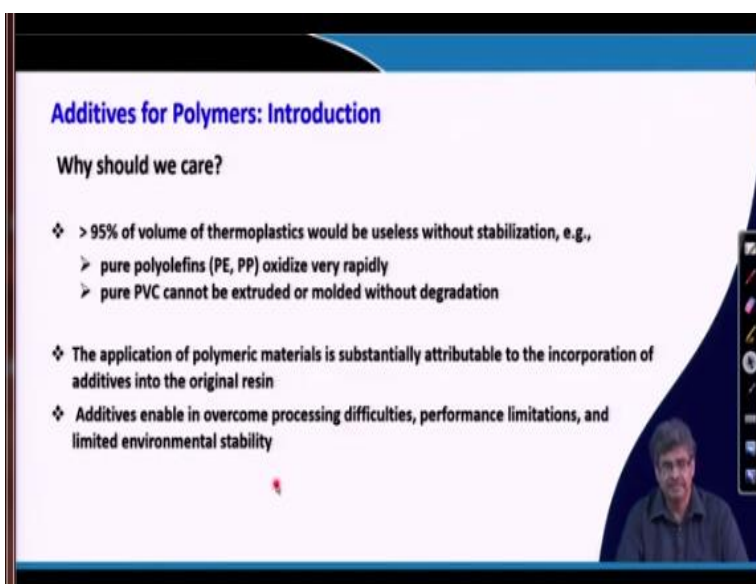


**Introduction to Polymer Science**  
**Prof. Dibakar Dhara**  
**Department of Chemistry**  
**Indian Institute of Technology-Kharagpur**

**Lecture-41**  
**Polymer Additives**

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

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The screenshot shows a presentation slide with a white background and a blue header. The title is 'Additives for Polymers: Introduction'. Below the title, the question 'Why should we care?' is posed. Three bullet points follow, each starting with a diamond symbol (❖). The first bullet point states that over 95% of the volume of thermoplastics would be useless without stabilization, with examples: pure polyolefins (PE, PP) oxidize very rapidly, and pure PVC cannot be extruded or molded without degradation. The second bullet point states that the application of polymeric materials is substantially attributable to the incorporation of additives into the original resin. The third bullet point states that additives enable in overcoming processing difficulties, performance limitations, and limited environmental stability. A small video inset of a man is visible in the bottom right corner of the slide.

**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 volumes of thermoplastics would be useless without stabilization, for example, pure polyolefins like polyethylene and polypropylenes oxidize very rapidly. So, 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.

So, we required to add thermal stabilizer or to PVC to have a effective processing. So, the application of polymeric materials is substantially attributed to the incorporation of additives into the original resin. Additives enable in overcoming processing difficulties, performance limitations and limited environmental stability. So, we add actually additive to overcome this limitations as described here and I will describe more about this limitations little later.

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**Additives for Polymers: Introduction**

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

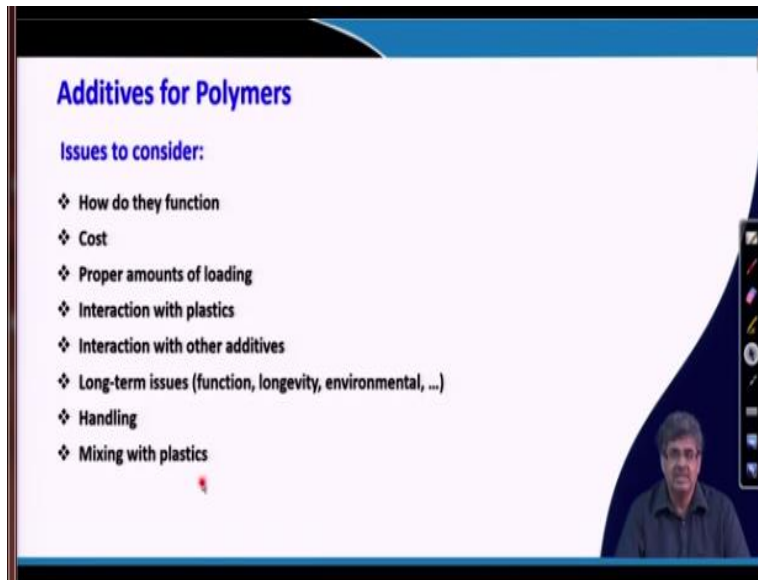
- ❖ Chemical composition of the polymer
- ❖ Processing conditions
- ❖ Its targeted application
- ❖ Mechanism of degradation of a polymer when subjected to heat, light, shear, moisture, either during its manufacture or during its life cycle.

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.

Now 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 its manufacturing and entire life cycle. So, we need to understand how polymer degrades during processing or during its use in for a outdoor application or some other application?

So, unless we do not understand the mechanism of degradation 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 fluoride make them prone to degradation by variety of environmental agents. Hence these polymers generally require protection against oxidation, light, thermal degradation etc as I just discussed now.

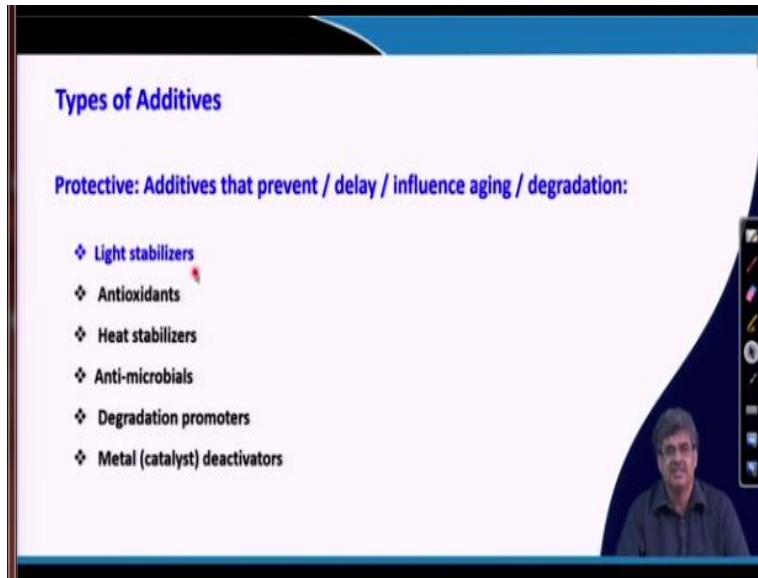
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This some issues to be considered when we design or add additives to polymer samples, how do they function? What is the cost of the additives? Proper amount of loading need to be added, so that it actually does it function it does not deteriorate the function of the base polymer. How the additives interacting with the based polymer material that to be understood. Interaction with other additives if there are multiple additives; then how the multiple additives interact with each other that needs to be understood as well long term.

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

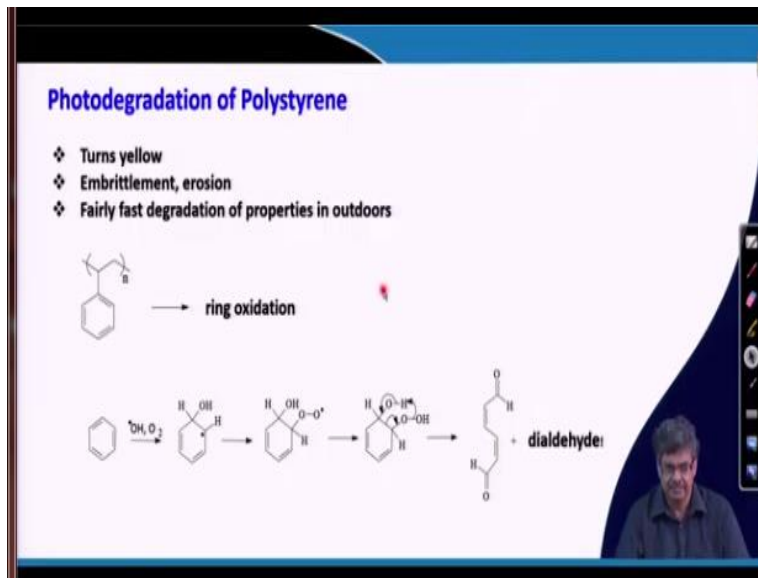
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As I said there are different types of role of additives can play and accordingly we add additives to the base material. For example protective additives, these additives generally prevent or delay or influence the aging or degradation behavior of the base polymer. And some examples of given light stabilizer with act against light exposure, antioxidants which basically prevent oxidative degradation, heat stabilizers which actually prevent or slow down the heat related degradation, especially during processing.

Similarly anti-microbials which basically protect the polymer from microbial attack and so on. So what I will do in this lecture? It is not possible for me to give example and discuss the mechanism of this additives the function of these additives, all these additives that is not possible. And that will require many lectures and which is also not required for this introductory course as well. So, what I decided? I will talk about one example for each case, so in this case let me discuss about light stabilizers.

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The light stabilizer actually required when the polymers is prone to deteriorates it is property in the influence of light. For example photo degradation 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 this light, the contact of light or and is actually more prominent.

And 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.

And obviously 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

*Fries rearrangement*

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 hour, one year, two, one and a half years exposure in outdoor. And that is happens because of light induced freeze rearrangement or fries rearrangement. So, basically there is a organic rearrangement reaction named as. So, this is fries rearrangement that happens in presence of light and as a result the sample becomes yellow and you get lot of color product and this path A is driven by light which is less than 300 nanometer.

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

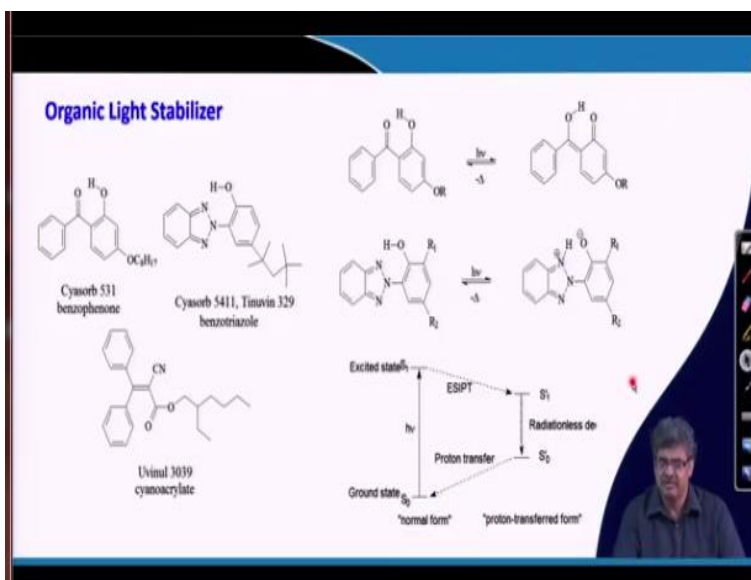
**Light Stabilizer Types:**

- 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 are light stabilizers. So, it is an additive which to reduce or eliminate the reaction caused by visible or UV light radiation. And most engineering plastics typically contents and aromatic groups which has intense UV absorption around 290 and that is the reason for that is the most dominating factor for this degradation because that has higher energy.

And as I said the exposure to lights generally result in yellowing in polymer. So, different types of light stabilizer are available in the markets and they are UV absorbers UVAs and they actually absorb and effectively screen UV light. Hindered amine light stabilizer or HALS they arrest chemical chain reaction resulting from free radicals. Also they have that is why they are called free radical scavengers. And we can add both together to have a synergistic benefit in a engineering plastics.

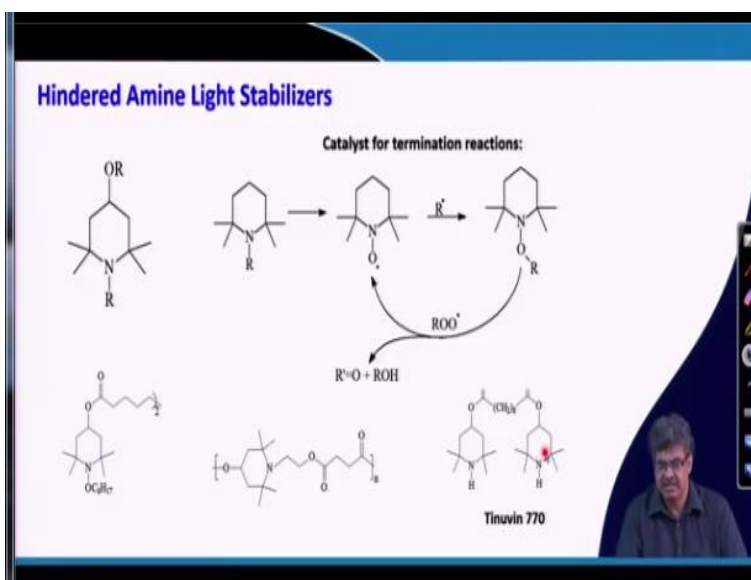
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Some of the examples are given here organic light stabilizers, this is a commercial name and this is the compound type. So, this is benzophenone dye molecule, this is benzotriazole and this is cyanoacrylate containing molecules. And these actually a stop or prevent UV light absorption by excite state proton transfer. So, in this case the normal form get excited by absorbing the light and then add in excited state it actually undergo a excited state intra molecular proton transfer at is shown here.

And then it comes back to the normal form by radiation less pathway and reverse proton transfer. So, by doing these it can actually prevent the engineering polymers from getting degradation.

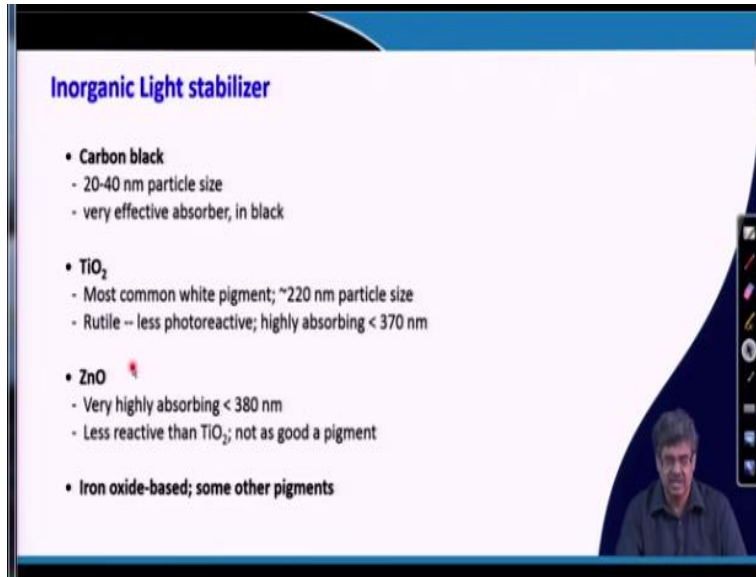
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Similarly the HALS, they actually stop these radicals for doing oxidative reactions, so that is why they are called these radical scavengers. In some of the commercial HALS are shown the examples are shown here then this is the commercial name of this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

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**Inorganic Light stabilizer**

- Carbon black
  - 20-40 nm particle size
  - very effective absorber, in black
- TiO<sub>2</sub>
  - 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<sub>2</sub>; not as good a pigment
- Iron oxide-based; some other pigments

There are some inorganic stabilizer can be added to prevent photo degradations like carbon black TiO<sub>2</sub> and ZnO and they are basically very effective in nature. But remember if we want the polymer or material to be you know in the application which is transparent or clear application then we cannot add this type of inorganic stabilizer. Because when you add this carbon black TiO<sub>2</sub> as they removed invariably the transparency comes down.

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**Types of Additives**

Additives that provide enhanced performance:

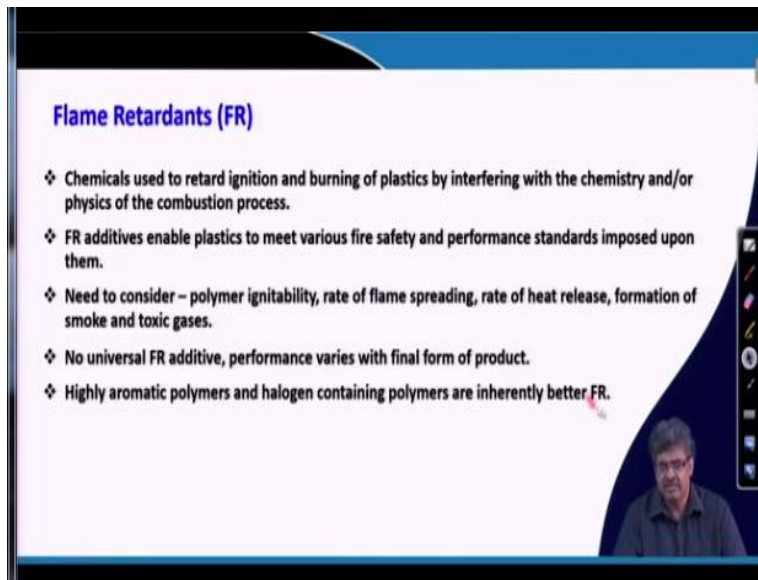
- ❖ Flame retardants
- ❖ Impact modifiers
- ❖ Optical brighteners
- ❖ Pigments and colorants
- ❖ Plasticizers
- ❖ Reinforcements
- ❖ Coupling agents

There are other types of additives we just discussed about the stabilizers. Now I will move to the other types of additives which enhance performance. So, basically it enhances the performance of the base polymer. For example flame retardants, these actually improve the flame performance. So, basically the flammability of a polymer actually becomes lower as we add these flame retardants to the base polymer.

Similarly we can add impact modifier 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 case as well I will just talk about one example in little detail. I will skip the discussion on others because it is not possible for me to discuss all how does all these additives work? So, let me discuss about flame retardants.

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**Flame Retardants (FR)**

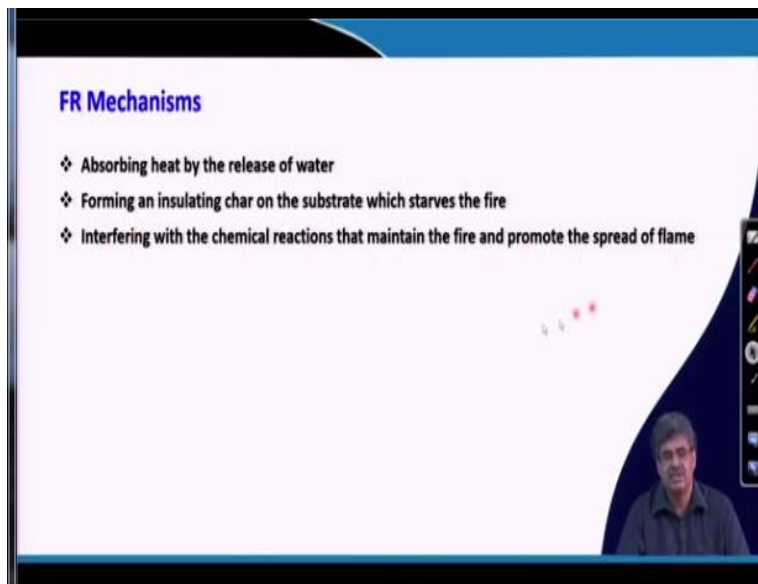
- ❖ Chemicals used to retard ignition and burning of plastics by interfering with the chemistry and/or physics of the combustion process.
- ❖ FR additives enable plastics to meet various fire safety and performance standards imposed upon them.
- ❖ Need to consider – polymer ignitability, rate of flame 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.

So, flame retardants are chemical use to retard ignition and burning of plastics by interfering with the chemistry and or physics of the combustion process. So, we need bond a plastics or polymer the combustion process happened and somehow by adding this FRs this actually returned the ignition and burning of the plastic materials. Now these FR additives enable plastic

to meet various fire safety and performance standard imposed by several regulatory authority. And without these basically these plastics material cannot be used in many applications, indoor applications or in transport and so on.

So, the factors we need to consider is this polymer ignitability rate of flame spreading, rate of heat release, formation of smoke and toxic gases all of these we need to consider. And as a result there is no universal FR additive for different sample. It basically depends on the type of application and depends on type of base polymer we are thinking. Highly aromatic polymers and halogen bond containing polymers are inherently better fire retardants.

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The mechanism, how this fire retardency occurs by different possible mechanisms, one is by absorbing heat by release of water. So, additives actually release water and as a result a heat is absorbed which prevents a inability of the material. Forming an insulating char and thereby preventing further burning of the substrate which basically stop the fire which basically stop giving fuel to the fire.

If we have insulating char on the polymer sample this possibility that it can interfere with the chemical reactions that maintain the fire and promote thus spread of fire. So, basically it can stop or it can prevent the chemical reactions which maintain the fire and promotes the trading of flame.

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**Examples of FR additives**

- ❖ Alumina Trihydrate,  $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$  – releases water at around 200 C which inhibits combustion
- ❖ Forming an insulating char on the substrate
  - Phosphorous flame retardants
  - Phosphate esters  $(\text{RO})_3\text{PO}$
  - 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 degree centigrade which inhibits combustion. There are other additives which actually improve the charring basically increase the amount of char on burning on the substrate as a result as I discuss that it prevents the polymers come in contact with the fire. So, basically fire will be starved of any further fuel and it will diminish.

And the examples are phosphorus flame retardants like phosphate esters and they are very useful in this type of polymer materials. So, the phosphate flame retardant works by promoting char formation on the substrate. Similarly this is brominated aromatics which emits HBr during decomposition which interferes with the chemical reaction which maintains 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.

$$LOI = \frac{\text{vol. O}_2}{\text{vol. O}_2 + \text{vol. N}_2} \times 100$$

How we quantify the flammability of polymers? There are 2 different types of testing, one is by generally done for the products by and done for actual applications and those are mandated by UL standards. So, there are very different you know protocols are there which I am not discussing here. And 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. So, 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 bonding process is done when the oxygen amount is very low this bonding will not happen.

So, slowly the oxygen amount will increase and the minimum amount of oxygen which is required to maintain this burning that is called limiting oxygen index. So, this is which most versatile small scale testing minimum percentage of oxygen required for bonding. So, LOI limiting oxygen index is given by the volume of oxygen and volume oxygen plus volume of nitrogen.

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

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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 requires 95% oxygen that means the flammability of polytetrafluoroethylene is very low, as you can see these are used for a nonstick coating. So, you can these polymers generally do not bond very quickly. Similarly, the polyoxymethylene polyethylene oxide they require very low amount of oxygen to bond. So, these polymers are highly flammable polymer. So, lower is the value of LOI, the flammability of the polymers is high or higher.

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**Mold Release Agents**

- ◆ Additives for improving processing – Lubricants/Release

PETS

GMS

**Lubricants**

- ◆ Additives for decreasing CoF/improve wear resistance

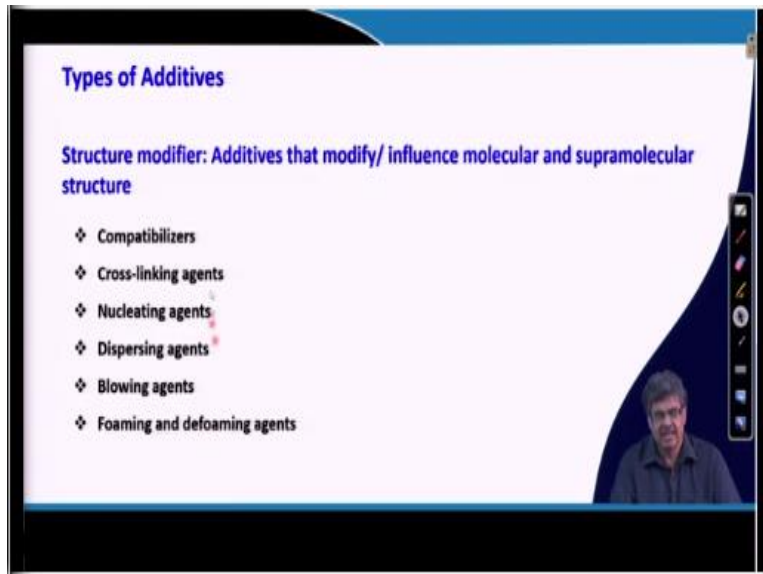
PTFE

There are some other additives which help in processing, fabrication and assembly of polymers. And they are like mold release agents which help in releasing the polymer from mold of the product from mold. Lubricants which effect or help in processing by basically if we add lubricant then the polymer can flow through the barrels easily. And 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 poly tetraethylene tetrastearate and this is GMS glyceryl monostearate. So, because of this presence of these long hydrophobic chains, they actually come or blot to the interface between the metal mold and the polymer. As a result these actually help releasing the polymer material from mold and they also help in processing of the polymer sample.

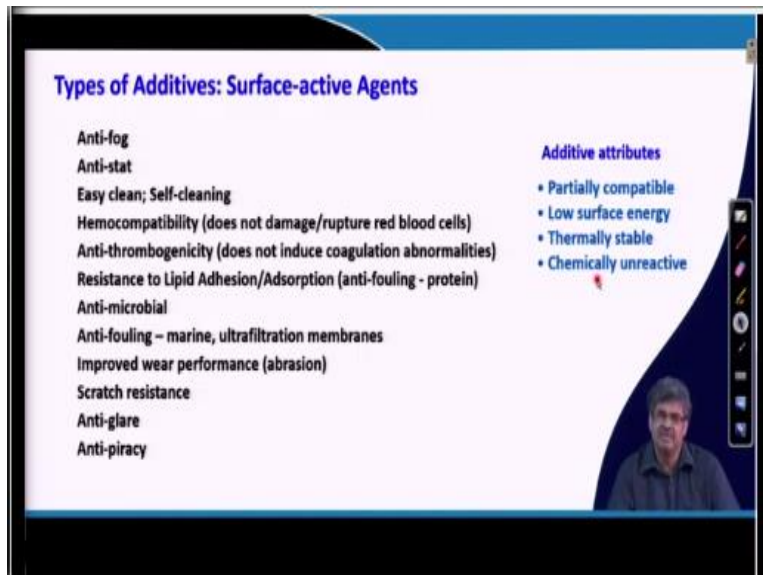
Similarly when you add this small molecule of polytetrafluoroethylene they actually reduce the friction between the metal barrel or metal skew and the polymer. So, coefficient of friction comes down as a result the lubrication happens.

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The other types of additives which are used for polymers are like compatibilizers, crosslinking agents, nucleating agents, dispersing agent, blowing agents. They have a definite role to play and I am not going to discuss any of this because you know it is require a lot of time and effort which is not available for this course.

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There are a significant amount of additives which has surface active agents which means the additives which are added in the polymer. They tend to come to the interface between the two phases like the example I gave that PETs or the GMS molecules which comes to the mold surface mold the interface between mold and the polymer matrix which helps in releasing the mold from polymers or samples from the mold.



Similarly there are other surface active agents which helps in several properties like anti fog it is helped is in basically preventing fogging on polymers samples like polymer film and so on. Anti static agent it basically prevents generation of static charge on polymer surface easy clean, self cleaning is basically prevent or basically help in self cleaning of polymer material. We can add surface active agents to improve hemocompatibility or blood compatibility.

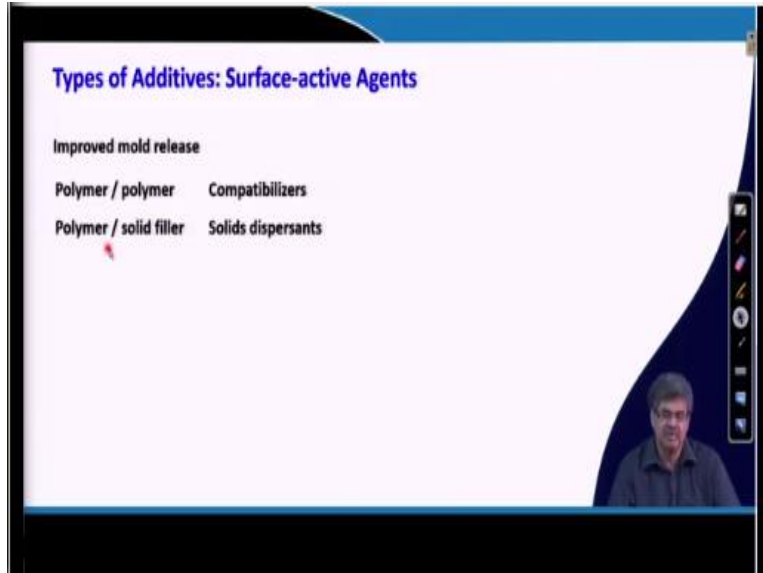
So, that it does not the sample when polymer sample comes in contact with blood it does not damage or rupture blood cells. Similarly we can add additives which prevent the polymer or plastic induced coagulation, resistant to lipid adhesion or absorption which prevents absorption or fouling by protein molecules. Anti microbial additives which basically at help in killing the viruses and microbials when come into the contact with surface.

Anti fouling, this is like very much applied in the marine applications where when in contact with water, this actually prevents fouling of many implants to grow on the plastic surface. And there are other like abrasion resistance, cast resistant, anti glare, anti piracy, there are many other properties which are achieved by adding surface active agents in the base polymers.

And as I again said that these require dedicated discussion of each of these additives to tell you the mechanism, how does it work and what are the types of additives? What are the chemical structures required for these type of additives which are not possible for this lecture? And this surface active agents need to have few common attributes like they should be partially compatible, they should not be soluble or very much miscible.

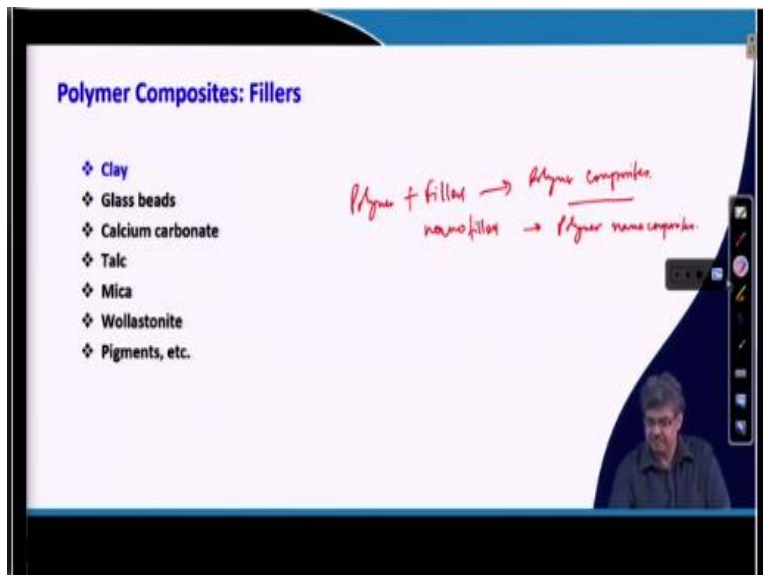
So, that it does not come to the surface or it should not be at all it immiscible. So, that it does not mix at all with the polymer sample it is a partial compatibility required. Low surface energy, so that it comes to surface it preferably. Thermal, it has to be thermal stable, so that it can withstand the processing of the polymer and it should be chemically unreactive, it should not react with the base polymer otherwise it will degrade the properties of the base polymers.

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These surface active agents can also be used as a compatibilizer between 2 immiscible polymers when you make a blend of two immiscible polymers. Then we can add compatibilizer to compatibilize to immiscible blends or invisible 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 see interface between the polymer sample and the filler and help in dispersing the filler within polymer matrix.

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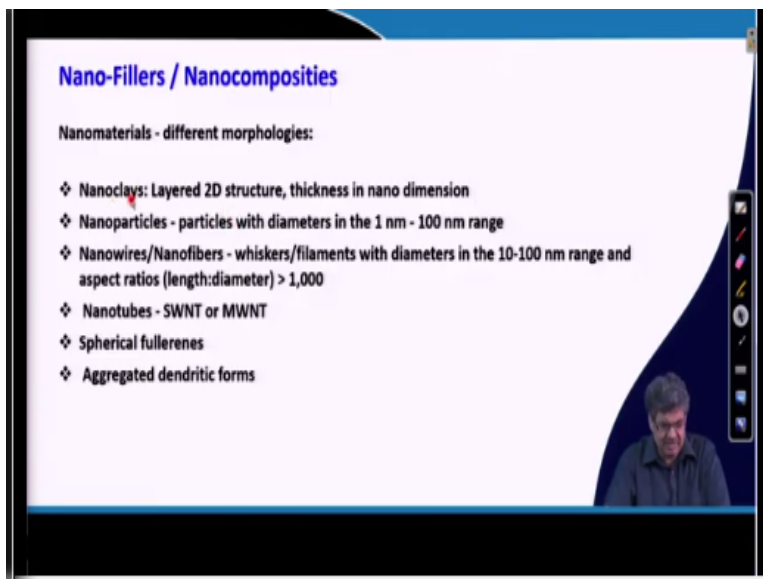
There are other fillers are added, now there is a difference when we use the term additives and fillers. In case of additives generally the agent or the additives are added in much lower concentration. For example typically less than 1% or 2% additives are added in the base

polymers maximum maybe 5%. But in case of fillers these fillers are added in much larger quantity, much higher than the additive molecules.

So, just the difference between additives and fillers, additives are generally added that much lower concentration whereas fillers are generally added and much larger concentration. And 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. And they are added specifically for improving some performances.

And I will talk about clays a little bit and specifically on nanoclays and when also 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 composite. So, when we add polymer plus filler we get polymer composites. And when we add nanofiller, nanofiller that mean fillers which have dimension in nano-region on nano-dimension, then we call those composite at polymer nanocomposites.

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So, we now talk about 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. And there are specific role these fillers actually take place for example when we

add these nanotubes, carbon nanotubes. They actually increases electrical conductivity of the base polymer when you add nanoparticle the increases several properties like scratch resistant and so on.

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**Nano-Fillers / Nanocomposites**

Presence of nano-fillers brings following improvement over base polymer

Improved -	Loss of -
• Strength	• Transparency
• Toughness	• Elongation at break (ductility)
• Heat distortion temperature	• Thermal stability, etc
• UV resistance	
• Barrier properties	
• Thermal and electrical conductivity	

So, I will discuss a little bit about nanoclays, when you add nanoclays on other in fact nanofillers they generally improve these properties like increases the strength, toughness HDT heat distortion temperature, UV resistance, barrier properties, thermal and electrical conductivity. But at the same time by adding this nanofillers we lose transparency, we lose ductility or elongation at break and also lose thermal stability especially because of the impurities present in these type of fillers.

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**Nano-Fillers / Nanocomposites**

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

Layered Clay

Polymer

Intercalated Nanocomposite

Exfoliated Nanocomposite

Improvement in -

- Modulus
- Tensile strength
- Barrier
- FR

Drawbacks -

- Transparency
- Elongation at break (ductility)

I will talk about nanoclays as example, nanoclays have these types of layered structures and when they are added in polymer. We add some additives along with these are we try to match the chemistry between the polymer and the clays. So, that the polymer chains can go and sit and basically separate this layer. Otherwise unless we can separate this layer and disperse this clay layer then we will not get the improvement in properties.

So, this is a intercalated nanocomposite and this is exploited nanocomposite where the layers are separated and dispersed in the polymer matrix. And one example like if we have a situation like these and if gaseous wants to pass through these polymer matrix. Then they will come and get resistant from this nanoclay. So, if gas wants to pass through this, then they will stop here, then there is to take this another length.

And there is to take a longer path to pass through this polymer matrix. Hence it is expected to increase the barrier property of the base polymer. So, it increases modulus because this has higher modulus, inorganic substances have much higher modulus than the polymeric substances. It also increases tensile strength as they describe that is because of this, it creates torturous paths for the gaseous to move increases the barrier property is also help in increasing or improving the fire retardant performance of the base polymer.

But drawback is that it decreases the transparency and this decreases the ductility. So, maintaining the ductility or elongation have increasing modulus is a challenge. Or in otherwise creating a high modulus ductile polymeric sample is remains a challenge. So, with this I will stop this class and I will talk about blends a little bit in the next class.