodegradation of Polystyrene

- Turns yellow
- Embrittlement, erosion
- Fairly fast degradation of properties in outdoors

The light stabilizer is actually required when the polymer properties are prone to deterioration by the influence of light. For example, photodegradation of polystyrene. If we keep polystyrene under light for long duration it turns yellow, it becomes brittle, and this degradation of properties become fast in outdoor applications, because outdoor is where there is direct contact with light.

That happens because of the ring oxidation of this aromatic ring and the mechanism of oxidation is shown here. You can see in more detail later when you spend time on the slides. So, we need to add additives which will prevent this ring oxidation, or actually we can protect the polymer from exposure of this harmful light, you know, remember, when you talk about light, the light will have different electromagnetic radiation.

For example, if you compare between a UV light and visible light, UV light will have a higher energy. So, UV light will have more prominent effect in degradation of polymer samples than a visible light. So, if you want to protect this polymer sample if you can somehow protect the exposure to UV light then it will be easier for us to stop or prevent or retard this degradation.

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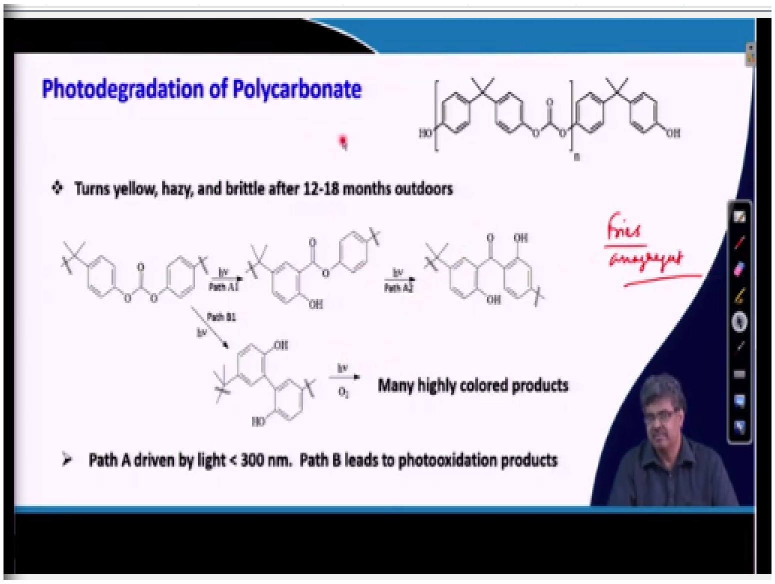

Photodegradation of Polycarbonate

- Turns yellow, hazy, and brittle after 12-18 months outdoors

Many highly colored products

- Path A driven by light < 300 nm. Path B leads to photooxidation products

Similarly polycarbonate, the structure is shown here, it becomes yellow, hazy and brittle after about say one year to one and a half years exposure in outdoor conditions. This happens because of light induced Fries rearrangement or Fries rearrangement. As a result, the sample becomes yellow and you get a lot of colored products, and this path A is driven by light which is less than 300 nm.

So, basically it is done mostly by the UV light, and part B leads to photo-oxidation products. So, somehow if we can stop these reactions then we probably would be able to protect the polycarbonate from photo-degradation. How is it done?

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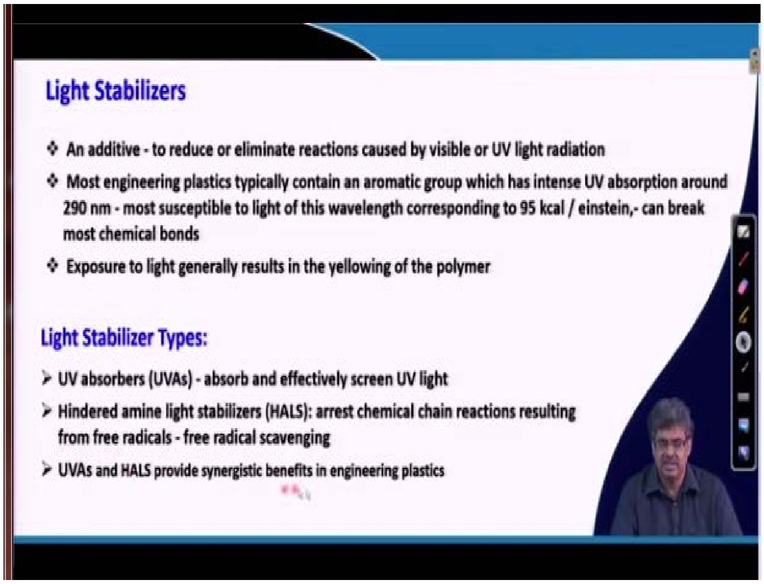

Light Stabilizers

- An additive - to reduce or eliminate reactions caused by visible or UV light radiation
- Most engineering plastics typically contain an aromatic group which has intense UV absorption around 290 nm - most susceptible to light of this wavelength corresponding to 95 kcal / einstein,- can break most chemical bonds
- Exposure to light generally results in the yellowing of the polymer

Light Stabilizer Types:

- UV absorbers (UVAs) - absorb and effectively screen UV light
- Hindered amine light stabilizers (HALS): arrest chemical chain reactions resulting from free radicals - free radical scavenging
- UVAs and HALS provide synergistic benefits in engineering plastics

It is done by adding additives and we call those as light stabilizers. It is an additive which is used to reduce or eliminate the reaction caused by visible or UV light radiation. Most engineering plastics typically contents aromatic groups which has intense UV absorption around 290 nm and that is the reason for, that is the most dominating factor for this degradation because that has higher energy. As I said that exposure to light generally results in yellowing of polymer. Different types of light stabilizer are available in the market, and they are UV absorbers or UVAs and they actually absorb and effectively screen UV light. Hindered amine light stabilizer or HALS arrest chemical chain reaction resulting from free radicals. That is why they are called free radical scavengers. We can add both together to have a synergistic benefit in engineering plastics.

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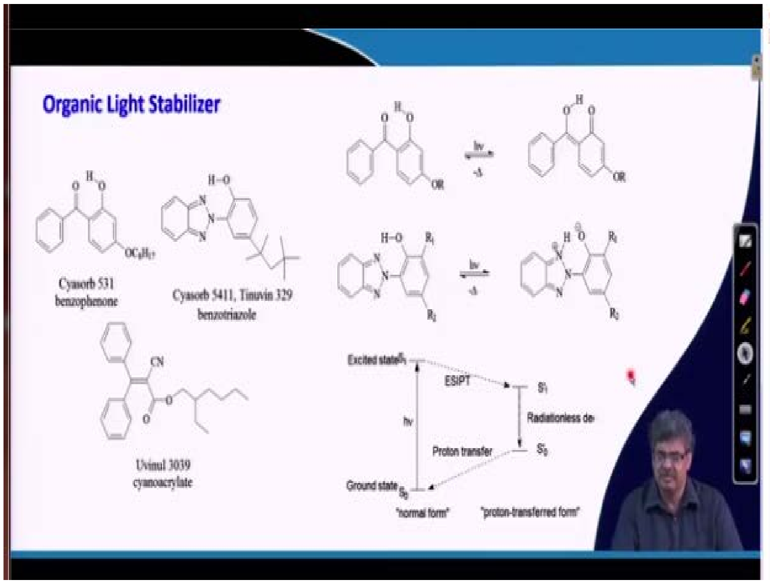

Organic Light Stabilizer

Some of the examples are given here, organic light stabilizers, this is a commercial name and this is the compound type. This is benzophenone dye molecule, this is benzotriazole and this is cyanoacrylate containing molecules. These actually stop or prevent UV light absorption by excited state proton transfer. So, in this case the normal form gets excited by absorbing the light and in excited state it undergoes an excited state intramolecular proton transfer at is shown here. Then it comes back to the normal form by radiation less pathway and reverse proton transfer. So, by doing this it can actually prevent the engineering polymers from getting degraded.

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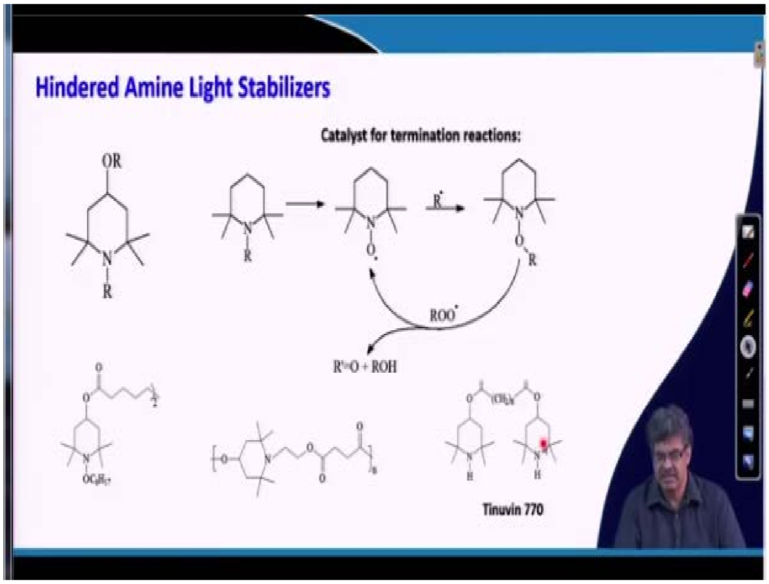

Hindered Amine Light Stabilizers

Catalyst for termination reactions:

Tinuvin 770

Similarly, the HALS, they actually stop these radicals for doing oxidative reactions, so that is why they are call radical scavengers. Some of the commercial HALS are shown here, this is the commercial name of this particular stabilizers.

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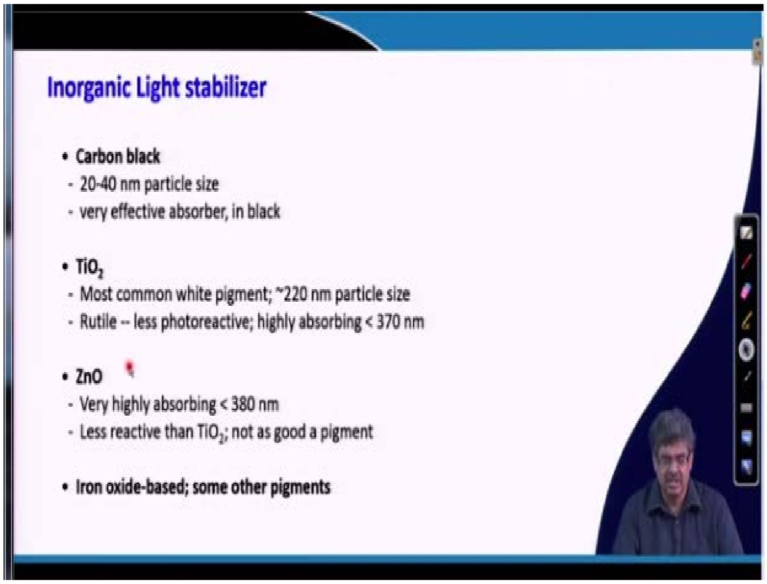

Inorganic Light stabilizer

- Carbon black
  - 20-40 nm particle size
  - very effective absorber, in black
- TiO_2
  - Most common white pigment; ~220 nm particle size
  - Rutile -- less photoreactive; highly absorbing < 370 nm
- ZnO
  - Very highly absorbing < 380 nm
  - Less reactive than TiO_2; not as good a pigment
- Iron oxide-based; some other pigments

There are some inorganic stabilizers can be added to prevent photodegradation like carbon black, TiO_2, ZnO and they are very effective in nature. Remember if we want the polymer or material to be used in the transparent or clear application, then we cannot add this type of inorganic stabilizer. Because when you add this carbon black, TiO_2, invariably the transparency comes down.

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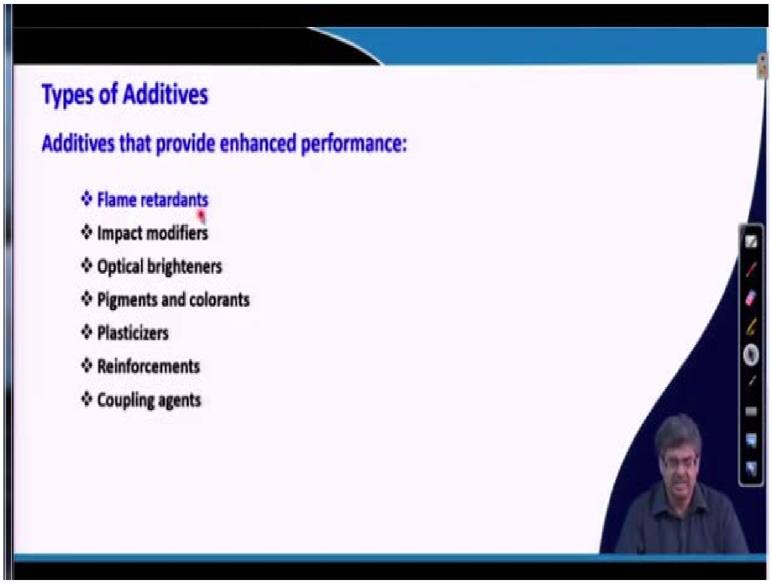

Types of Additives

Additives that provide enhanced performance:

- Flame retardants
- Impact modifiers
- Optical brighteners
- Pigments and colorants
- Plasticizers
- Reinforcements
- Coupling agents

There are other types of additives which enhance performances. They enhance the performance of the base polymer. For example, flame retardants improve the flame performance. The flammability of a polymers becomes lower as we add these flame retardants to the base polymer. Similarly, we can add impact modifiers which will increase the impact resistance of the base polymer, optical brightener which actually increases the brightness of the base polymer. Obviously, pigments, colorants added for aesthetic issue, plasticizers can be added to decrease the T_g and increase the ease of processing of the base polymer. Similarly, the other reinforcement and coupling agents can be added to improve the performance of the base polymer. So, as I discussed earlier, I will just talk about one example in little detail. how does all these additives work. So, let me discuss about flame retardants.

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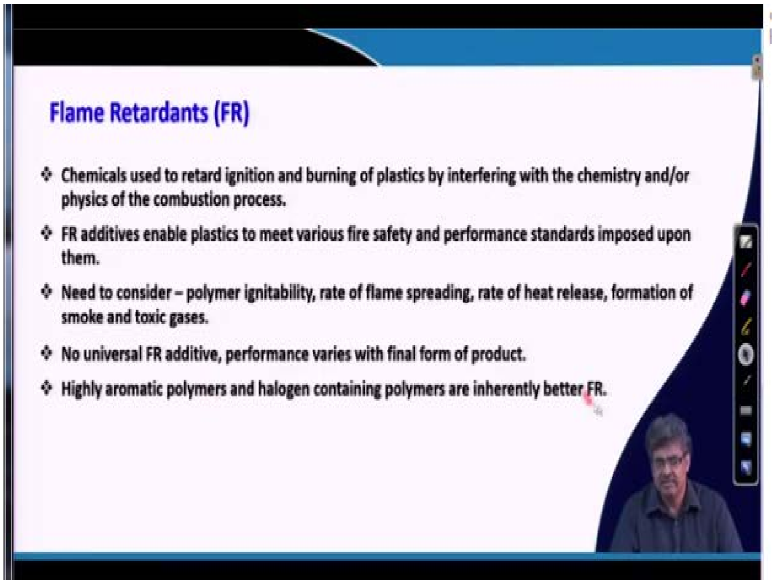

Flame Retardants (FR)

- Chemicals used to retard ignition and burning of plastics by interfering with the chemistry and/or physics of the combustion process.
- FR additives enable plastics to meet various fire safety and performance standards imposed upon them.
- Need to consider – polymer ignitability, rate of flame spreading, rate of heat release, formation of smoke and toxic gases.
- No universal FR additive, performance varies with final form of product.
- Highly aromatic polymers and halogen containing polymers are inherently better FR.

Flame retardants are chemicals used to retard ignition and burning of plastics by interfering with the chemistry and or physics of the combustion process. When we burn a plastics or polymer the combustion happens and somehow by adding these FRs, actually retard the ignition and burning of the plastic materials. Now these FR additives enable plastics to meet various fire safety and performance standards imposed by several regulatory authority. Without these basically, these plastics material cannot be used in many applications, indoor applications or in transport and so on.

The factors we need to consider is this polymer ignitability, rate of flame spreading, rate of heat release, formation of smoke and toxic gases. As a result, there is no universal FR additive for different samples. It basically, depends on the type of application and the base polymer under consideration. Highly aromatic polymers and halogen containing polymers are inherently better fire retardants.

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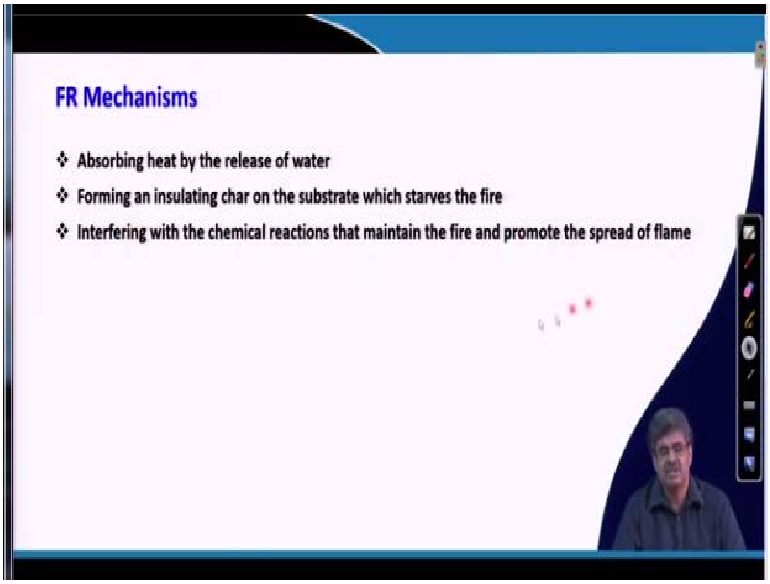

FR Mechanisms

- Absorbing heat by the release of water
- Forming an insulating char on the substrate which starves the fire
- Interfering with the chemical reactions that maintain the fire and promote the spread of flame

This fire retardancy occurs by different possible mechanisms, one is by absorbing heat through release of water. Additives actually release water and as a result heat is absorbed which prevents flammability of the material. They also work by forming an insulating char and thereby preventing further burning of the substrate which stops the fire due to the insulating char on the polymer surface. There is a possibility that it can interfere with the chemical reactions that maintain the fire and promote the spread of fire. It can stop or it can prevent the chemical reactions which maintain the fire and prevent the spreading of flame.

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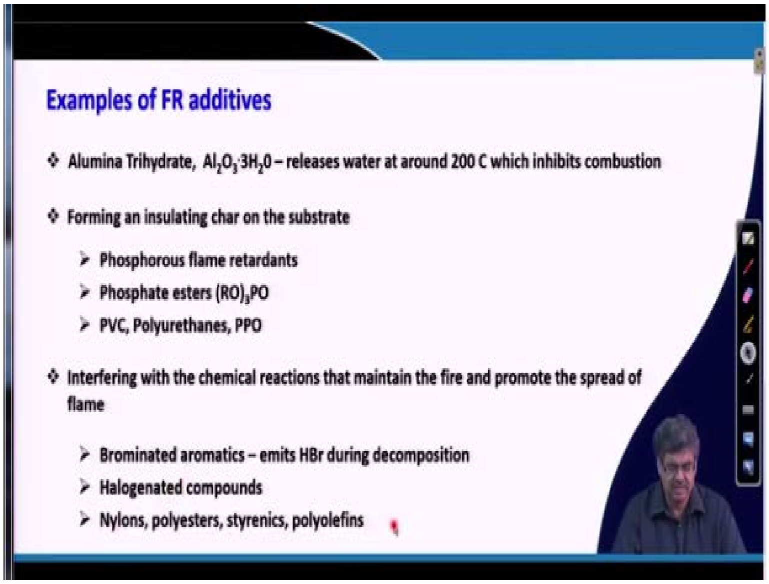

Examples of FR additives

- Alumina Trihydrate, $Al_2O_3 \cdot 3H_2O$ – releases water at around 200 C which inhibits combustion
- Forming an insulating char on the substrate
  - Phosphorous flame retardants
  - Phosphate esters $(RO)_3PO$
  - PVC, Polyurethanes, PPO
- Interfering with the chemical reactions that maintain the fire and promote the spread of flame
  - Brominated aromatics – emits HBr during decomposition
  - Halogenated compounds
  - Nylons, polyesters, styrenics, polyolefins

For example, aluminium trihydrate releases water at around 200 °C which inhibits combustion. There are other additives which actually improve the charring, basically increases the amount of char on burning of the substrate as a result, as I discussed, that it prevents the polymers to come in contact with the fire. So, basically fire will be starved of any further fuel and it will diminish. Examples are phosphorus flame retardants like phosphate esters and they are very useful in this type of polymer materials. The phosphate flames retardants work by promoting char formation on the substrate. Similarly, these brominated aromatics emit HBr, which during decomposition interfere with the chemical reactions, which maintain the fire. Halogenated compounds also work that way and they work better for these types of polymers like nylons, polyesters, styrenics and polyolefins.

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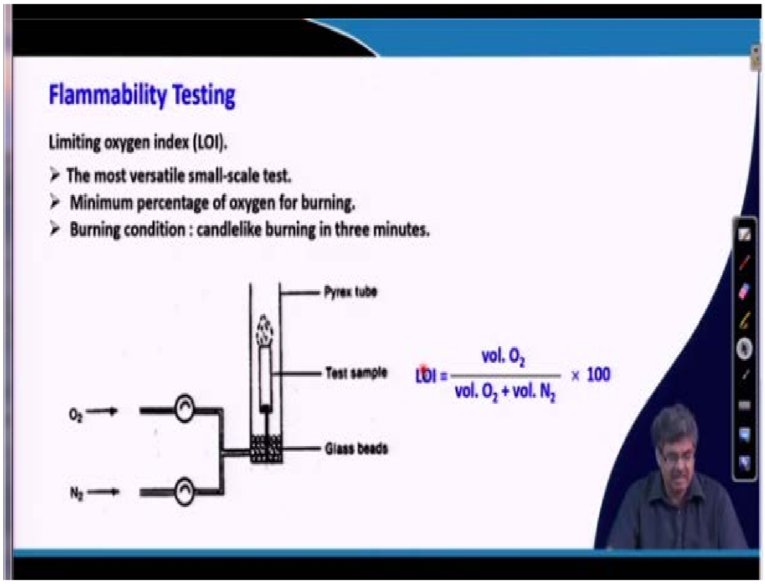

Flammability Testing

Limiting oxygen index (LOI).

- The most versatile small-scale test.
- Minimum percentage of oxygen for burning.
- Burning condition : candlelike burning in three minutes.

$$LOI = \frac{vol.\ O_2}{vol.\ O_2 + vol.\ N_2} \times 100$$

How we quantify the flammability of polymers? There are two different types of testing, one is generally done for the products, done for actual applications and those are mandated by UL standards. So, there are very different protocols are there which I am not discussing here. Based on those protocols we can actually classify the polymeric materials at V_0, V_1, V_2 like levels where V_0 is the better sample.

But in laboratory to find out the flammability, there is, another test is done which is called limiting oxygen index, basically, is quantifying the minimum amount of oxygen is required to maintain the flammability. So, in this case oxygen is passed along with nitrogen and within this mixture the burning process is done. When the oxygen amount is very low this burning will not happen. Slowly the oxygen amount will increase and the minimum amount of oxygen required to maintain this burning is called limiting oxygen index. This is the most versatile small-scale testing, minimum percentage of oxygen required for burning. LOI, limiting oxygen index, is given by the volume of oxygen and volume oxygen plus volume of nitrogen.

$$LOI = \frac{vol.O_2}{vol.O_2 + vol.N_2} \times 100$$

So, the higher is the value of LOI, that means higher amount of oxygen is required to flame the polymer, which means the polymer is less flammable. If the polymer can burn with low amount of oxygen that means the polymer is more flammable.

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Limiting Oxygen Indexes (LOI) of some common polymers

Polymer	LOI
Polyoxymethylene	15
Poly(ethylene oxide)	15
Poly(methyl methacrylate)	17
Polypropylene	17
Polyethylene	17
Polystyrene	18
Poly(1,3-butadiene)	18
Poly(vinyl alcohol)	22
Polycarbonate	27
Poly(phenylene oxide)	28
Polysiloxane	30
Poly(vinyl chloride)	45
Poly(vinylidene chloride)	60
Polytetrafluoroethylene	95

Some of the values of some polymers, LOI value is given here. PTFE is requiring 95% oxygen that means the flammability of polytetrafluoroethylene is very low. As you can see these are used for a nonstick coating. So these polymers generally do not burn very quickly. Similarly, the polyoxymethylene, polyethylene oxide, they require very low amount of oxygen to burn. So, these polymers are highly flammable polymer. Lower is the value of LOI, the flammability of the polymers is higher.

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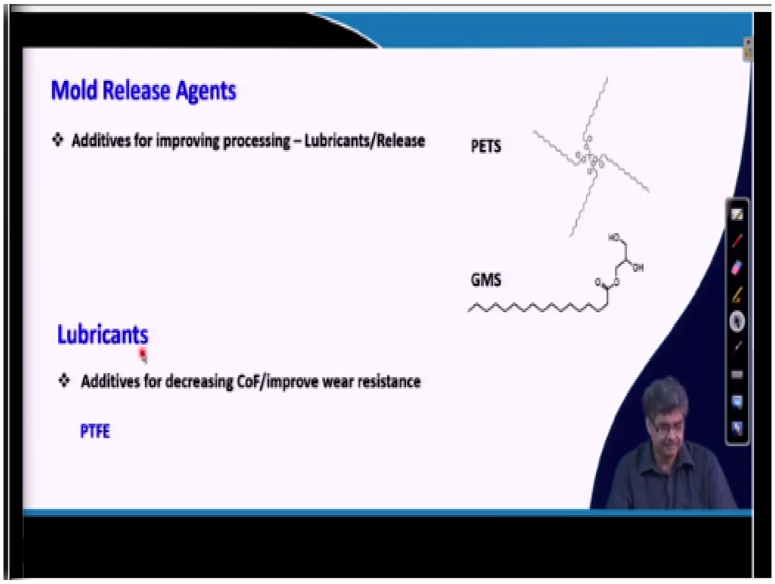

Mold Release Agents

- Additives for improving processing – Lubricants/Release

Lubricants

- Additives for decreasing CoF/improve wear resistance

PTFE

There are some other additives, which help in processing, fabrication and assembly of polymers. They are like mold release agents which help in releasing the polymers from mold or the products from molds. Lubricants which help in processing i.e. if we add lubricant then the polymer can flow through the barrels easily.

There are other polymer additives, which are added during processing or fabrication. I will just give two examples of mold release agent and lubricants. Like this is the molecule PETS, pentaerythritol tetrastearate, and this is GMS, glyceryl monostearate. So, because of the presence of these long hydrophobic chains, they actually come or blot to the interface between the metal mold and the polymer. As a result, they actually help releasing the polymer material from mold and they also help in processing of the polymer sample.

Similarly, when you add this small amount of polytetrafluoroethylene, they actually reduce the friction between the metal barrel or metal screw and the polymer. Coefficient of friction comes down, as a result, the lubrication happens.

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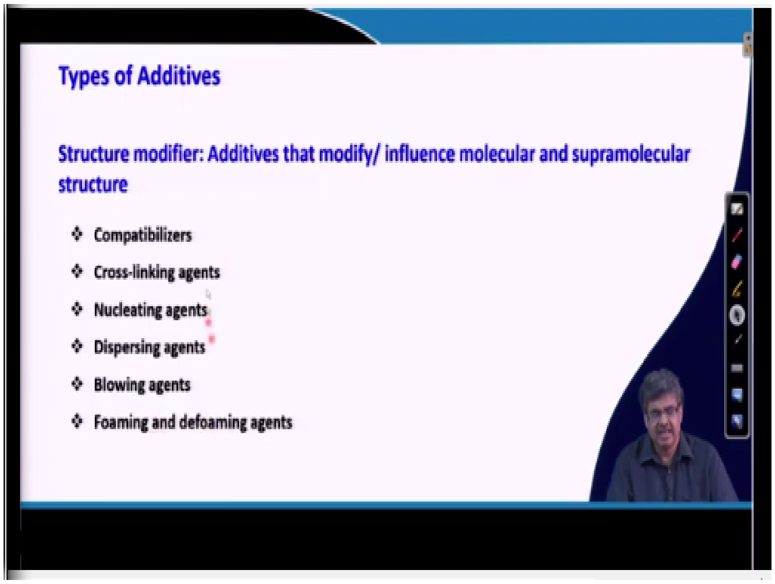

Types of Additives

Structure modifier: Additives that modify/ influence molecular and supramolecular structure

- Compatibilizers
- Cross-linking agents
- Nucleating agents
- Dispersing agents
- Blowing agents
- Foaming and defoaming agents

The other types of additives, which are used for polymers are compatibilizers, crosslinking agents, nucleating agents, dispersing agent, blowing agents.

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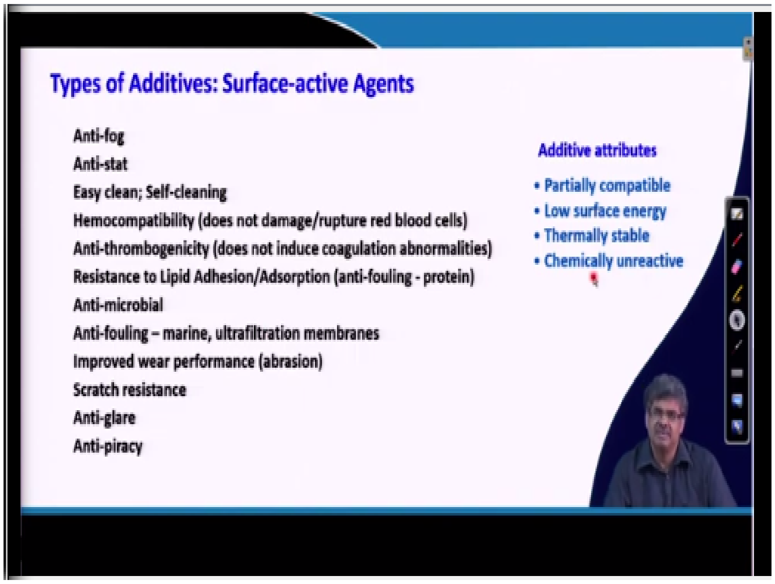

Types of Additives: Surface-active Agents

Anti-fog
Anti-stat
Easy clean; Self-cleaning
Hemocompatibility (does not damage/rupture red blood cells)
Anti-thrombogenicity (does not induce coagulation abnormalities)
Resistance to Lipid Adhesion/Adsorption (anti-fouling - protein)
Anti-microbial
Anti-fouling – marine, ultrafiltration membranes
Improved wear performance (abrasion)
Scratch resistance
Anti-glare
Anti-piracy

Additive attributes

- Partially compatible
- Low surface energy
- Thermally stable
- Chemically unreactive

There is a significant amount of additives which are surface active agents which means the additives when added to the polymer, they tend to come to the interface between mold and the polymer matrix and helps in releasing the molded plastic part from the mold.

Similarly, there are other surface active agents, like anti-fog that helps in preventing fogging on polymers samples like polymer films etc; anti-static agent that prevents generation of static charge on polymer surface; self-cleaning agents that help in self-cleaning of polymer material. We can add surface active agents to improve haemocompatibility or blood compatibility so that when the polymer sample comes in contact with blood it does not damage or rupture blood cells. Similarly, we can add additives that prevent plastic induced blood coagulation, provide resistance to lipid adhesion or adsorption, prevent fouling by protein molecules, etc. Anti-microbial additives help in killing the viruses and microbials when come into the contact with surface. Anti-fouling agents are very much applied in the marine applications where this actually prevents fouling of marine plants to grow on the plastic surface. There are others like abrasion resistant, scratch resistant and anti-glare agents. There are many other properties which are achieved by adding surface active agents in the base polymers.

It requires dedicated discussion to answer questions like, how do additives work? What are the types of additives? What are the chemical structures required for these types of additives? These are beyond the scope of this lecture due to time constraints. These surface-active agents need to have few common attributes like they should be partially compatible, they should not be soluble or very much miscible so that they do not come to the surface. They should not be totally immiscible with the polymer sample; a partial compatibility is required. They must have low surface energy so that they come to the surface preferably; they need to be thermally stable for withstanding the processing conditions of the polymer and must be chemically unreactive with the base polymer or otherwise will lead to degradation of the properties of the base polymer.

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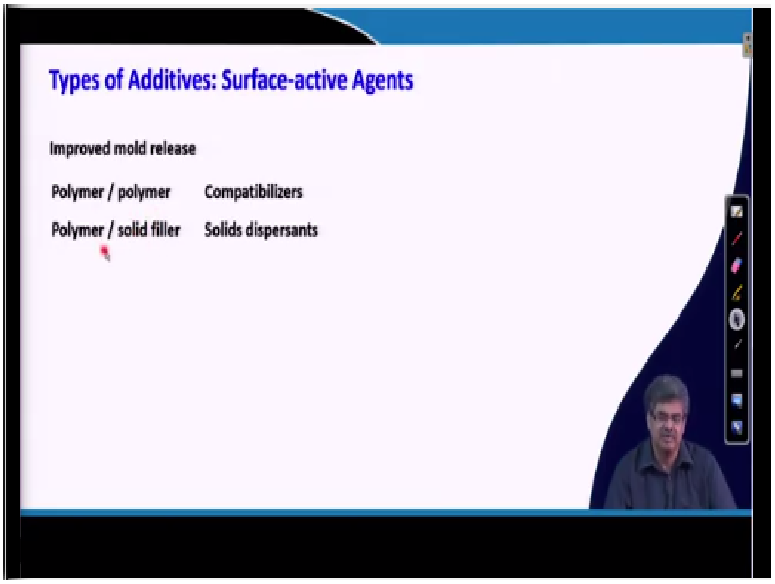

Types of Additives: Surface-active Agents

Improved mold release

Polymer / polymer	Compatibilizers
Polymer / solid filler	Solids dispersants

These surface active agents can also be used as a compatibilizer between two immiscible polymers, when you make a blend of two immiscible polymers. Then we can add compatibilizer to compatibilize the two immiscible blends or immiscible phases. Similarly, we can use these surface active agents to compatibilize or disperse solid fillers inside polymer matrix. In this case these agents actually go and seat in interface between the polymer sample and the filler and help in dispersing the filler within polymer matrix.

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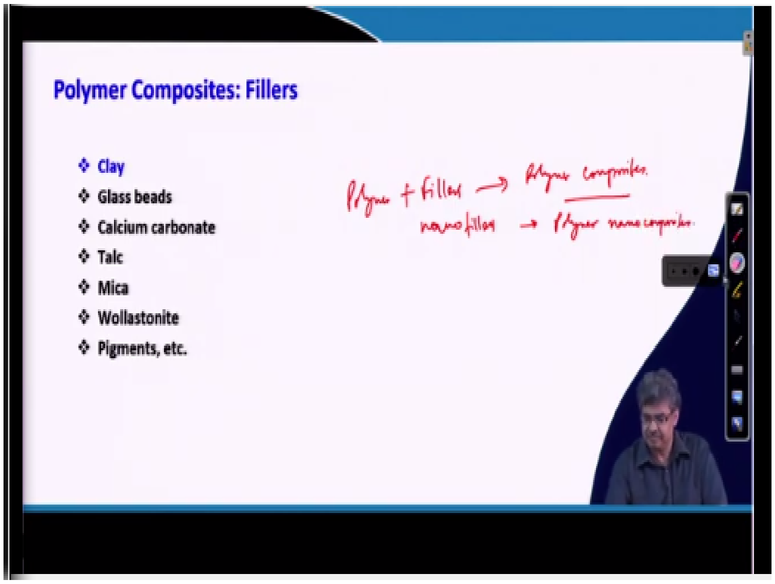

Polymer Composites: Fillers

- Clay
- Glass beads
- Calcium carbonate
- Talc
- Mica
- Wollastonite
- Pigments, etc.

Polymer + fillers → Polymer composites

nanofillers → Polymer nanocomposites

There are other fillers that are added. Now there is a difference when we use the term additives and fillers. In case of additives, generally the agent or the additives are added in much lower concentration. For example, typically less than 1% or 2% additives are added in the base polymers, maximum maybe 5%. But in case of fillers, these fillers are added in much larger quantity, much higher than the additive molecules.

Just the difference between additives and fillers: additives are generally added at much lower concentration whereas fillers are generally added in larger concentration. There are many types of fillers, which are added to improve the performance like clay, glass beads and calcium carbonate, talc, mica and so on. When we add fillers to the base material, we actually generate a composite. So, when fillers are added to polymers, polymer plus fillers, we get polymer composites. When we add nanofillers (dimension in nano-region on nano-dimension), then we call those composite as polymer nanocomposites.

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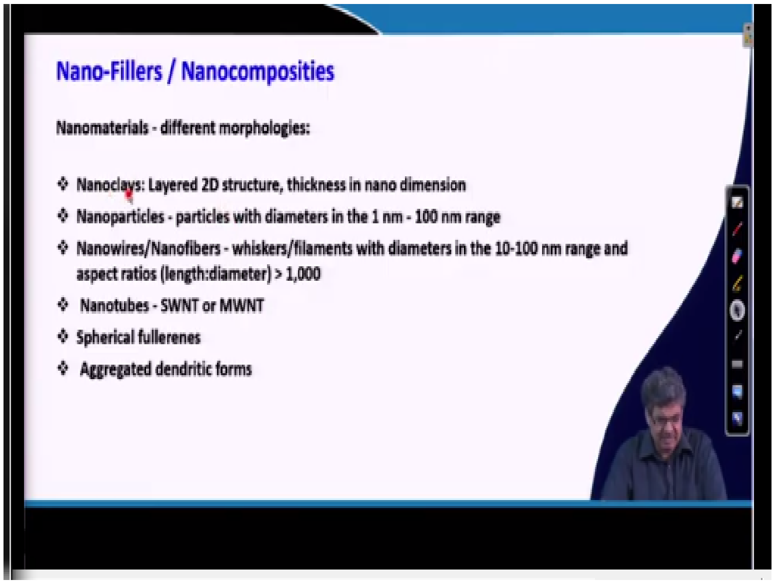

Nano-Fillers / Nanocomposities

Nanomaterials - different morphologies:

- Nanoclays: Layered 2D structure, thickness in nano dimension
- Nanoparticles - particles with diameters in the 1 nm - 100 nm range
- Nanowires/Nanofibers - whiskers/filaments with diameters in the 10-100 nm range and aspect ratios (length:diameter) > 1,000
- Nanotubes - SWNT or MWNT
- Spherical fullerenes
- Aggregated dendritic forms

So, we now talk a little bit about this nanofiller and nanocomposites and there are many nanomaterials which are added to polymer based material to improve their properties like nanoclays, nanoparticles, nanowires or nanofibers, nanotubes, spherical fullerenes, aggregated dendritic forms. There is specific role these fillers actually take, for example, when we add these nanotubes, carbon nanotubes, they actually increase electrical conductivity of the base polymer, when you add nanoparticle they increase several properties like scratch resistance and so on.

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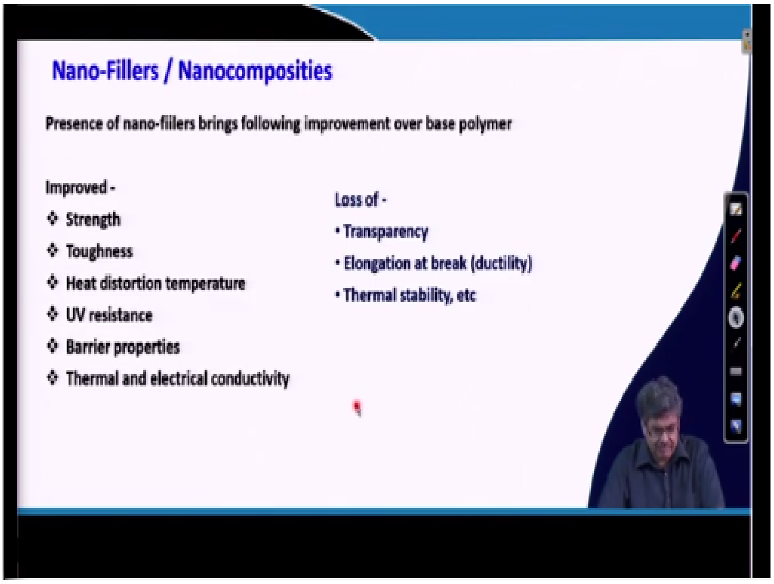

Nano-Fillers / Nanocomposities

Presence of nano-fillers brings following improvement over base polymer

Improved -
- Strength
- Toughness
- Heat distortion temperature
- UV resistance
- Barrier properties
- Thermal and electrical conductivity

Loss of -
- Transparency
- Elongation at break (ductility)
- Thermal stability, etc

I will discuss a little bit about nanoclays. When you add nanoclays, they generally improve properties e.g. increase the strength, toughness, HDT heat distortion temperature, UV resistance, barrier properties, thermal and electrical conductivity. At the same time by adding these nanofillers we lose transparency, we lose ductility or elongation at break and also lose thermal stability especially because of the impurities present in these types of fillers.

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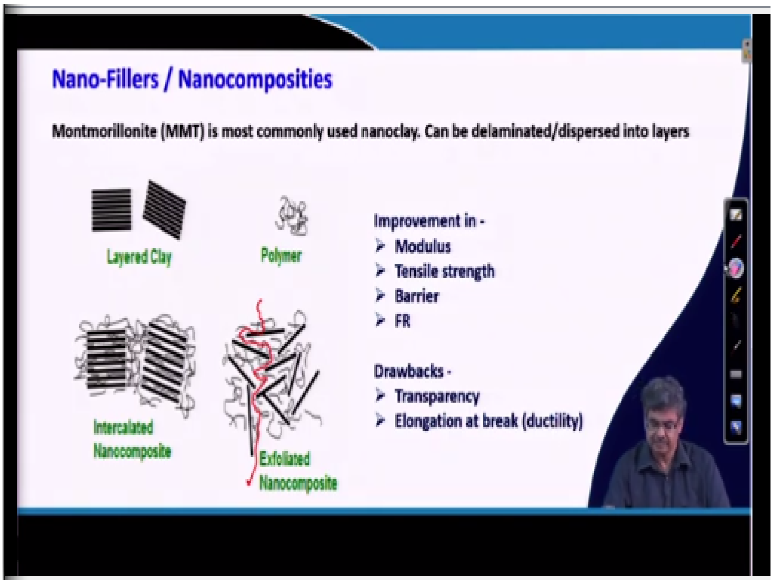

Nano-Fillers / Nanocomposities

Montmorillonite (MMT) is most commonly used nanoclay. Can be delaminated/dispersed into layers

Improvement in -
- Modulus
- Tensile strength
- Barrier
- FR

Drawbacks -
- Transparency
- Elongation at break (ductility)

Nanoclays have these types of layered structures and when they are added to polymers, we add some additives along with these or we try to match the chemistry between the polymer and the clays, so that the polymer chains penetrate and separate these layers. Unless we can separate the layer and disperse this clay layer then we will not get the improvement in properties. So, we get intercalated nanocomposite and exfoliated nanocomposites where the layers are separated and dispersed in the polymer matrix. One example like if we have a situation where a gas has to pass through this polymer matrix, then it will face resistance from these nanoclays. So, if gases want to pass through this, then they will stop here, then they have to take this another path which is a longer path to pass through the polymer matrix. Hence, it is expected to increase the barrier property of the base polymer. It increases modulus because the clay has higher modulus than the polymeric substances. It also increases the tensile strength because it creates torturous paths for the gases to move that increases the barrier property. It also helps in increasing or improving the fire retardant performance of the base polymer. Drawback is that it decreases the transparency and decreases the ductility. So, maintaining the ductility or elongation with increase in modulus is a challenge. Or in otherwards, creating a high modulus ductile polymeric sample is remains a challenge. We will talk about blends a little bit in the next class.