Introduction to Polymer Science
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Lecture-40

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

Welcome back. In this lecture, we will discuss about other polymer properties like optical properties, electrical properties, barrier properties, chemical resistance and weathering of polymers. We will briefly discuss about these properties.

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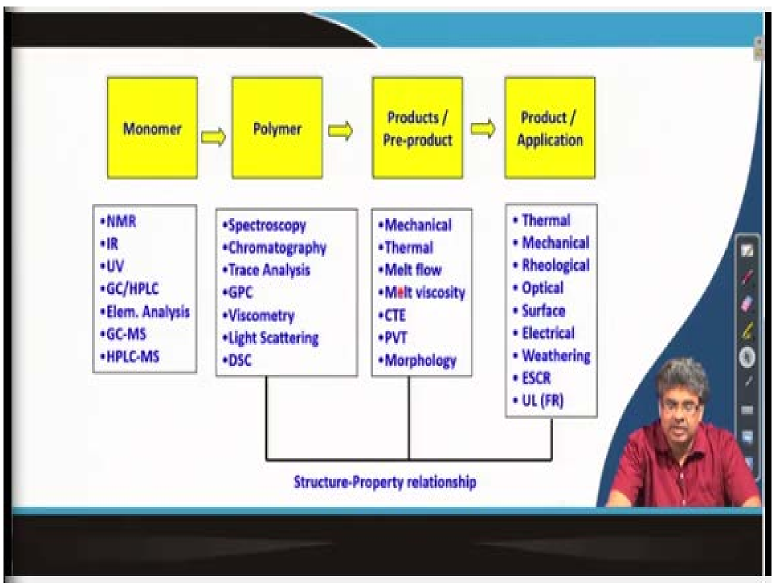

If we look at this chart, we have studied how to synthesize the polymers and then we have studied different techniques, which can be utilized to characterize the synthesized polymer. Then we discussed also different properties like mechanical properties, thermal properties, rheological properties, viscoelasticity. We did not discuss these properties in details because of lack of time. These are the properties of polymers which must be characterized before we think about any application and so these are inherent properties in a polymer sample. Once we have these 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 we discussed earlier.

We need to also characterize the sample fully in terms of their mechanical properties specially for the type of application it is meant to. We have discussed many mechanical properties but which of the 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.

Then we need to 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. These properties are related to the structure of polymer molecules, which are characterized by these techniques, as discussed earlier. These help us to understand the structure-property relationship between a polymer molecule and a product.

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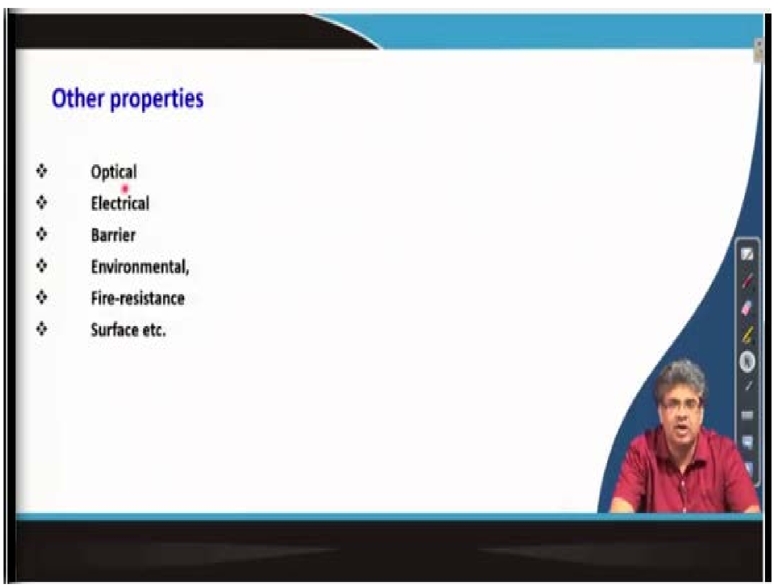

We will quickly discuss the other properties. We have already discussed mechanical, thermal, rheological properties in previous lectures. Now we will quickly go through these properties, let us begin with optical properties.

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Now an optical property is a very important property especially for the 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 appeals more than if it is a dark. There are other examples, like if we are using several applications 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 or different properties within optical properties like transmission as I discussed, refraction, reflection, scattering, absorption, clarity, haze, gloss, yellowish index, optical coefficient, birefringence, color. There are several things, depending on the application we need to characterize for the polymer sample.

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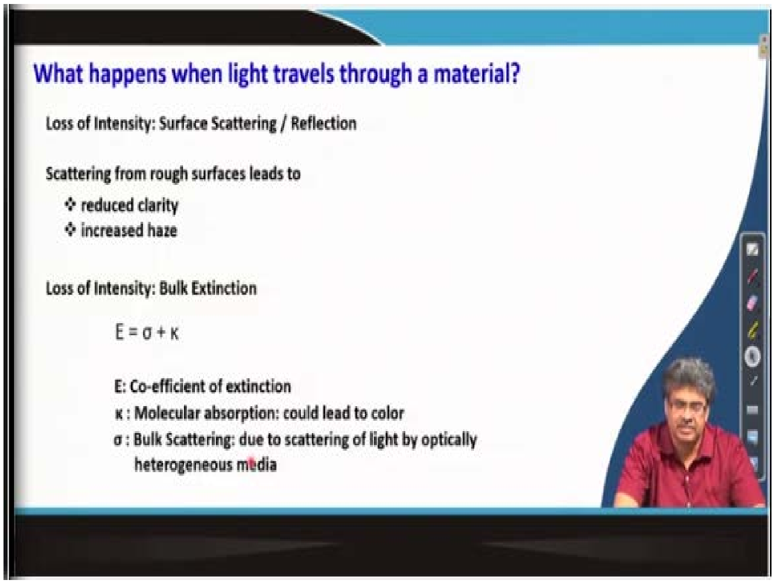

Now before we discuss the optical properties, we need to find out or we need to understand what happens when light travels through a material or when light interacts with materials. Invariably there will be loss of intensity due to surface scattering or reflection and due to the bulk scattering or extinction.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

Similarly, loss of intensity happens because of bulk extinction where 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. This scattering is due to optically inhomogeneous medium. If there are more than one component and if the refractive indices are different, then there will be bulk scattering. That will depend upon the difference in the refractive index and the size of the scatterer.

$$E = \sigma + k$$

Where, E is the coefficient of extinction, k is molecular absorption, σ is bulk scattering.

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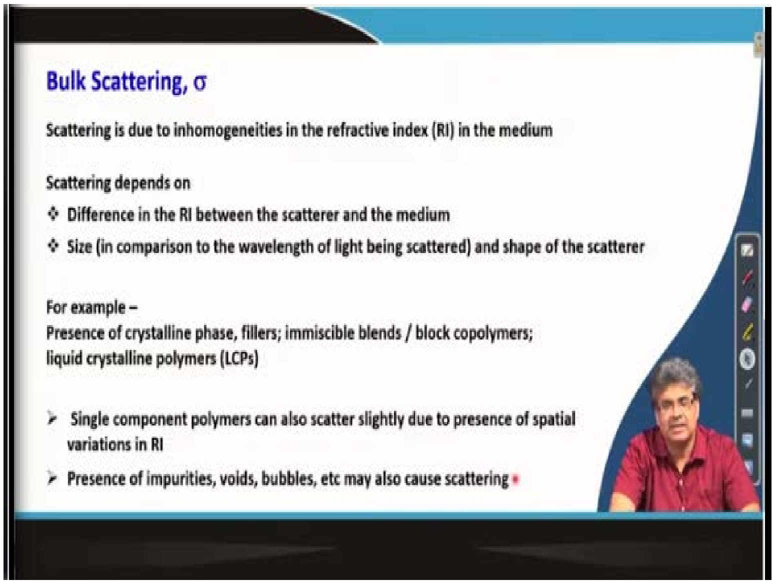

Let us talk about bulk scattering. Now bulk scattering is due to inhomogeneities in the refractive index of the medium. If the medium has more than one component and their refractive index values are different then the sample will actually scatter light. This scattering depends on the difference in the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

For example, presence of crystalline phase and fillers will scatter light. Similarly immiscible blend or block copolymers. If we have immiscible blends or immiscible block copolymers then there will be inhomogeneity in the medium. 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.

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

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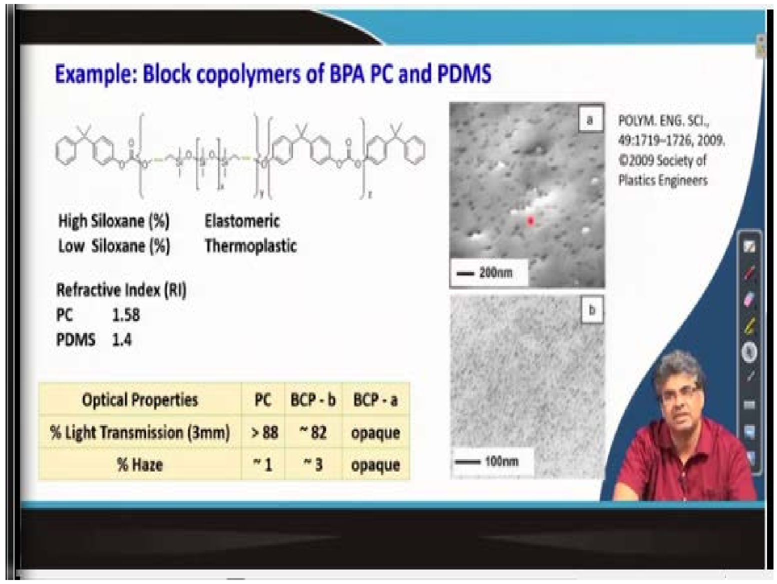

Take an example of block copolymer of bisphenol A and polydimethylsiloxane. So this is PDMS block and this is bisphenol A block. Now if the siloxane percentage is high then this is elastomeric polymer because the elastomeric component has much low T_g and the glassy component which has a much higher T_g compared to this polydimethylsiloxane. If it has low siloxane then it behaves like thermoplastics and if you have high siloxane the behavior of PDMS dominates, so it behaves like an elastomer. Now the refractive index of PC is 1.58 and PDMS is 1.4,. Thus there is a significant difference of R.I. between these two components. So, unless their domain sizes are extremely low, there will be scattering happening as these two are immiscible with each other.

If you compare two samples, where the base is polycarbonate matrix and these domains are polydimethylsiloxane, then you can see that the size of the polydimethylsiloxane domains are higher in one sample compared to the other sample where the size of PDMS domains is much lower. Also, you see the optical properties for a pure bisphenol A polycarbonate where these domains are not present. The light transmission for a 3 mm thick sample is greater than 88% and percentage haze is about 1%. For the block copolymer sample where the domain sizes are much lower compared to this, the transmission value is about 82%, haze is about 3%. 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 a result of that, the opacity or the percentage transmission depends on the difference in the refractive index between the two phases. If the difference is higher, then there will be higher scattering and if the domain size is higher then the scattering will be higher and as a result the haziness or opacity will go up.

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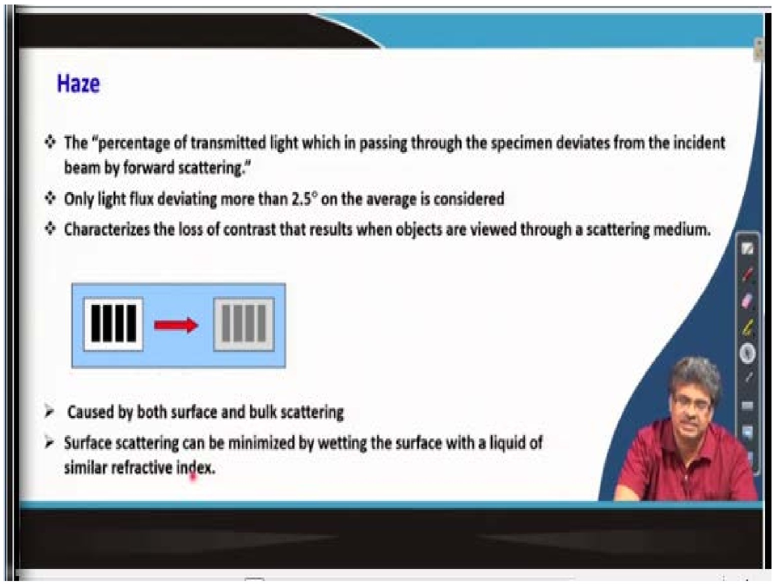

Now we talked about haze, what is haze? Haze is a percentage of transmitted light which while passing through the specimen deviates from the incident beam by forward scattering, where only light flux deviating more than 2.5° on an average is considered. It characterizes the loss of contrast when objects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

If you take a plastic material and view through it, the loss of contrast is related to the percentage of haze in the sample. Percentage is or haze is caused both by surface and bulk scattering, surface scattering can be minimized by wetting the surface which will basically minimize the roughness. 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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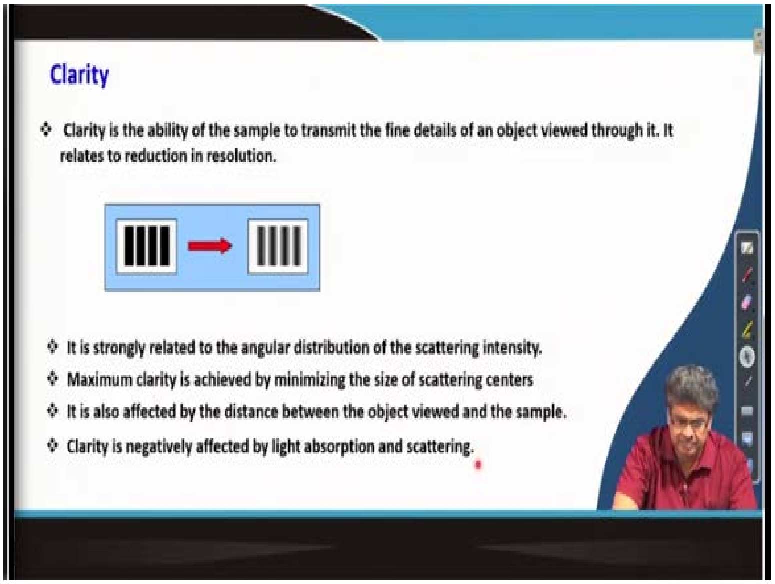

We often use the term clarity. What is the actual meaning of clarity? Clarity is the ability of a sample to transmit the fine details of an object viewed through it. If you are seeing through a polymer glass then it's ability to transmit the fine details of an object is related to the clarity of the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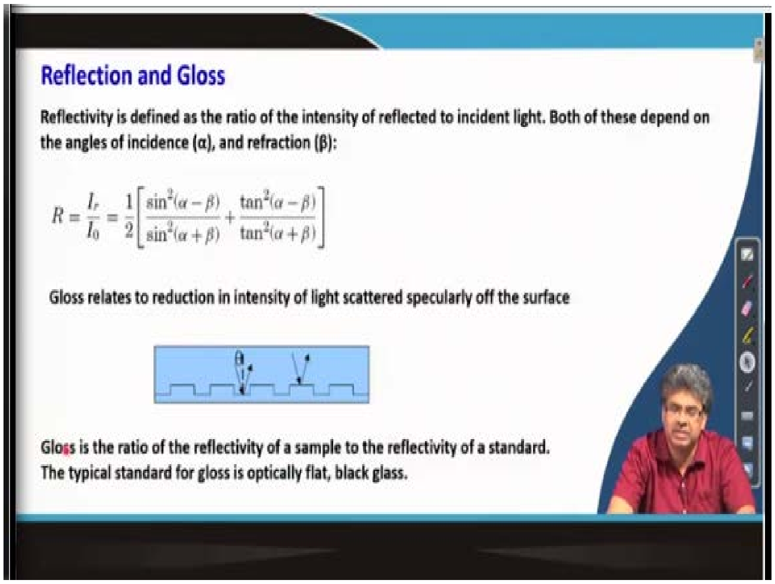

We will also talk about the terms reflection and gloss. Reflectivity is defined as the ratio of intensity of the reflected to the incident light. Both of these depend on the angle of incidence and refraction, α and β. This is related to the intensity of the reflected light, to the intensity of the incident light and this is given by this expression where angle of incidence is α and angle of refraction is β.

$$R = \frac{I_r}{I_0} = \frac{1}{2}\left[\frac{sin^2(\alpha-\beta)}{sin^2(\alpha+\beta)} + \frac{tan^2(\alpha-\beta)}{tan^2(\alpha+\beta)}\right]$$

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. 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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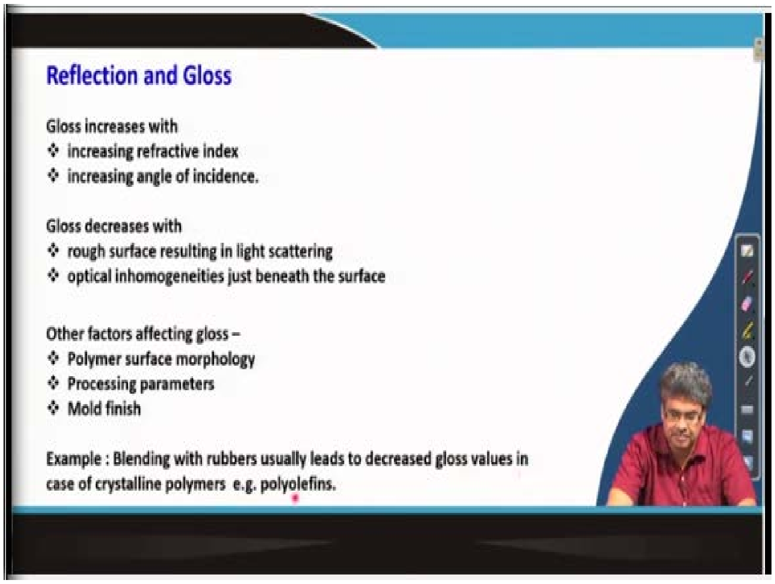

Gloss increases with increase in refractive index, increase in angle of incidence, and gloss decreases with rough surface resulting in light scattering, optical inhomogeneities just beneath the surface. Other factors which affect gloss are polymer surface morphology, processing parameters, mold finish.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

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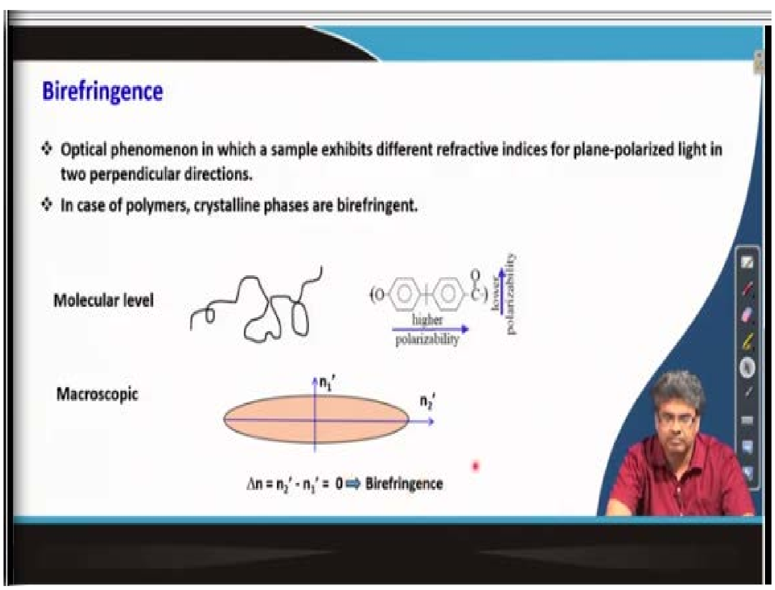

There is also another term related to optical properties, that is birefringence**.** This is related to the optical phenomena in which a sample exhibits different refractive index for plane polarized light in perpendicular directions. If we use two differently plane polarized light and if it shows different refractive indices for those two-plane polarized light, then we call the sample have birefringence and this happen if the polymer contains crystalline phases.

As crystalline phases are aligned in a particular direction, hence, 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 like Bisphenol A, then in this direction the polarizability is higher whereas in another transverse direction the polarizability is lower, so we have birefringence.

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

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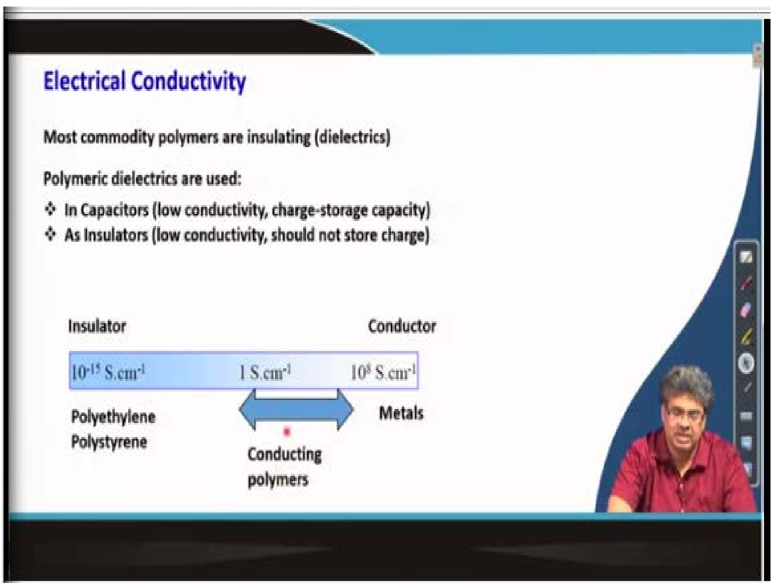

We will move to next to electrical property of polymers. Most common polymers or commodity polymers are insulating dielectric and this is very advantageous because polymers are used for many applications as electrical, electric insulators. As a result, polymer dielectrics are used in capacitors, low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

Typical values of polymers are like insulators, 10^{-15} S cm^{-1} whereas conductors, which are metals have very high conductivity values. About few decades back, conducting polymers were discovered and they have a conductivity value around this region and some examples of conducting polymers are shown here.

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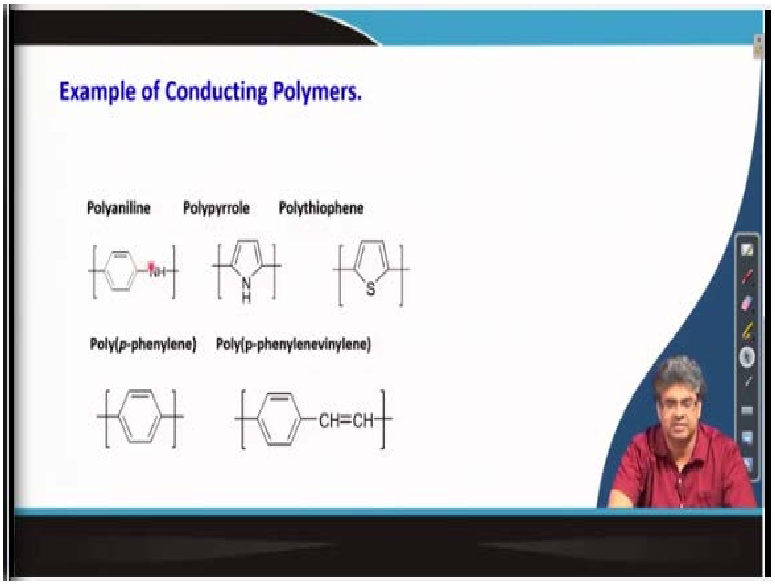

Like polyaniline, polypyrrole, polythiophenes. They actually do not conduct or behave like conducting polymers as such but when they are doped, e.g., if polyaniline is doped with proton or acidified then it shows conductivity because of the movement of electrons through the backbone due to possible resonating structures.

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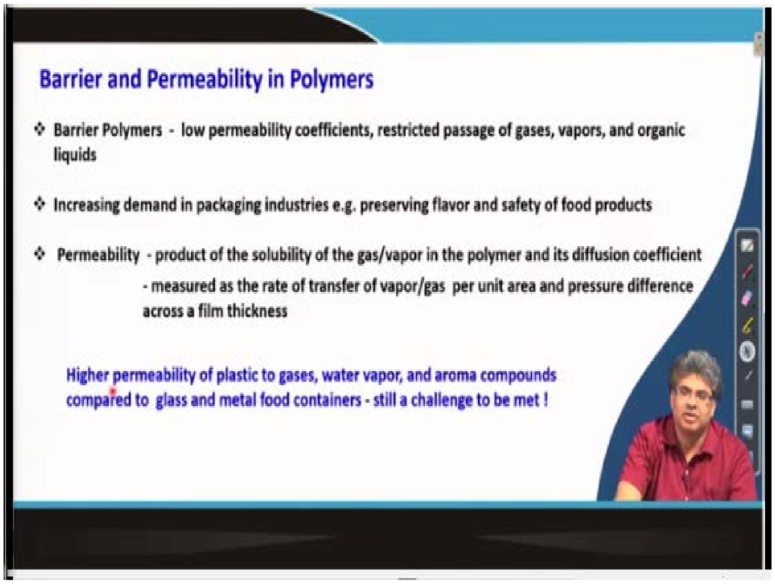

We will now discuss about barrier and permeability in polymers, this is also very important because in several cases, the container must have barrier property towards several gases. For example, if we are using a vial of a drug, then the storage time of that particular drug will depend on the vial's barrier property towards oxygen which may react with the drug molecules. 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.

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. Barrier properties implies having low permeability coefficient, restricted passage of gases, vapors and organic liquids. With increasing demand for packaging industries for preserving flavor, smell and safety of food products or even pharmaceutical products, this is very important now. 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. Permeability measures the rate of transfer of a gas or vapor per unit area and pressure difference across a film thickness. For a given pressure difference across the thickness, the permeability is expressed as the rate of transfer of gas or vapor per unit area. Due to higher permeability of plastics to gases, vapor, water vapor and aroma compounds compared to glass and metal food containers, so, instead of using a plastic 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 have a long way to go to match the barrier performance of glass and metal food containers. Still a challenge to be met, and there are many approaches like addition of clay type materials which increases the barrier property. We can increase the crystallinity to also increase the barrier property in polymer sample.

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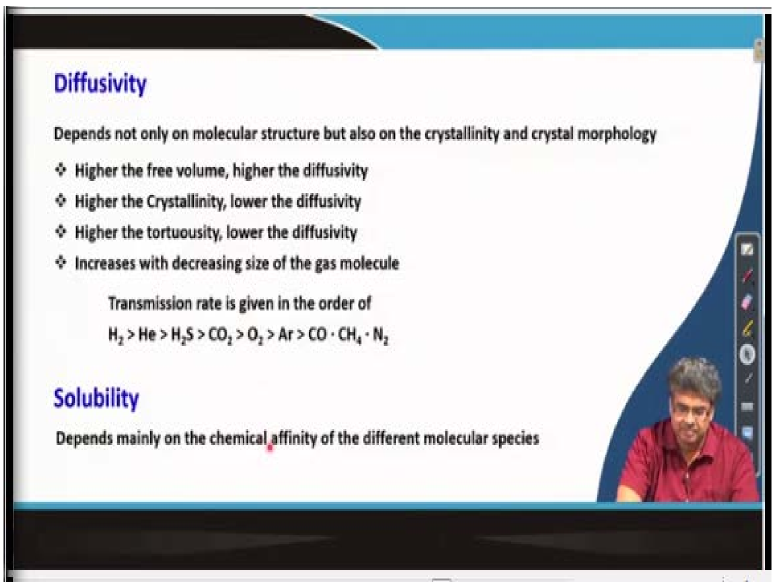

We talk about diffusivity. Diffusivity depends not only on the molecular structure but also on the crystallinity and crystal morphology of the polymer sample. Higher the free volume, higher the space, so higher will be the diffusivity. Higher is the crystallinity lower would be diffusivity as one can easily understand. If the diffusion path is torturous, so if we add some clay materials in between, then the diffusion of the gases through the matrix will be torturous, that means the gas molecule has to pass through way around those obstructions. So, the diffusion length will be much higher compared to a pure matrix where these obstructions or obstacles are not there. So higher is tortuosity, lower would be the diffusion.

Increase in diffusivity with decreasing size of the gas molecule is understandable. If the size of the gas molecule decreases, then diffusivity will increase. For example, transmission rate is given in this order, H_2> He> H_2S> CO_2> O_2> Ar> CO. CH_4. N_2. As the size increases the diffusivity comes down. Solubility of the gases depends on the chemical affinity of different molecular species. As we have seen that, these two factors in combination determine the barrier property or permeability of the sample.

So, if you want 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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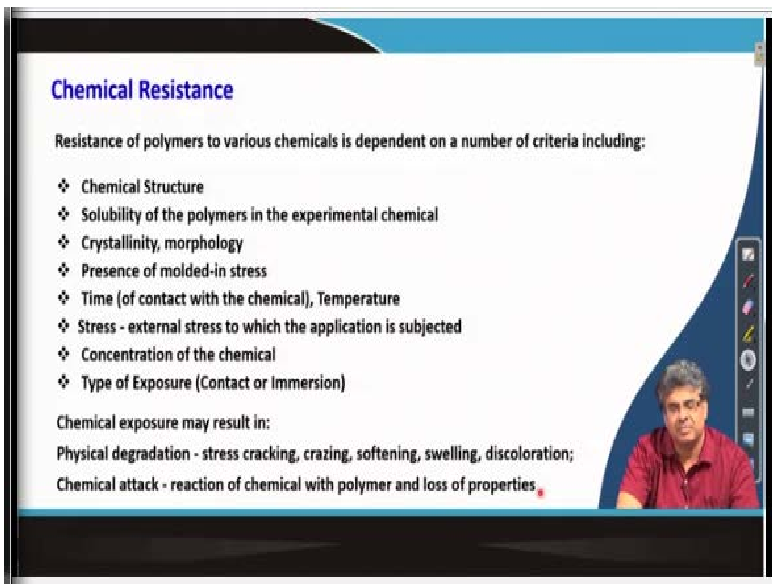

Next, we will move to the next property, chemical resistance. Chemical resistance is resistance of polymers to various chemicals, which depends on a number of criteria which includes chemical structure, solubility of the polymer in the experimental chemical. Obviously if the polymer is more soluble,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

Crystallinity will obviously prevent these chemicals to interact with the polymer chains, hence resistance will be higher. If there are molded in stress, that means during the molding process, if stress is built up and it is not released, then those places act as a kind of a crack and when we apply an external chemical, those stress will actually 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.

Types of exposure is also important. Whether you are taking the sample and immersing in the chemical or you are just contacting, that will also determine the chemical resistance of the sample. What actually happens 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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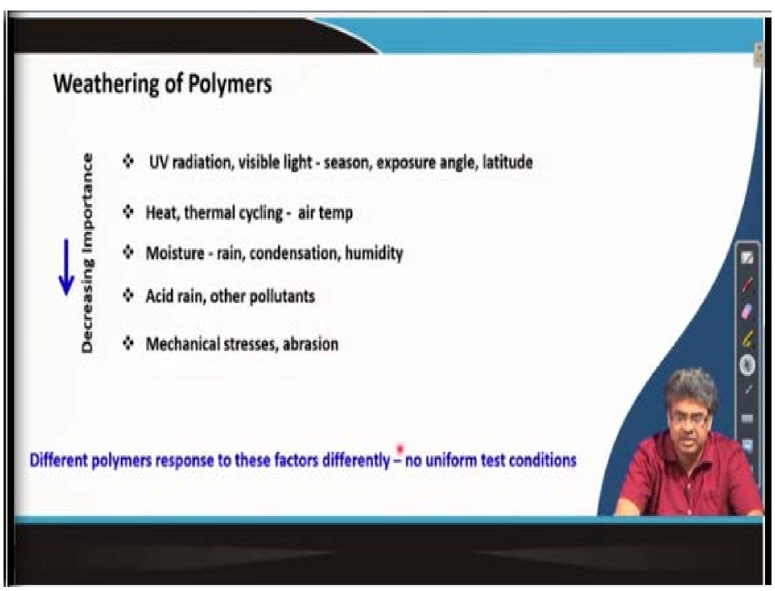

Next we will move to weathering of polymers and weathering means there are several polymers which are applied in outdoor applications. If you are talking about a stadium, say football stadium covered with polymer sheets, or car dashboard etc, the polymer samples will come in contact with several harsh conditions e.g. UV radiation or visible radiation. The extent of this radiation will of course depend upon season, summer, autumn or winter and what angle of exposure and what latitude we are in, which part of the world we are in etc. So, the plastic or the polymer will behave differently at different places or different sessions.

The other factors which causes weathering of polymers, i.e. degradation of polymer properties are heat and thermal cycling, air temperature etc that cause the polymer samples to lose it's good properties. 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 be affected by the amount of rain or condensation or humidity in the medium.

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

The UV radiation is highly important factor for outdoor application because of the high energy of the UV radiation actually cause lot of damage. Then comes heat, and moisture that are less vital. Since this is very subjective evaluation and it depends on various factors, so for weathering of polymers no uniform test condition is applicable.

There are some indicative test conditions are suggested by different standard organizations and those are followed in laboratory. So, we conclude this lecture and next lecture we will talk about few other properties.