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

Lecture-40
Optical, Electrical, Barrier Properties: Chemical Resistance and Weathering of Polymers

Welcome back. In this lecture I will talk about other polymer properties like optical properties, electrical properties, barrier properties, chemical resistant and weathering of polymers. Now we will briefly discuss about these properties because for this introductory course I will not have enough time to go through in details for all these properties. Hence my plan is to go through these properties quickly and briefly.

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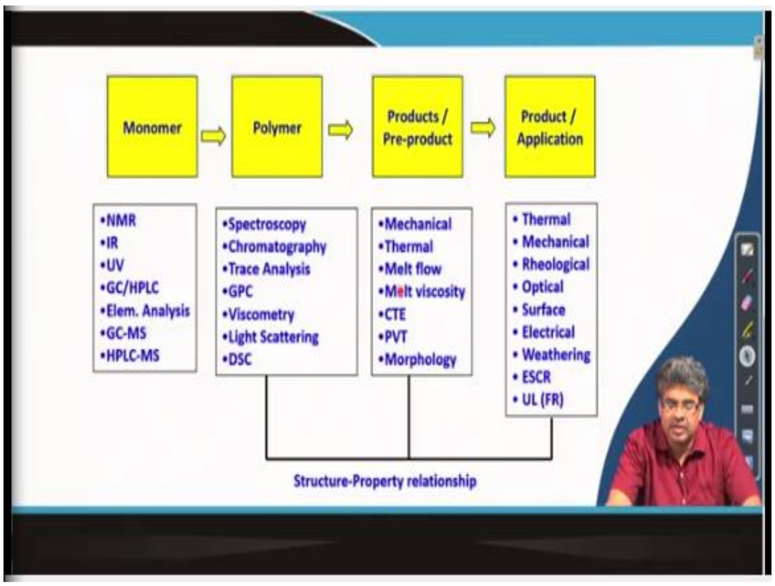

If we look at this chart, we have studied how to synthesize the polymer and then we have studied different techniques which can be utilized to characterize the synthesized polymer. And then we discussed also different properties like mechanical properties, thermal properties, rheological properties viscoelasticity. We did not discuss these properties in details because we lack of time.

And these are the properties of polymer which must be characterized before we think about any application, so these are inherent properties in a polymer sample. Now once we have this data, we can think about going into testing the properties of polymers relevant to product or applications. For example we can talk about the thermal characterization other than T g and T m like HDT or other thermal characterization which I discussed earlier.

We need to also characterize the sample fully in terms of their mechanical properties specially the type of application it is meant to. You know we have discussed many mechanical properties but which properties need to be characterized completely that will depend on the application for which the sample or the material is prepared for. We also need to be studying the rheological properties because that will basically bridge between the polymer performance and product performance and the polymer structure.

This also gives a lot of ideas in terms of polymer processing. And then we need to calculate or need to basically determine all other properties like optical, surface, electrical, weathering. Now these properties need to be determined or evaluated depending upon the application of the polymer. And these properties are related to the structure of polymer molecules which are characterized by these techniques which we have discussed earlier. So, these help us to understand the structure property relationship between a polymer molecule and a product.

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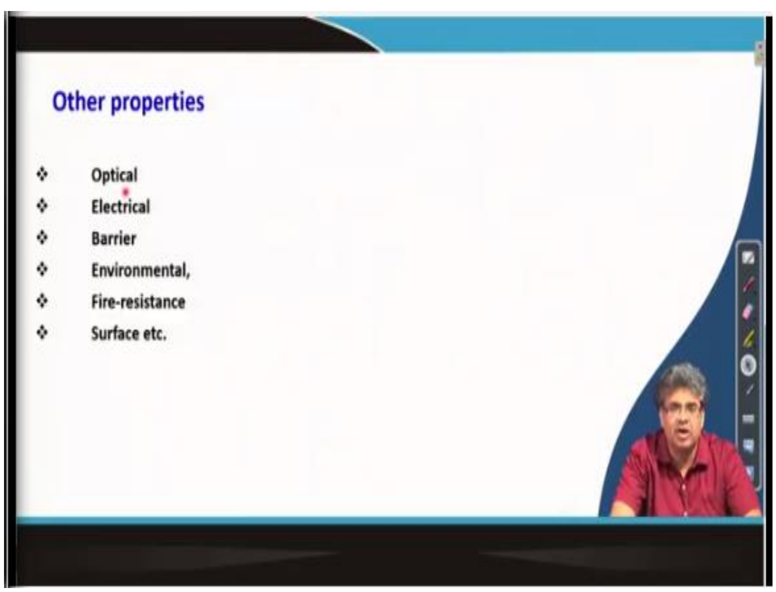

So, I will quickly discuss the other properties, I have already discussed mechanical, thermal, rheological properties in previous lectures. Now I quickly go through these properties, let us begin with optical properties.

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Now an optical property is a very important property specially for the polymer samples which are or polymer materials which are required to be aesthetically important. For example if we are using a bottle then obviously if it is a clear then it happens more than if it is a dark. There are other examples, like if we are using several application where we require complete transparent plastic material or polymer material.

Then obviously transmission is a very important property for that particular sample. Similarly we have several other aspects of different property within optical properties like transmission as I discussed, refraction, reflection, scattering, absorption, clarity, haze, gloss, yellowish index, stress - optical coefficient, birefringence, color. There were several thing depending on the application we need to characterize for the polymer sample.

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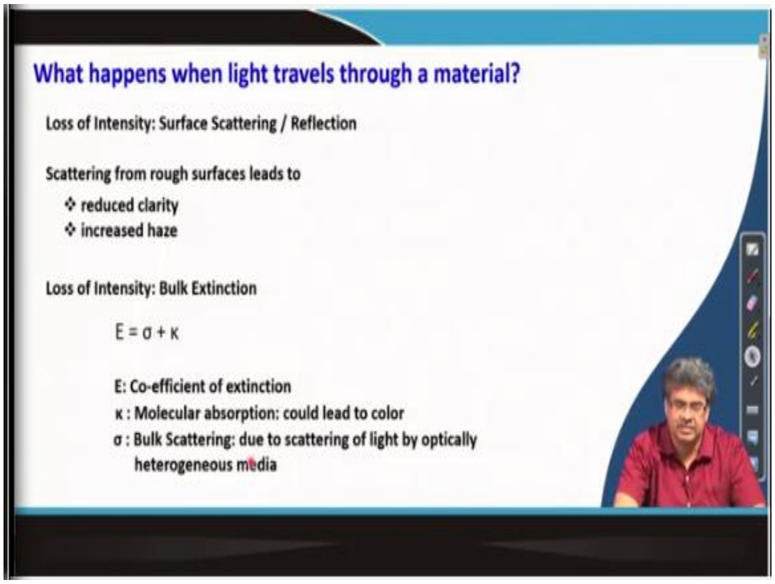

Now before we discuss the optical properties, we need to find out or we need to understand what happens when light travels through a material or when light interact with material. Invariably there will be loss of intensity due to surface scattering or reflection and due to the bulk scattering or extinction. So, let us talk about the surface scattering, the surface scattering happens because of the rough surface and these actually reduce clarity and also increase haze in the polymer sample.

Similarly loss of intensity happened because of bulk extinction, extinction means decrease in intensity and that may happen due to absorption. Molecular absorption which leads to color formation or it could be due to bulk scattering and this scattering is due to optically inhomogeneous medium. If there are more than one component and if the refractive index as different, then there will be bulk scattering. And that will depend upon the difference in the refractive index and the size of the scatter.

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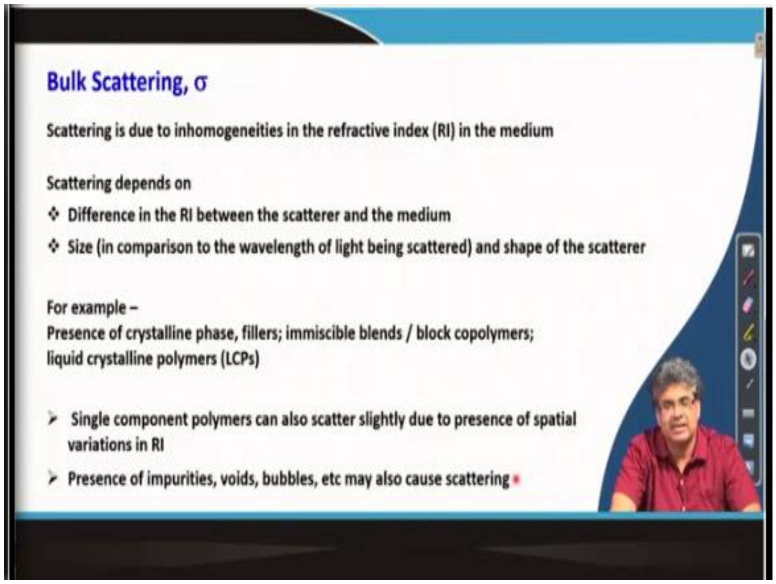

Let us talk about bulk scattering, now bulk scattering is due to in homogeneities in the refractive index of the medium. If the medium has more than one component and their refractive index values are different then the sample will actually scatter light. And this scattering depends on the difference in the refractive index between the scatter and the medium. And of course on the size in comparison to the wavelength of the light being scattered and the shape of the scatter.

For example presence of crystalline phase, fillers will scatter light, similarly immiscible blend or block copolymers. If we have immiscible blend or immiscible block copolymer then there will be inhomogeneity in the medium. And as if the differences in the refractive index between the components are enough then there will be scattering bulk scattering, that may happen also in case of liquid crystalline polymers.

Now, even single component polymers can also scatter light due to presence of spatial variation in refractive index which might appear due to moulding variation. And also the single component might actually be scattered because the presence of impurities, voids, bubbles, etc which may basically gives inhomogeneity and scatter light.

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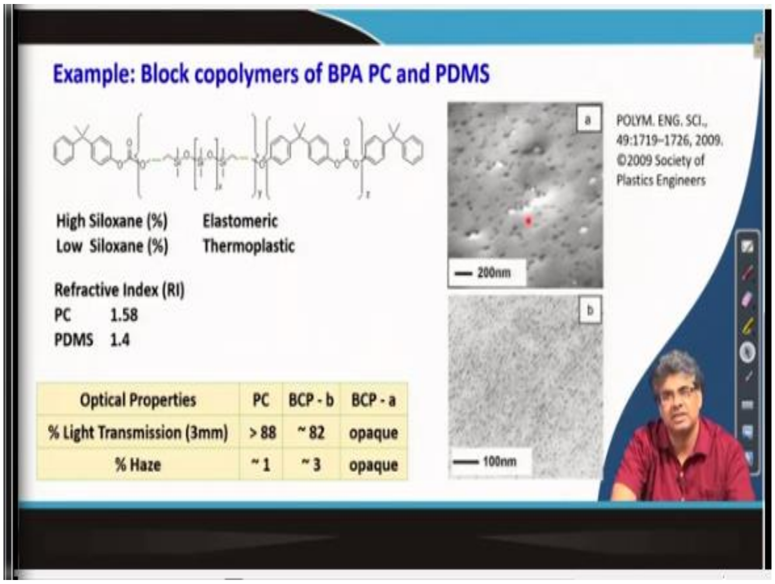

Optical Properties	PC	BCP - b	BCP - a
% Light Transmission (3mm)	> 88	~ 82	opaque
% Haze	~ 1	~ 3	opaque

We will give example, take example of block copolymer of bisphenol A and A polydimethylsiloxane, so this is PDMS block and this is bisphenol A block. Now if the siloxane percentage is high then this is a elastomeric polymer, elastomeric sample because this has much low T g and this is elastomeric component. And this is a glossy component which has a much higher T g compared to this polydimethylsiloxane.

And if it is a low siloxane then it behaves like thermoplastics, this dominates and if you have high siloxane this behavior of PDMS dominates, so it behaves like a elastomer. Now the refractive index of PC is 1**.** PC means this part is 1.58 and PDMS is 1.4 which is having a significant difference between these 2 components. So, unless their domain size, the size is extremely low, there will be scattering happening if immiscible as this 2 are immiscible with each other.

If you compare 2 samples where the base is polycarbonate matrix and these domains are a polydimethylsiloxane. In this case as you can see the size of the polydimethylsiloxane domains are higher compared to this sample, where the size of these domains for PDMS domains is much lower compared to this. So, if you look for the optical properties for a pure bisphenol A polycarbonate when these domains are not present.

The light transmission for a 3 millimeter thick sample is greater than 88% and haze percentage haze is about 1%.. For this block copolymer sample where the domain sizes are much lower compared to this, the transmission value is about 82%, haze is about 3%. But in this case the transmission is so low that the sample is completely opaque and haze is very high and this is opaque.

So, this means that the scattering and as the result of that opacity or the percentage transmission depends on the difference in the refractive index between the 2 phases as the difference is higher. Then there will be higher scattering and if the domain size is higher than the scattering will be higher and as a result the haziness or opacity will go up.

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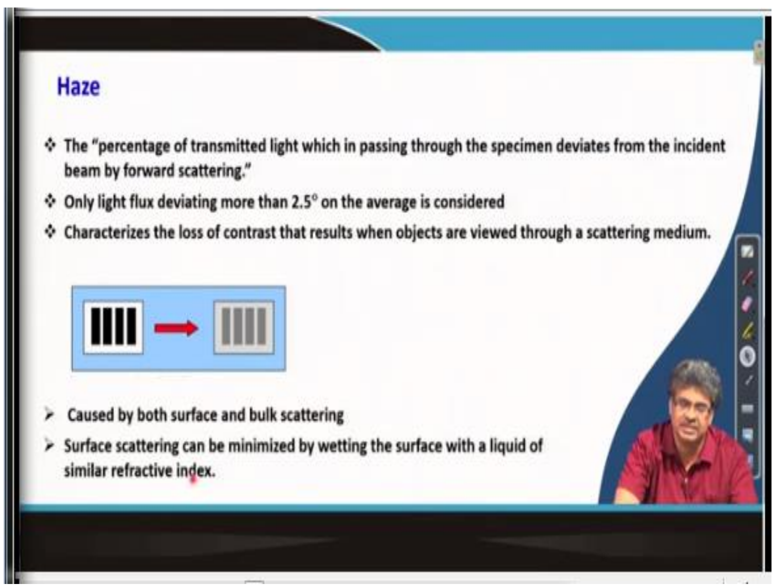

Now we talked about haze, what is haze? Haze is a percentage of transmitted light which is passing through the specimen deviates from the incident beam by forward scattering, which means only light flux deviating more than 2.5 degree on average is considered. It characterizes the loss of contrast that results in objects are viewed through a scattering medium.

So, if you take a plastic material and view through it the loss of contrast is related to the percentage of haze in the sample. And percentage is or haze is caused both by surface and bulk scattering. And surface scattering can be minimized by wetting the surface which will basically minimize the roughness. And we can also use a liquid of similar refractive index of the polymer material which will also reduce the surface scattering and as a result increase the transparency or reduce the haze.

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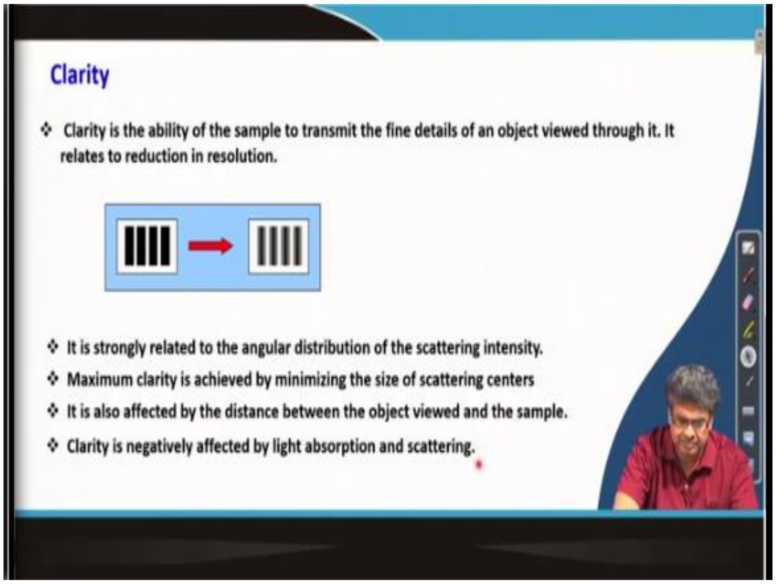

We often use the term clarity, what is the actual meaning of clarity? Clarity is the ability of a sample to transmit the fine details of an object viewed through it. So, if you are being through a polymer glass then this ability to transmit the fine details of an object is related to the clarity of the polymer sample through which we are viewing and it relates to the reduction in resolution. So, you can see this graph to understand this, this sketch to understand this.

It is strongly related to angular distribution of scattering intensity, maximum clarity is achieved by minimizing the size of the scattering center. It is also affected by the distance between object viewed and the sample as it is related to the angular distribution of the scattered intensity. Clarity is negatively affected by light absorption and scattering.

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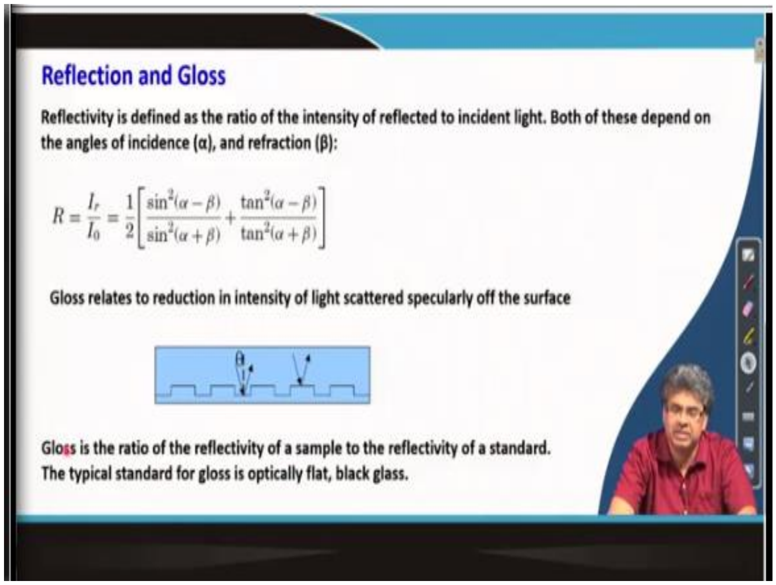

We will also talk about the terms reflection and gloss, reflectivity is defined as the ratio of intensity of the reflected to the incident light. Both of these depends on the angle of incidence and refraction alpha and beta. And this is related to the intensity of the reflected light to the intensity of the incident light and this is given by this expression where angle of incidence is alpha and refraction, angle of refraction is beta.

Gloss relates to the reduction in intensity of light scattering specularly off the surface. Gloss is the ratio of reflectivity of a sample to the reflectivity of a standard sample. And the typical standard for gloss is optically flat black glass. So, if you compare the reflectivity between the standard sample and the particular sample we can measure the value of gloss quantitatively.

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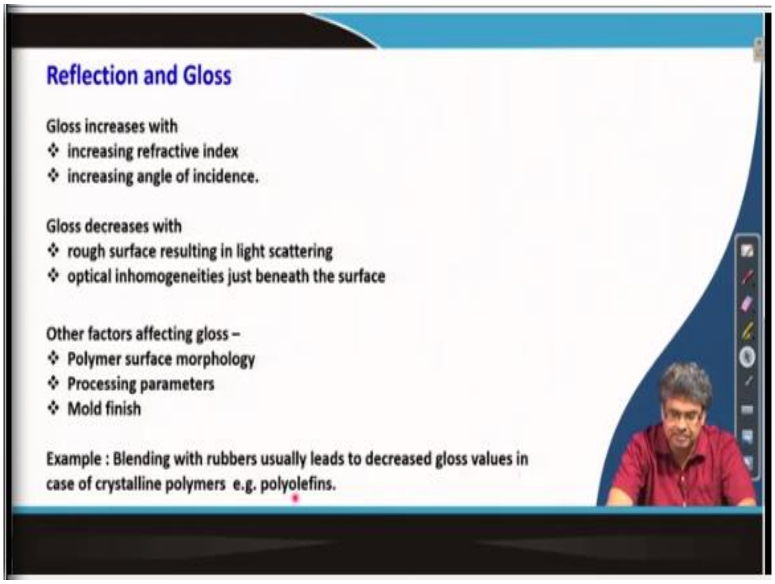

Gloss increases with increasing refractive index, increasing angle of incidence and gloss decreases with rough surface resulting in light scattering, optical inhomogeneities just beneath the surface. And other factors which affects gloss are polymer surface morphology, processing parameters, mold finish. For example blending with rubbers usually lead to decrease in gloss value in case of crystalline polymers like polyethylene.

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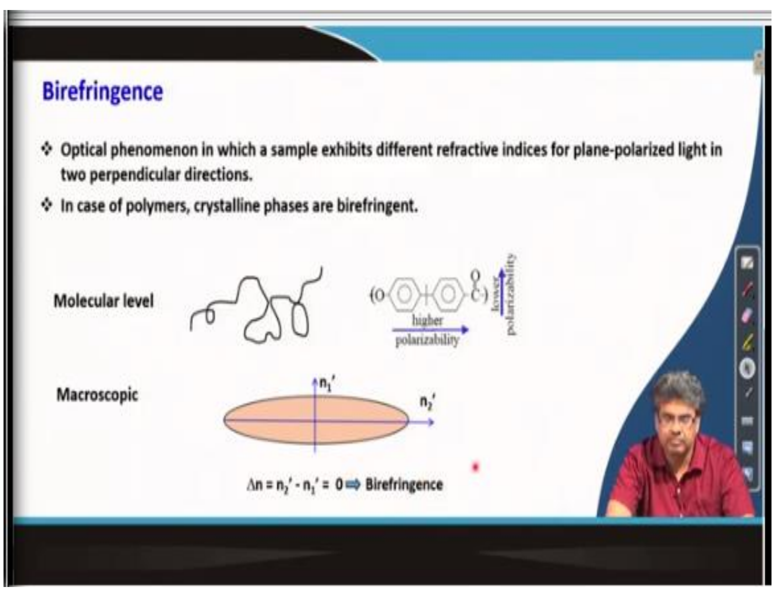

This also another term related to optical properties is birefringence**.** This is related to the optical phenomena in which a sample exhibits different refractive index for plane polarized light into perpendicular direction. If we use 2 differently plane polarized light and if it is show different refractive index for those 2 plane polarized light. Then we call the sample have birefringence and this happen if the polymer contains crystalline phases.

Because the refractive index will be because they are aligned crystalline phases are aligned in a particular direction. Hence if the refractive index towards different plane polarized light will be different, if the polymers have crystalline domains. For example if I have this type of polymer for like Bisphenol A, then in this direction the polarizability is higher whereas in a other transverse direction the polarizability is lower, so we have birefringence.

See in macroscopic way, we can actually look for the refractive index values in 2 direction. If they are not equal then the polymer sample source birefringence.

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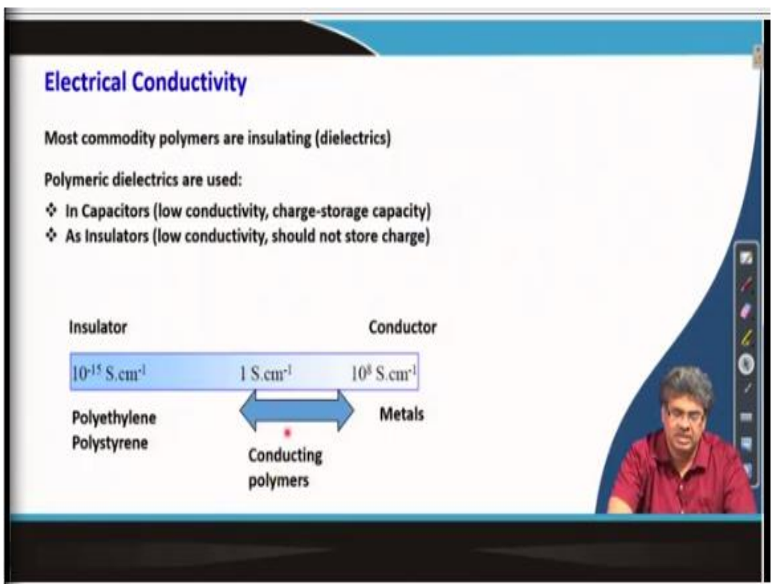

We will move to next property electrical property and again I will just briefly touch these properties. Most polymers or commodity polymers are insulating dielectric and this is very advantageous because polymers are used for many applications as electrical, electric insulators. And as a result polymer dielectrics are used in capacitors, low conductivity, charge storage device and as an insulator which require low conductivity and should not store charges.

So, typical value of polymers are insulated 10 to the power - 15 Siemens per centimeter whereas conductor which are metals have very high conductivity values. And recently not very recently but about few decades back conducting polymers were discovered and they have a conductivity value around this region. And some of this example of some conducting polymers are shown here.

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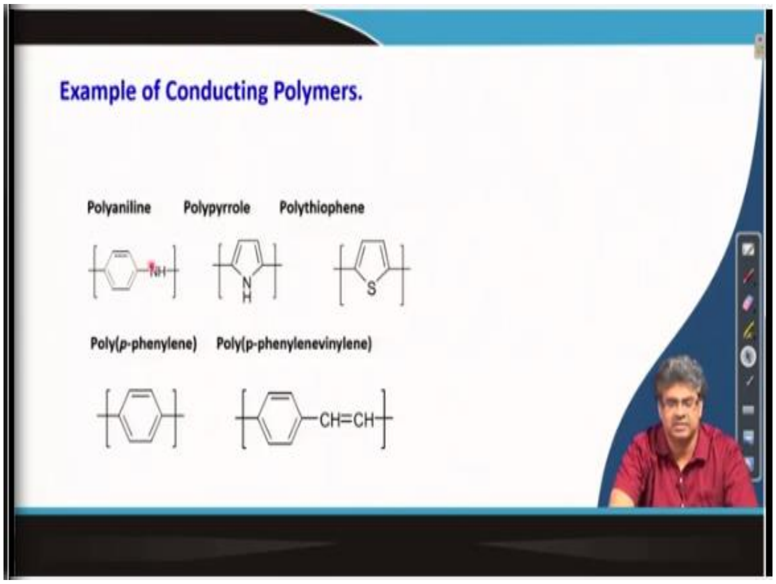

Like polyaniline, polypyrrole, polythiophenes and these they actually do not connect or behave like conducting polymer as such. But when they are doped for example, if and when is doped with a proton or acidified then it shows conductivity because of the movement of electron through the backbone due to possible resonating structures.

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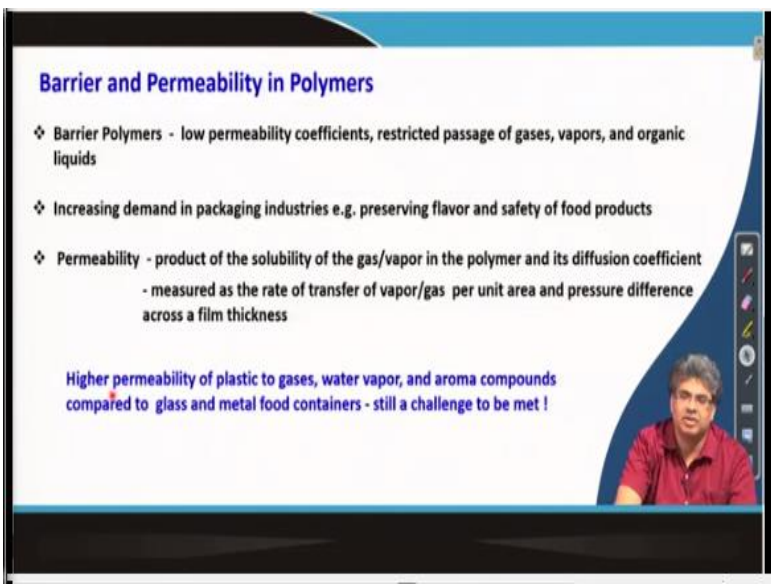

We will now discuss about barrier and permeability in polymers, this is also very important because in several cases the container must be barrier having barrier property to several gases. For example if we are using a vial of a drug, then if the drug reacts with oxygen then the storage time will of that particular drug will depend on how good is the vials barrier property if it can sufficiently barrier the passage of or diffusion of oxygen from outside to inside.

Then the stability or lifetime of the drug will be higher, so barrier is very important. Similarly in some cases permeability also important if for example we are using for some medical applications where the polymers need to actually allow oxygen to diffuse in and out in that case, permeability is also important for polymer samples. So, barrier properties having low permeability coefficient, restricted passage of gases, vapors and organic liquids.

Increasing demand for packaging industries preserving flavor, smell and safety of food products or even pharmaceutical products, this is very important now, various properties. Permeability is required for products where the solubility of gases or vapors in a polymer and it is diffusion coefficient. So, permeability of a polymer sample depends on the solubility of the gas or vapor in that polymer matrix.

And the diffusion coefficient of the gases or vapor through the polymer matrix. And permeability measures the rate of transfer of a gas or vapor per unit area and pressure difference across a flame thickness. So, for a given pressure difference across the thickness the permittivity is expressed as the rate of transfer of gas or vapor per unit area. Higher permeability of plastics to gases, vapor, water vapor and aroma compounds compared to glass and metal food containers.

So, instead of using a plastics container, if we use the glass container and metal food container then the permeability will be lower or the barrier property will be higher in general. So, plastics actually lose out or still some way to go to match the barrier performance of glass and metal food containers. So, still a challenge to be met and there are many approaches like addition of clay type materials which increases the barrier property. And we can increase the crystallinity to also increase the barrier property in polymer sample.

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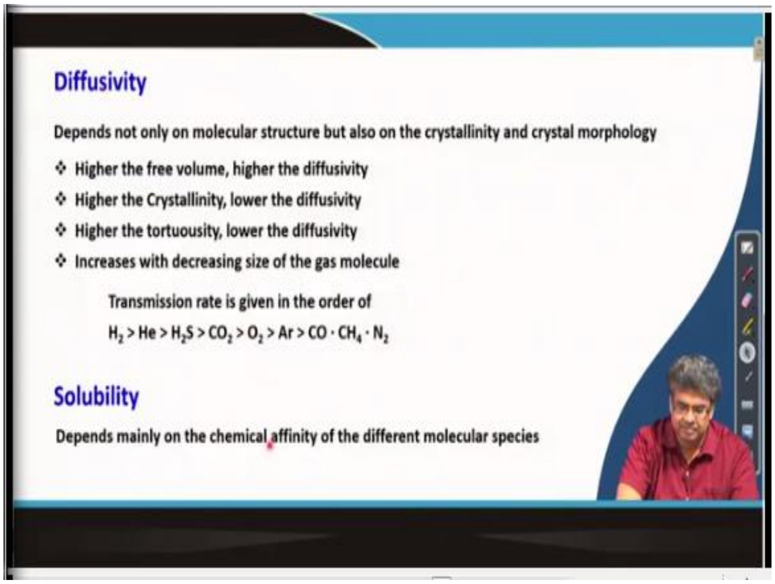

We talk about diffusivity, diffusivity depends not only on the molecular structure but also on the crystallinity and crystal morphology of the polymer sample. Higher the free volume of obviously the space is higher, so how higher will be the diffusivity. Higher is the crystallinity lower would be diffusivity as one can easily understand. And if the path, diffusion path is torturers, so if we add some clay materials in between.

Then the diffusion of the gases through the matrix will be tortuous, that means the gas molecule has to pass through way around those obstructions. So, that length of basically diffusion length will be much higher compared to a pure matrix where these obstructions or obstacles are not there, so if higher is tortuosity, lower would be the diffusion. Increase with the decreasing size of the gas molecule obviously these understandable.

If the size of the gas molecule decreases, then diffusivity will increase. For example, transmission rate is given when the this order as the size increases the diffusivity comes down. Solubility of the guests depends on the chemical affinity of different molecular species. As we have seen that, these 2 factors in combination determined the barrier property or permeability of the sample.

So, if you want to the polymer samples to be effective as a barrier property, we need to decrease the solubility and decrease the diffusivity of the gases through the polymer matrix.

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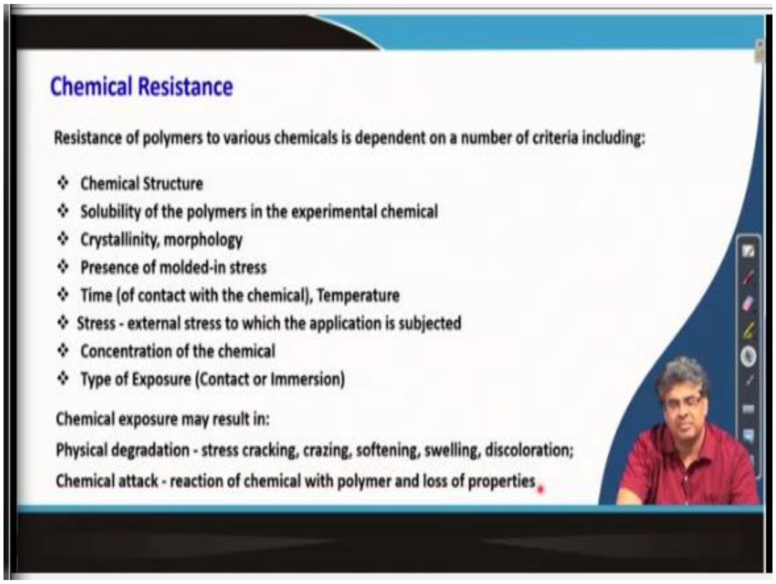

Next we will move to the next property chemical resistance. Now chemical resistance is a resistance of polymers to various chemicals. And which depends on a number of criteria which includes chemical structure. Solubility of the polymer in the experimental chemical obviously if the polymer is more soluble the chemical will have chance to degrade or interact with the polymer in a more than if it was not soluble.

Crystallinity, morphology, crystallinity will obviously prevent these chemicals to interact with polymer chains hence resistance will be higher. If they are molded in stress, that means during the molding process, if stress is built up and it is not released then those places which acts as a kind of a crack and when we apply a external chemicals, harsh chemical those stress will actually will basically facilitate the breakage of the polymer sample when it comes in contact with the harsh chemicals.

And time of course the higher is the time, higher will be the or lower will be the resistance and temperature if the temperature is higher lower will be the resistance. Stress obviously, if we apply more stress the condition be harsh then the resistance will also come down. Obviously the concentration of the chemical is higher, then the resistance of the polymer sample will be lower.

And types of exposure obviously if it is whether you are taking the sample and immersing in the chemical or you are just contacting that will also determine the exposure the chemical resistance of the sample. The chemical what it may cause on chemical exposure? It may result in physical degradation, for example stress cracking, crazing, softening, swelling, discoloration, these are the physical degradation in terms of loss of physical properties.

It can also degrade chemically, that means it can decrease or it can degrade the chemical nature of the polymer, decrease the molecular weight and react with the chemical. And as a result, it can decrease the properties, good properties of the polymer.

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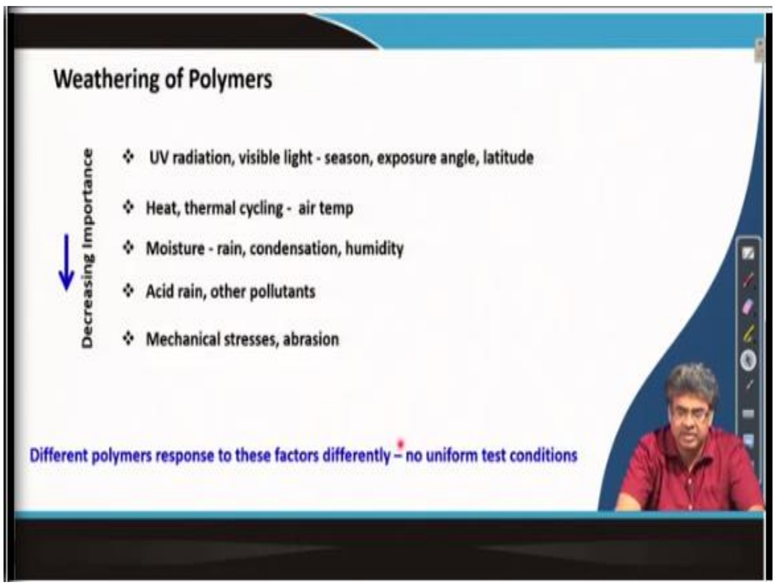

Next we will move to weathering of polymers and weathering means there are several polymers which are applied in applications which are outdoor applications. If you are talking about a stadium, football stadium covered with polymer seats or you know plenty of car dashboard there are many example we can give where the application of polymers are in outdoor application.

And which as a result the polymer sample will come in contact or come in exposure with several in harsh condition. For example UV irradiation, visible radiation and the extent of this radiation will of course depend upon which session the summer, autumn or winter and what angle of exposure and what latitude we are in which part of the world we are in that will. So, basically you know the plastic or the polymer will behave differently at different places or different sessions.

The other factor which causes weathering of polymers, weathering of polymer mean degradation of polymer properties. The heat and thermal cycling, air temperature these also cause the polymer samples to lose it is good property. And another important factor is moisture when we are using the polymers in outdoor application. Then the amount of moisture in the environment will also affect polymer properties and the amount of moisture is basically affected by the amount of rain or condensation or humidity in the medium.

The more humidity is bad for the polymer samples in the acts with the property gets degraded faster in a high humidity environment. Other factors like acid rain, pollutants they also actually degrade the polymer samples and as a result polymer good properties of polymers actually get destroyed. Sometimes mechanical stresses, abrasion also may cause damage to the polymers.

And the importances of these factors are in these directions, so decrease importance. For example the UV radiation is very highly important for outdoor application because of the high energy of the UV radiation they actually cause lot of damage and then heat and then moisture in this direction. And because this is very subjective evaluation and it depends on various factor, so weathering of polymers no uniform test condition is applicable.

And there are some indicative test conditions are suggested by different standard organization and those are followed in laboratory. So, with this I will stop this lecture and next lecture I will talk about the other property few other properties.