Polymer Chemistry
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Lecture -39
Other Properties (Contd.)
And
Polymer Additives

Welcome back to this course on polymer chemistry. In last lecture, we were discussing about polymer properties and their evolution. And we did a detail discussion about mechanical properties, and we also discussed about thermal properties, and little bit of fire resistance properties of polymers.

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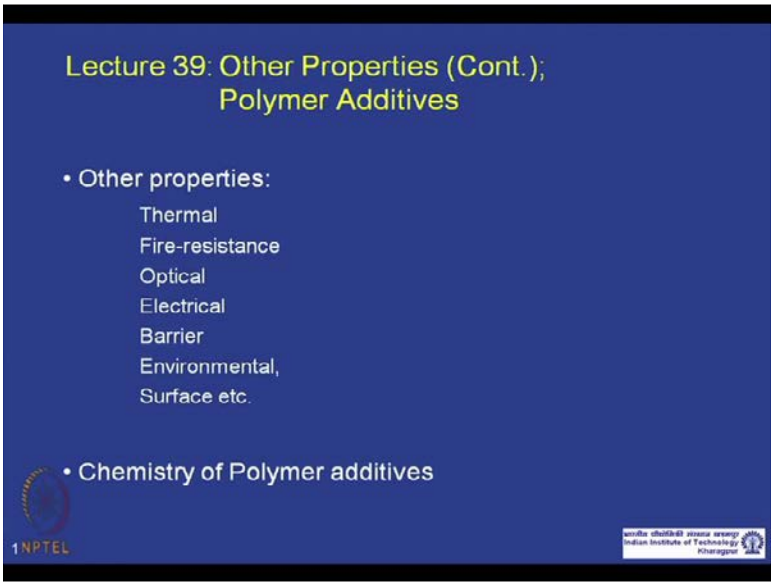

In today's class what we will do, is to go through the other properties, like optical properties, electrical properties, barrier properties, and environmental properties, surface properties. And not in detail just briefly, and then begin our discussion on chemistry of polymer additives.

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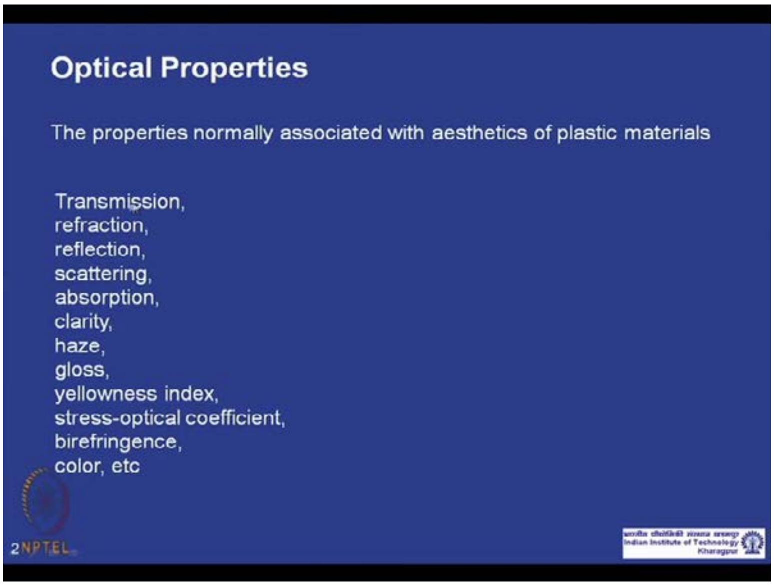

So, let us start our discussion on optical properties; now when you make a material out of the polymer, like plastic material. Now the look that sticks of the material, or the parts, depends upon several optical properties. For example, if we are going to make a plastic material or polymer material, which are intend to be a optically clear applications, then the plastic part or the polymer part has to be transparent. And if it is for absolutely clear application, then there should not be any haze or any yellowness in the material and so on.

And in opaque applications, there are other properties like gloss, reflectance, yellowness index and so many things, surface roughness. So those are the things, one must consider before for a, before you apply or before you have a polymer product out in the market. So, if we look at these optical properties of a plastic material, you can list a number of terms, transmission, refraction, reflection, scattering, absorption, clarity, haze, gloss, yellowness, index by premium color and so on. So, what I am going to do is, not to discuss each and every term, but pick up few important term, and then explain and then, see how the value of the particular property, or value of the particular parameter, depends on the chemical structures. For example, let us talk about transmission first.

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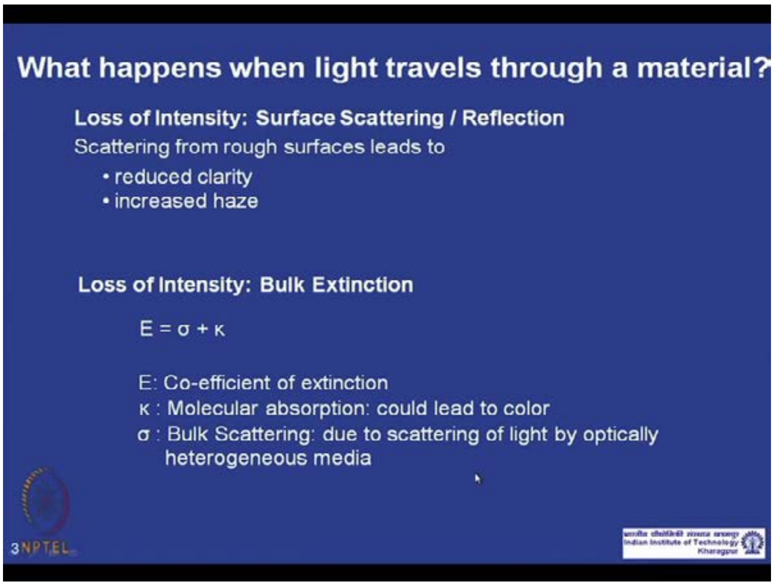

Now what happens when a light travels through a matter. If you are talking about the plastic material, obviously you are talking about a, you are thinking a plastic material or polymer material, when light travels through the, a polymeric material what happens? Obviously, first thing happened that it, when it just heat the polymer surface, or the part surface, it can get scattered from the surface of the polymer, if the surface is rough, and of course reflection, part of the light gets back to the original medium by reflection. So, basically when, a light travels through a material, in this case a plastic material or a polymer material.

First thing happen is, surface scattering or reflection, and because of that there will be loss of intensity, of the light passing through the main material, and scattering from rough surface, also will lead to reduction in the clarity of the material, and of course, increase in the haze. Now we will discuss, or define this term, clarity and haze in a minute. So, basically because of surface scattering and reflection your transmission comes down. In the bulk what happen, bulk they could be two thing happening; one is scattering can happen, and now because of scattering, there will be loss of intensity of light, and molecular absorption can happen, due to presence of some cromophrous, or some pigment in the material, which could lead to formation of color in the medium.

So, because of scattering and absorption, there will be loss of intensity. So, the bulk extension coefficient, is consist of bulk scattering, and molecular absorption. It may be noted that, this absorbed light can be reemitted, but that reemitted light is always less, or at best equal compared to the amount of absorbed light. So, there will be a drop in intensity, when light pass through the matter, due to surface scattering reflection, and bulk extension. Now let us discuss little about this bulk scattering phenomenon, which happens very frequently in a polymer material.

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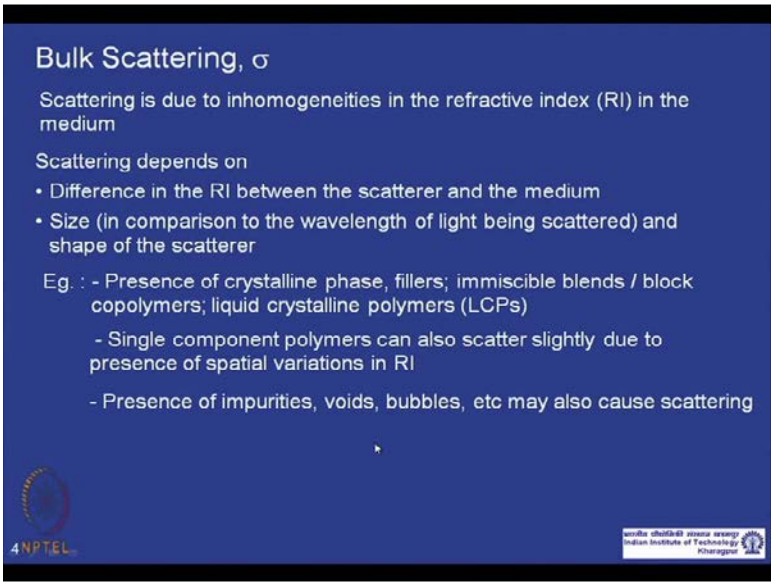

Now the scattering happen, due to in homogeneities in the refractive index in the medium. So, if there are in homogeneities present, in the polymeric material, there could be, or there will be, bulk scattering; for example, if you have some particles, so small particles which are, there are voids or some have bubbles are there, then in a homo polymer metrics. Then there will be a difference in the refractive index, within the media and those portions that just now I mentioned, there will be scattering, took to scattering to happen the two conditions has to meet; one they should be difference in I RI refractive index between the scatter and the medium.

Obviously, if there is a particle present in the medium, whose refractive indices is same as the polymer refractive index, then there will not be any scattering happening. So, first and foremost criteria for scattering to happen, is that there should be a mismatch, or in homogenates in, homogenates in the refractive index, between the scatterer and the medium. Second; obviously, the amount of scattering will depend upon, the size and the shape of the scatterer; the more the size, in comparison to the white plane length of the light being scattered, the higher would be the amount of scattering. For example, phases of crystalline phases, in a semi crystalline material, the amorphous in the crystalline phases will have a different refractive index, so that will cause scattering, and for this reason actually most of the crystalline polymers are opaque in nature, because of the heavy amount of light scattering. If you have fillers, which are having higher size, compare to, is not very small size, have a significant diameter, then their will scatter light. Immiscible blinds are block copolymers also have difference in, the refractive index between the, two phases form by the two homopolymers, or two blocks, they will also scatter. A liquid crystalline polymers, because they are different in homogenous in the refractive index, for a liquid polymer crystalline polymer, LCP'S. Now for a single component polymer; say for example, there is a homopolymer we were talking about, or a copolymer immiscible copolymer, they can also scatter slightly, due to presence in special variation of RI, due to presence of some stresses, moldered stresses, or reason vision, there could be some may be very small, but small in homogenates in the refractive indices value, across different places of the material, and therefore that reason there could be slightly, slight amount of refractive index. So, if you want to have, you want to make some polymeric material, which does not, or should not have any scattering, then your material must be very homogenous in respect to the refractive index value, across the inter medium. And as I said the presence of the impurities like voids, bubbles, etcetera may also cause scattering, obviously the refractive index values between, the material polymeric metrics, and the voids of the bubbles will be different, so depending on the size of these voids of bubbles, they will scatter a light.

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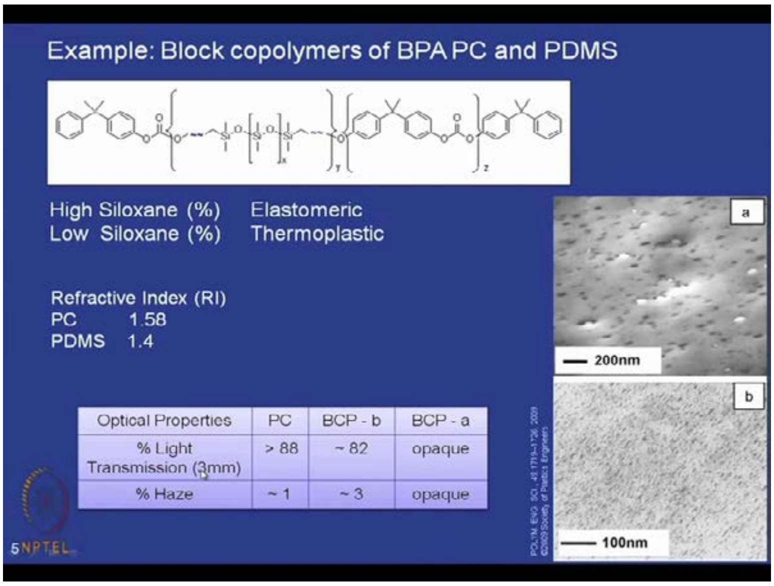

Just take a rear example of block copolymer, of BPA polycarbonate and PDMS. This is a structure of the block copolymer, where this block consist of a PDMS block, and a base phenyl polycarbonate block, depending upon, which is higher, this polymer may be a, as elastomeric or thermoplastic if, the amount of rubbery phase that is for PDMS is higher, high siloxane percentage, then this polymer BF block on a BF as elastomeric, and if the amount of siloxane is lower, than this block copolymer behave as thermoplastics. Now let us talk about low concentration of siloxane; say about 5 to 10 percentage, we are talking about thermoplastics. Now because these PDMS is stitched with the other block, then they do not face separate in such a way, that they come out or delaminate from the total matrix. So, they make this PDMS form small domains of PDMS, in the entire matrix, which is mostly BPA polycarbonate, we are talking the composition, where it is mostly BPA polycarbonate, and may be 5 percentage PDMS. Look at the refractive indices of this two, PC is 1.58, and PDMS is 1.4, so; obviously, there is a mismatching in refractive index, so they will scatter a light. And depending upon the amount of scatter, the transparency will come down, and higher the scattering, the transparency will be low less. Look at the transmittance T m, or transmission electron micrographs, these black portions are the siloxane domains, and the background is the BPA PC. Now in this case, this a, the block length of PDMS is higher, as a result this domains sizes are higher. So, it scatters more, and the transparency is transparency is very less, in fact, this is opaque. Whereas when the block length is small, then they also scatter, but the size, because of the size is so small their scattering amount is low, so this block copolymer, the polymer material made out of this block copolymer will look, transparent, but slightly hazy. So, if you look at the optical properties of the polycarbonate, light transmission is more than 88 percent for this 300 thickness pluck, and haze is about one percent whereas, in block copolymers b, where the domains are having smaller sizes, that is all that the scatterer size is very small. There transparency has come down, because of scattering, but not that much, haze has gone up. Whereas when there are scatterer size is much higher, then the polymer is become completely opaque. So, basically what I again telling that, the scattering amount of scattering, depends upon the refractive this mismatch. If there is, you can make a block copolymer or a two phase system, where the two phases same refractive index, no matter what is the size of the scatterer, it will not scatter, but if there is difference in refractive index, the higher is the size of the scatterer, it will scatter more, and it may turn opaque whereas, if the scatterer size small, it will scatter less. So, there will be drop in transparency, but it will not, may not be opaque. Now let us talk about, little bit about, the transparency of a polymeric matrices.

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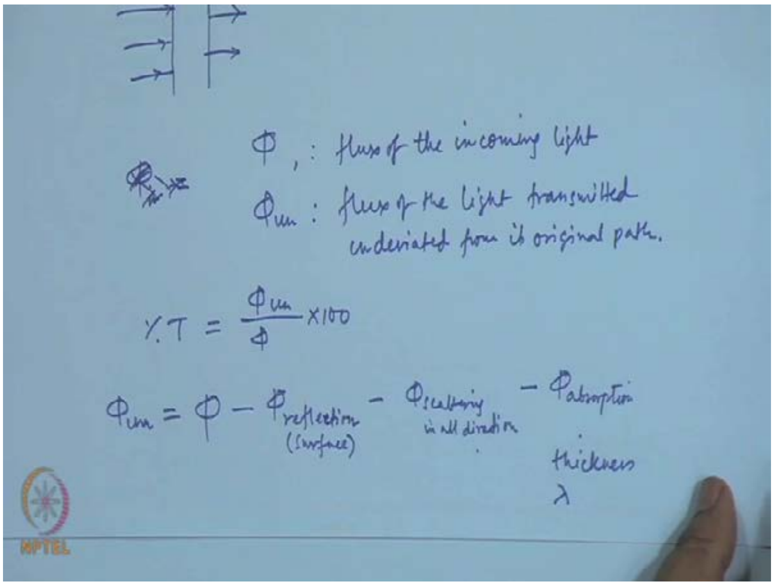

Now we just learn that, when light falls; say in a plastic material, or any material, there could be three possible phenomena happen; one is, the scattering are reflection from surface, second is, the scattering bulk scattering, and the third is your absorption. So, the total flux, of the light coming in. Let us terribly part of light, which will gets transmitted. Now if I consider phi, as the intensity of the, or flask of the incoming light, and. So, this is the flask of the incoming light, and if I consider phi u n, is the flux of light, transmitted and deviated, from its original path. Then percentage of transparency, is given by the fraction of light, transmitted, and deviated, through the metrics. Now we can also write, that the light, the flux of the transmitted light, which went out and deviated, would be phi, is the flask of the incoming light minus, the phi d 2 reflection, from surface, minus phi scattering in all direction. We discussed about, what is the cost for scattering, and phi absorption. If there are some mities or some (()) which absorb light, then it will absorb light, and it will decrease the intensity of the, out flask of the outgoing transmitted light, this might give you color in the medium. Now, this depend, these two depends on the thickness of your material, and also lambda, the wavelength of the light, which are used. So, obviously, this valued percentage, and hence the percentage transmition, we will also depend upon the thickness, and the lambda of the, or the wavelength of the light used. Now, if we have no scattering, or no scatter present in the medium, in the polymer material, and also there is no nothing which is absorbing. Then obviously, this transparency is, only given by the loss due to the reflection. So, if you can find out theoretically, what will be the extent of reflection, then we can find out, what will be maximum transparency, of any material or a plastic material, and that is theoretically given by fractional equation.

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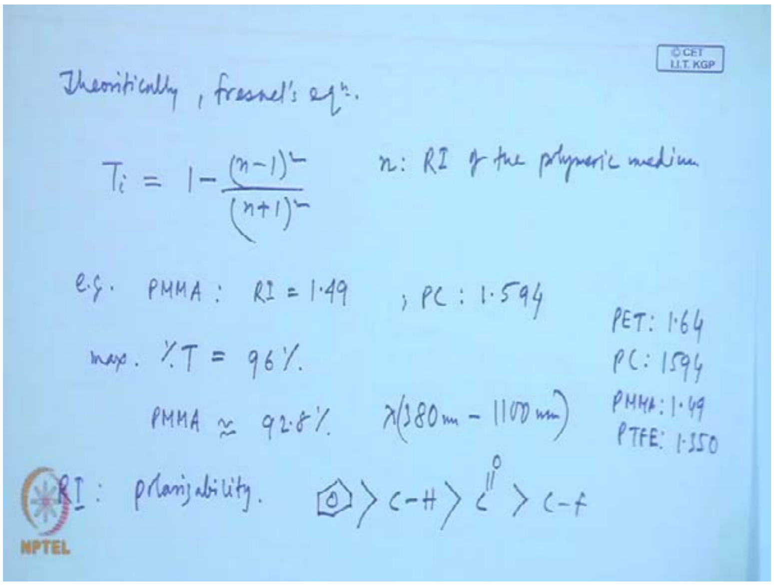

So, theoretically from fractional equation; the maximum transparence is given by this, where n is the refractive index of the polymeric media. So, obviously, if we talk about say for example, take a case of PMMA poly methane methylculate, which as RI 1.49, then percentage T maximum. So, the maximum percentage T of a PMMA, if you put this value here, it will come around 96 percent. So, this is the maximum transparence you can get, out of a PMMA material. So, higher is the refractive index, lower is the maximum transparency, one can get, when a light pass through a polymeric material, but you one can never get this high amount of transparence through a polymeric material, because there will be some in homogeneity in the refractive index the medium, even this for a homo polymer, and that will cause some amount of loss of flask of, the incoming light or transmitted light, due to scattering. So, maximum transparence for PMMA in real case, we get about 92.8 percents. So, that 3 percent transparence is lost due to, presence of scatterer, and this value is for lambda around 380 diameters to 110 meter; say lambda changes, beyond that this value, might change. So, what do you learn from here that, less then, if there is no scatterer present, or no nothing is present which is or observing light, in the polymer metric then, the transparences dictated, mainly by the value of the reflect index. So, if you compare, shall I PMMA with a BP PC, which have a reflective index 1.594, then obviously the maximum transparence possible, for PMMA is higher than a (()). So, if you want make a transparent, or you want to increase correspondent poly metric material, then you should look for a polymer, which has have lower reflective. Now in this, what is reflective means, it relates to the polarisability of the molecules present, polarisability of the molecules present, and that the order of polarisability depends upon, normally size of the group present, so polarisability of different groups will be of like this. So, the values of reflective index, if it is right, then say PET (()), we will have a value of 1.64, PC equal 1.594 PMMA 1.49, and say PTFE (()) will have even lower reflective index. So, if the polarisability is less, the refractive index will be also lower. If you want to make a transparent polymer, then; obviously, for a given thickness, and for given wavelength, it’s always preferable to use a polymer, having lower refractive index, then a polymer with having a higher effective index.

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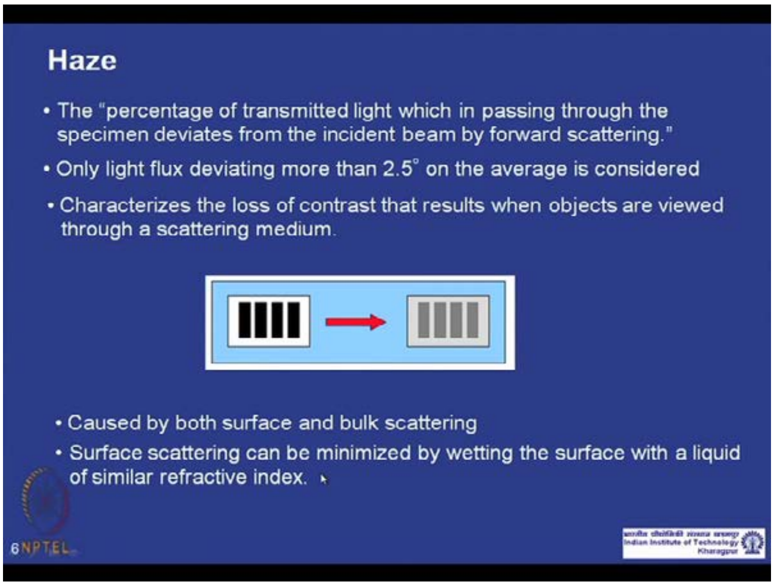

So, just discuss about the transmission and talk about Haze. Haze is defined as a percentage of the transmission light, which is passing through the specimen, deviates from the incident beam, by forward scattering. So, obviously if there is something present in the medium polymeric material which is scattering, and it typically scatter in all the direction, then amount of forwards scattering, the amount of lights which is scattered, is, and which deviates from the incident beam, by forward scattering is, what is Haze. Now, for calculating are defining Haze, we will only considered forward scattered light flask, which deviates more than 2.5 degree, on average than the incident light beam. So, original. So, with the lights, the forward scattered lights, which is scattered beyond 2.5 degree, compare to the incident light, would be taken as the value for Haze, and Haze characterized the loss of contrast, that result when object are viewed through the scattering medium. So, for example if this is a loss of Haze, because of Haze, lose of contrast, so if you are using two plastic material to view this two, then; obviously, there will loss of contrast. If you are looking through a Hazy material. .Now Hazy is cost by both surface scattering, and balls scattering, and you can remove if you want to know what is the contribution from surface and balls scattering, in the Haze, then what can be done. You can actually deep that plastic material, in a liquid or similar refractive index. Now in that case, that will minimize the surface scattering, because the surface is now smooth, because they are dipped in liquid. So, the Haze is mainly because of the balls scattering. So, from that value you can exchange, distinguish between, or find out what is the contribution from the surface scattering, and balls scattering on the Haze value.

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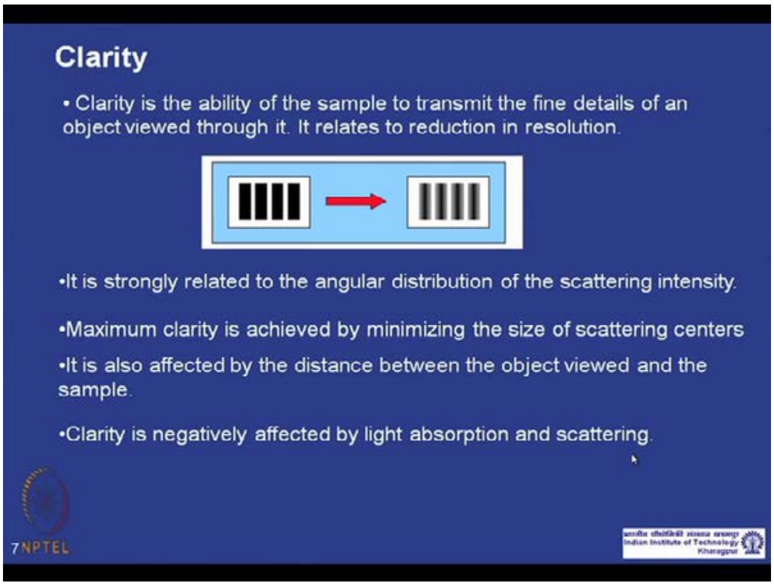

What is clarity, clarity of ability of the sample, to transmit the find details of, the object view through of. It's basically, is a resolution, how good resolution, you can get, when you going through a plastic material, so if the clarity is less, then the material or the resolution will come down. So, a material if it look at through material, which has lower clarity, then you will low resolution of the object will come down. It is tongue relatives to the angular the distribution of the scattering light, as scattering intensity, and if the size of scatter is large, the angular distribution of scattering intensity will be higher, so it is always prefer to minimize the size of the scattering center, to get maximum value of the clarity. And obviously, depends on the distance between the object viewed and the sample, and there is, if there is light absorption in scattering visibly, clarity will be lost.

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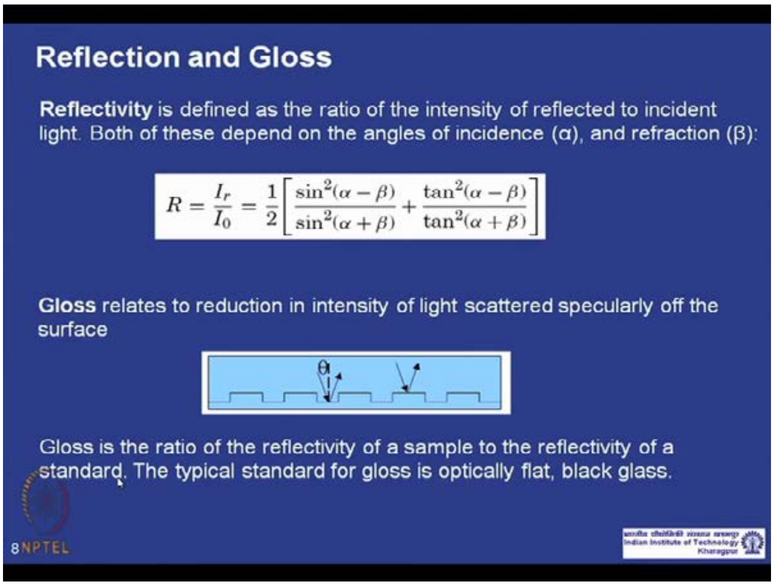

Next terms we be discussion about reflection and gloss; reflect reflectivity is defined as the ratio of the intensity of reflected light, to the incident light. So, the more amount of incident reflected light. More reflection means the reflective will be higher, and that depends upon angle of incident of the light, and angle of refraction, which in turn depend on the refracting index of the medium. So, in this case also if you, your refracting index of the material, or polymer is higher then, the reflects reflectivity is also higher. And if your angle of incident is higher, the reflectivity is higher, and this reflectivity is given by this expression, where alpha is your angle of incident, and beta is your angle of refraction. Gloss relates to the reduction of intensity of lights scatters specularly of the surface. Specularly means the angle of incident is same as, angle of refraction like a perfect mirror. If the a surface is not smooth; say it has rough, then the lights which are getting reflected specularly, from different region, they will have different distance to travel to the observer. So, they will be a phase difference and as a result they will be decreased in the intensity. So, if the sample is half, then the amount of, or intensity of the light, which is specularly reflected will be lower, and there will be reduction in the value of gloss. So, it is better if you want to make a glossy surface, then the surface should be smooth. And also if your, the sample is having a larger refractive index then, as a result of higher reflection value, your gloss will be also higher, how do you measure gloss. Gloss is measured, are related to the intensity. It basically measured as a ratio of reflectivity of it's, of a sample, to the reflectivity of a standard, and typically the standard is taken as a optically flat black glass, for a particular incident angle. So, basically this is considered a perfectly reflecting material. Then the reflectivity compare to this, for a material would be given by, will give the value of gloss.

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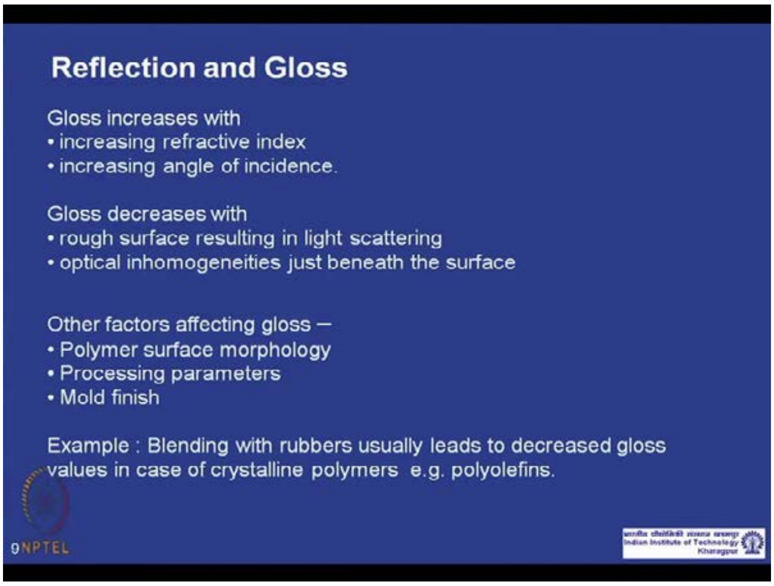

So, gloss will increase with the increasing refractive index, as I discussed that increasing refractive index, the amount of reflective light is higher, so obviously, gloss increases. Has increases with the angle of incidence, gloss decreases with the roughness; obviously, the reason that I said that the distance, travel from the surface to the observer, would different from different region, as a result they will phase difference, and intensity will come down. And if there a optical homogeneities just beneath the surface; obviously, the amount of light scattered, reflected will be different, and the gloss will come down. Other factors like polymer surface, morphology, processing parameter mold finish, which would give us the smoothness of, which basically dictates the smoothness of the molded parts, so they also affect the value of gloss. For example, blending with rubbers usually leads to decreased gloss values, in case of crystalline polymers like polyolefin.

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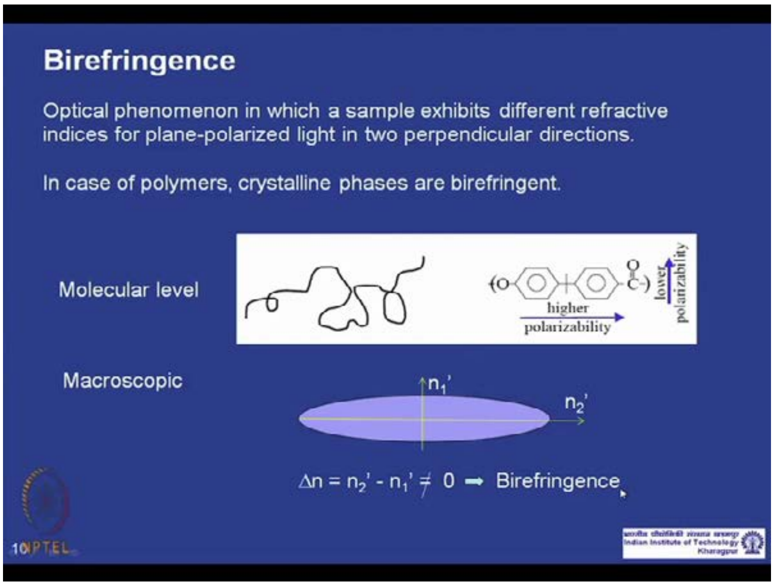

So, you know gla we now discussed, we know the, what is haze clarity reflection, and gloss. One more time we want to discuss in optical properties; birefringence. Birefringence is basically, optical phenomena, which a sample exhibit different refractive indices, for differently plane-polarized light. So, refractive index value for two perpendicularly polarized light, we will have different value. So, crystalline polymers, they have different refractive index, in particular perpendicular directions, so they will have different values, they will be birefringent. In terms of molecular level, the polariziability in one direction, and the perpendicular direction; say for example, one very higher aromatic polycarbonate, where they are different, so their molecularly birefringent, but we do not measure the molecular birefringent, we measure the microscophic birefringent for example, and that is given by the difference in the refractive index, in the two different direction. So, if this not zero, then we consider the sample is birefringence, and for very optically useful material, it is commonly that, the birefringence should be lower.

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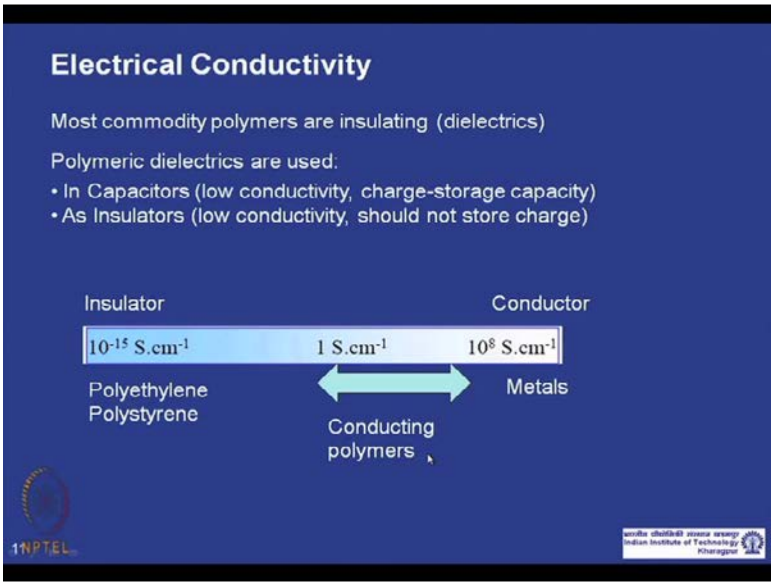

Just if we talked about the electrical properties of polymers, and we just talked about electrical conductivity, and we know that most polymers are insulating, and so they are dielectric. And polymeric dielectric used in capacitors, and as a insulators, so basically this are the two main use of polymers, in polymers, in electrical samples. And the value of electrical conductivity, you have the normal poly polymers; like polyethylene polystyrene, they have values of electrical conductivity just like insulator. Whereas, the other end, extreme other end; the metals the metals which are having much higher conductivity, and they are perfect conductor. In between there are few polymers, which highly conjugative polymers, they have conductivity in the range of semi conductor, and they are called conducting polymers, and they basically not the commodity, or they are not produced in large amount. They very they produced in small volumes, and we are not going to discuss much about conducting polymers.

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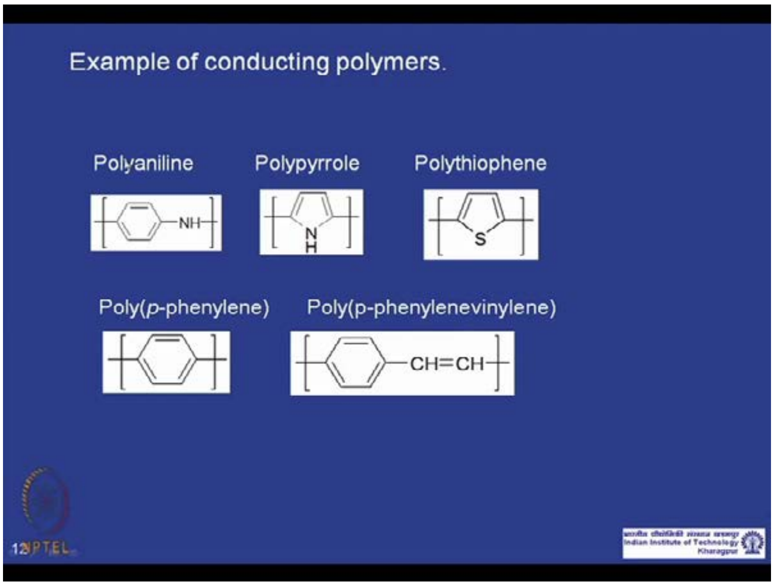

The only thing what I want mention, is the examples of few conducting polymers like; polyanile, ploypyrrole and structures are given here.

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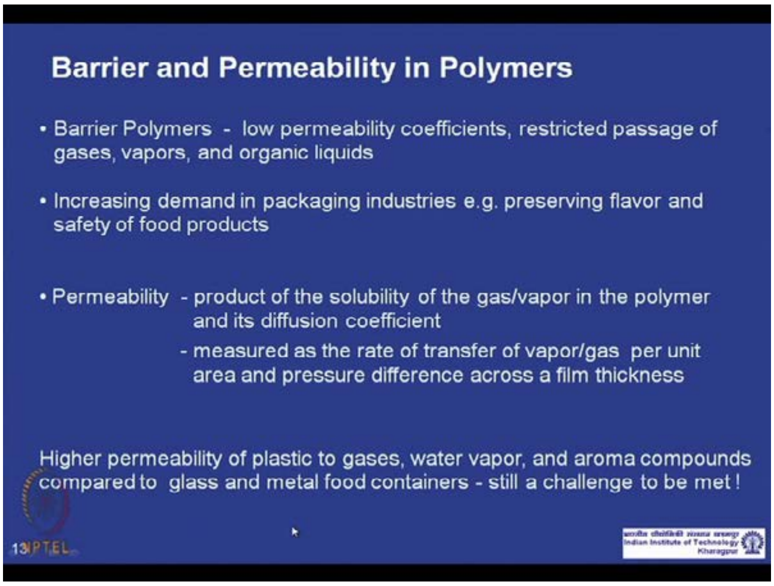

Next, we want to discuss little bit in brief, the barrier and permeability of the polymers. Now think about, that you making packing material out of polymers; for example, if you taking perfume bottle. Then if you want that, the perfume to be remains in the bottle for as long as possible. So, you want the polymer material to be behave as barrier to that perfume whatever is there inside. For example, polymer self, heavy used as a packing material for foods, and mainly. They are so many other applications, and for that it must have some properties, and foods especially, they has to be flexible, they mostly has to be transparent, and they also have a specific barrier properties. So, barriers polymers are having low permeability co efficient, and restricted passages of gases, vapors, and organic liquids. And if the polymers in barriers applications like, packaging industries, the demand going day by day, for preserving flavor, safety of food products. The permeability is opposite to the barrier, basically more permeable means less barrier, or more barrier means less permeability. The permeability is define has the product of, solvability of a gas or vapor, in the polymer matrix, and its diffusion co-efficient. So, basically permeability is given by, two factor; the solvability of the gas or vapor in the polymer, and the diffusion co-efficient of the gas in concern, and it is measured, as the permeability is measured, as the rate of transfer of the vapor or the gas per unit area of the material, and per unit measured difference across the flame thickness. So, basically it is normalized, with the area, as well as the pressure difference across the flame thickness. However, plastics are still not as good as barrier materials like, glass and metals. So, there is still necessity of making plastics, materials which can be as effective as like glass and metal, for barrier applications.

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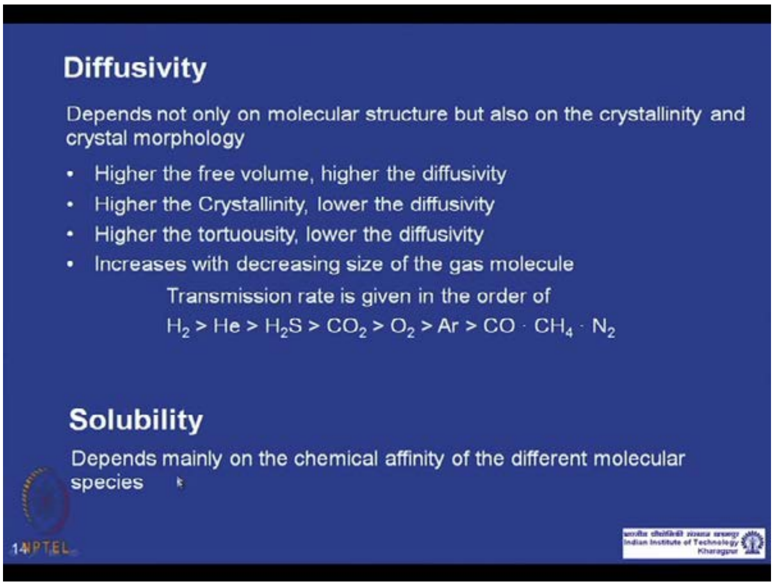

So, we just said that the barrier, or the permeability properties of polymers depends upon the, diffusivity of the gas concerned, and of course, the solvability of that gas in the particular polymer. Now the diffusivity of the gas depends upon chemical structures, so it does not. Only dependent upon the molecular structure, but also in the crystallity and crystal morphology. In a semi crystalline polymer, crystalline region are highly densed region, and basically it acts as very high barrier, to any diffusion through it. So, basically higher the crystality, higher is the barrier property for that polymer. And in fact, if you increase density of the polymer matrix, the barrier properties goes up. So, if the free volume is higher, which means they are the region, the free regions where the gas can diffused through, which means the diffusivity will be higher. As we discussed the higher the crystality, crystalline regions are inpermeable; hence lower is the diffusivity. Higher is tortousity, lower the diffusion. Tortousity means, is the path, one has to travel to cross that thickness. So, if I consider one example.

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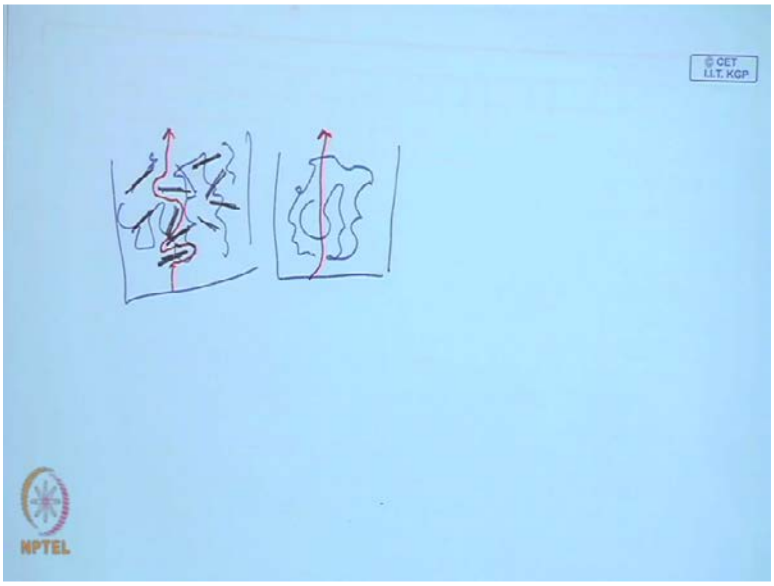

Now if I have a polymer metrics, and they are. So this is, for example, compare a polymer matrix, just plan polymer matrix, and a polymer matrix, with all this. These are; say for example, clays. These are clays, which are exfoliated in the matrix. Then, if a gas has to pass through this medium, then it has to take longer path, like this, compare to a path where, you do not have this clay materials. So this means this is a tortures path, and higher is this tortures path, the higher is the barrier, to the gas to pass through. And if diffusivity increases, with the decrease in the size of the gas molecules. Obviously, for well known reason, so transmission is follows, for everything is same. Given everything is other is same, transmission rate will go up for a smaller size gas, compare to a higher size gas. Second parameter, which is responsible for permeability is the solubility, and solubility of a gas in a polymer depend upon, the chemically affinity between gas, and the polymer we are talking about; that depends upon the solubility parameter of the gas, and the polymer metals, we discussed earlier, when we discussed the polymer solutions, we talked about the solubility parameter. So, basically the higher the solubility, it is higher is the permeability of the polymer matrix towards that gas.

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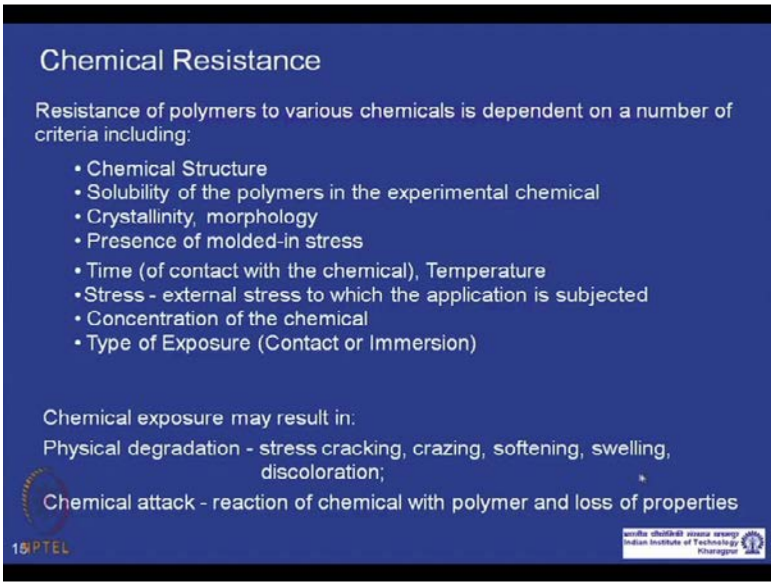

We also briefly talk about chemically resistance, chemical resistance is basically a property, where a polymer is being in contact with certain chemicals, and after a given exposure, time the property of the retention is measured. So, if you talk about mechanical property, then after the exposure, the mechanical property like, impact tension strength, there is a compact or the ductility. Those are compact with the value which was, before the exposure to the chemicals. And if there is less detoriation in the values of those property, then the polymer will be resistant to chemical, so this is as simply. You can talk about mechanical properties, or optical properties, like glass Haze, with in contact of the chemicals of the optical properties might change as well. And the resistance of the polymer, to varies chemicals depend on number of criteria’s. Obviously, it depends on the chemical structures; for example, if hydrolysable groups. If you bring contact, if you bring that polymer in contact with acids, or basis, then it will hydrolysis, and as the molecular degradation will happen, the properties will come down. Similarly it should not react with the chemical you are bringing in contact with. Solubility of the polymers with the experimental chemical; obviously, to be resistant, the polymer must be soluble, in the experimental chemical, and that depends on the crystallinity and the morphology. The higher is the crystallinity, normally the resistance to the chemical is higher. So, crystalline polymers are much more chemically resistant then, amorphous polymers. If you are modeled in stress; like while modeling, because of some other reason, because not good flow in the material you have a, built in some stress. Then obviously, in any given opportunity, the polymer will try to release that stress, and one opportunity of its come contact with the chemical, it might release that stress, by cracking or crazing and so on. So, modeled in stress is basically bad, for a polymer to be resistant, to a chemical. While testing the several test parameter must be consider, for comparing the chemical resistance, or resistance of different polymer for example, time, of the contact with chemical temperature, at which you are doing the experiment, the stress level. What is the external stress you are applying during the experiment, concentration of the chemicals which are using, type of exposure, whether you are just contacting, or emerging in that particular chemical. So, this all parameter has to be standardized, if you want to compare between, the chemical resistances of different polymers for particular chemical. If you want to make bottle, plastic bottle for a perfume, or say something else like, alcohol, then obviously, that plastic material has to be resistant to that of alcohol, to be survived for long time. So, these are the typical application, where we test for chemical resistance. Chemical resistance; obviously, chemical exposure may result in physical degradation, stress cracking, craze, swelling, discoloration, so many things can happen. And obviously, it can do chemical attack, and bring down the molecular weight. And if you decrease the molecular weight; obviously, there will loss of, lot properties including mechanical properties, thermal properties and so on.

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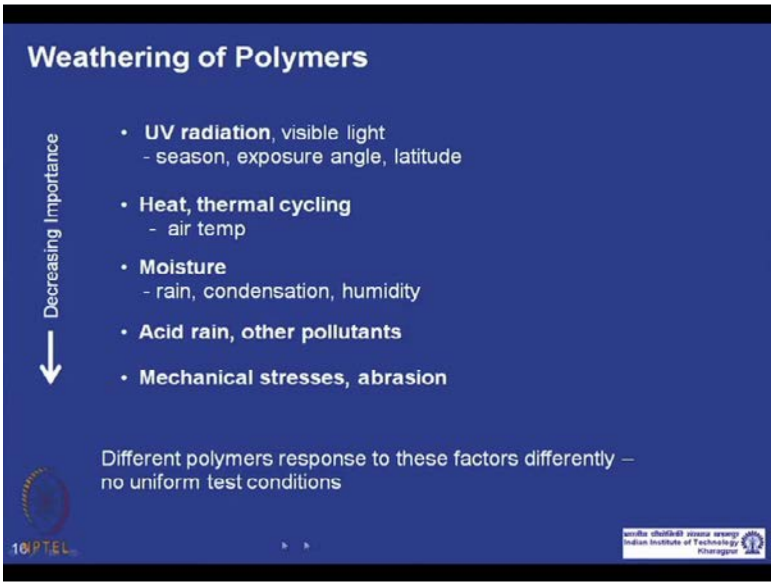

Just briefly discussed the weathering of polymer, with lot polymer are used in outdoor applications. So, for, to understand how long they will survive in that condition, outdoor condition, you must whether ability, or mechanism which a polymer gets weathered. So whether ability is basically noting, but the retention of property, of a particular polymer after it has gone through, or it has stayed outdoor, whether for some amount of time. So, the higher whether ability means, it has, it will retain, the polymer retained the properties for a longer period of time, in that given weather condition. What are the condition in weather which affect the polymer properties, is UV radiation in most extend, and that will depend upon, which session you are winter summer, what is the exposure angle, latitude, which latitude you are polymer exposed; heat cycles, so that will depend upon what temperatures, what is your air temperature and so on. The moisture content in the environment, and that will depend upon rain, condensation, humidity. It is also depend upon acid rain, other polythene. So all these things contribute to the weathering of the polymers, to different extent; for example, the UV radiation is the most important parameter for, responsible for weathering of polymer, so they decreasing importance is, this way. So, if you want to compare whether ability of different polymer, you must have a standard conditions, which is very difficult reproduce, and you must compare a conditions, depending upon, or looking at the final application. Basically you cannot say just your polymer is weather able or not. So, you are polymer can be weather able are not depending upon, where it is used, which place, and which condition and so on. And this are all factors which I listed here, it may not be responsible, you know have different response. So, different polymers response to these factors will be differently, so there is no uniformity condition as I was just mentioning. So, it will depend upon the final outdoor application, where these polymers are used. So, what I will do, one I will stop for this lecture, and in the next lecture, I will start the discussion of polymer additives, and some of the additives, which are used to basically protect the polymers from this weather conditions, including see UV radiation, and some additives which might use useful or added to polymer, to increase the perform of the polymer. So, let us stop for this lecture, and I will start the discussion of polymer additive in the next lecture.