Science and Technology of Polymers
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Lecture - 11
Structure and Properties of Polymers

How they can be made, how those can be exploited etcetera. So, let us discuss on the structure property, structure of polymers their properties and relation of this structures with the properties, how these are related?

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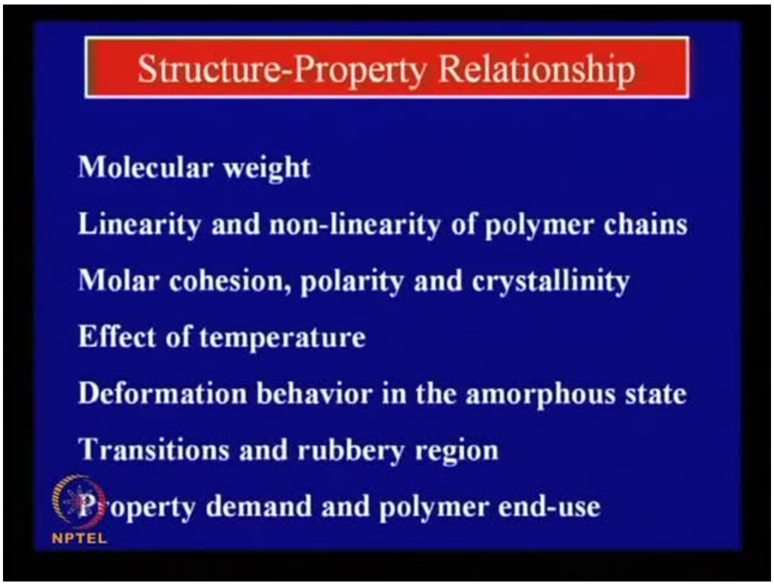

Structure-Property Relationship

Molecular weight

Linearity and non-linearity of polymer chains

Molar cohesion, polarity and crystallinity

Effect of temperature

Deformation behavior in the amorphous state

Transitions and rubbery region

Property demand and polymer end-use

There are few points, we will go through these points and we shall discuss the structure of the polymers, and their properties. The molecular weight comes first then we would not be able to know, what is the, what is the size of the polymer molecule is it mono disperse polymer. Means, the sample of polymers either it is having uniform molecular size, uniform molecular weight or not or that is a mixture of many different polymer spices, having different molecular weight.

Accordingly, you can expect a distribution of molecular sizes in the mass, if that be the case then how the properties of such type of polymers are influenced, by such molecular weight distributions, not only the properties of the polymer during service or during use, but how these polymers behave during the processing, and fabrication of any polymer product. So, there this molecular weight and molecular weight distribution, molecular size distribution has perform role to play.

Then comes the linearity and non-linearity of polymer chains. What happens if a polymer chain is linear? Linear you know, what I mean to say linear means a line like thread like, say think of a bamboo, think of a bamboo having branches. Bamboo is the longest grass, you know bamboo is a longest grass species. Now, you think of a bamboo having branches now, if you trim the branches what will happen, it will look like a rod or thread type of thing depending on diameter. So, that is a linear.

Now, if the branches are there it is not considered as linear, but rather it is as a branched structure. Now, if many bamboos are tied together tied with the help of rope, then it is a kind of inter bamboo linked system with the help of ropes, threads, studies that represent a cross linked three dimensional network system. So, linearity and non-linearity of the polymer chains actually, influence the properties of a polymer system, you understand properties of a polymer system. How the properties can be properties of those polymers be available, and in which way they influence their behavior linear polymer or branched polymer or non-linear crossing polymer. For example, take a simple example of polyethylene.

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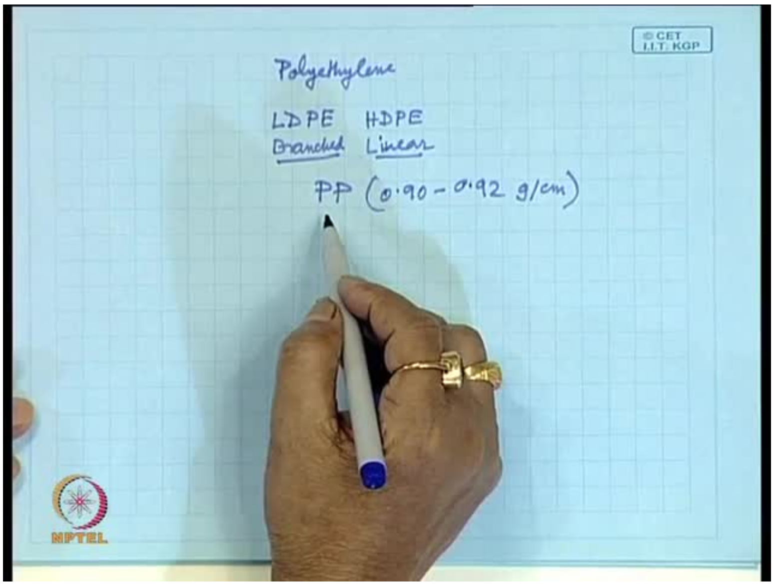

Polyethylene

LDPE HDPE

Branched Linear

PP (0.90 - 0.92 g/cm)

Polyethylene, take a simple example of polyethylene. How many different types are there as I mentioned LDPE let us take this two grades, low density and high density

HDPE. Now, this is a linear polymer, this is a branched polymer density becomes low due to presence of short branches or long branches. So, density is controlled density of the polymer is controlled or influenced by the presence of branches. If there are no branches there will be compaction. So, density will be more, density of a compact system is more bar density of the compact system is more. So, this LDPE is branched one. So, it is low density and HPDE is linear. So, it is high density.

Think of polypropylene P P, it is the lightest polymer. It is the lightest polymer density sometimes it is 0.09 to 0.091 or 92, this is the density or specific gravity of this polymer polypropylene. Why? Methyl group is there, this methyl group and some short branches also produced so, that makes this polymer providing lowest density lightest polymer, all the strong, all the very strong polymer.

Then next, point to be considered is molar cohesion. What do you mean by molar cohesion? Very simple phenomena, very simple phenomena try to follow this phenomena in simplest fashion you will understand. You think of a solid say ice think of ice it is solid at certain temperature and pressure, once the temperature is increased ice starts melting that is kinetic energy of the auto molecules are increased by increasing the temperature all right.

Now, that will continue till the entire mass of ice melts at that temperature and temperature remains same, if the pressure remains kept constant then the temperature of the liquid water gradually increases, till it is it reaches its boiling temperature say 100 degree Celsius at atmospheric pressure. Then the kinetic energy of the water molecules further increases, and becomes it is converted to vapor gas all right.

So, in the at that temperature water molecules same water molecules remains in a solid cohesion then, it remains in liquid phase then it remains in vapor phase. So, what is this cohesion? The force, forces surrounding each molecule forces surrounding each molecule, that interact with the surrounding molecule and helps in association of this molecule in a solid state, and liquid state. Even a methane gas can be liquefied and solidified, carbon dioxide can also be liquefied and solidified. And if cohesion force has to play I gave you a very good example of this ethylene gas, which is ethylene, which is gas at ambient condition of temperature and pressure.

Now, hence this ethylene is converted to polymer, polyethylene. This polyethylene again had the same ambient, ambience of temperature and pressure it becomes solid and strong, just compare between ethylene and polyethylene. Now, when it is converted to polymer it becomes strong and tuff it can be at load. Whereas, this ethylene gas cannot be a load it is a gas it is a fluid, but this polyethylene is not. How it happens?

It happens due to the molar cohesion, the molecular cohesion due to inter molecular forces of interactions, where from this inter molecular forces of interactions comes in to play. There is no polar bonds, it is non polar bonds and this is due to London dispersion force. What is the genesis of this London dispersion force, you think of this carbon-carbon bond in polyethylene bonds present at carbon and carbon, and carbon and hydrogen, both are covalent bonds both are covalent bonds, but there is a difference in electro negativity or electro positivity, between carbon and hydrogen because these two elements are not placed at the same position in the periodic table.

So, there is a gap between the placement the positions of these two elements. That is why some polarity is there as a result of that what happens it actually, it provides some induction force yeah sorry induction effect over the bonds. So, that is called the dispersion force. And when it is present in polymer, that it is it take a sum of this total inductive force or dispersion force surrounding each, carbon-carbon and carbon-hydrogen bonds, the total quantity of force will be enormous. So, that makes it viscous, that makes it stronger all right. So, that is called molar cohesion, you cannot forget you cannot ignore this molar cohesion in polymer, while dealing with polymer you have to consider this molar cohesion.

Again, if you want to dissolve this polyethylene in a solvent, you take water put polyethylene in water does it dissolve there no, what is the reason behind that thing you think of very simple, desolation. What is the desolation process? You when you add a solute in a solvent what happens, solvent provides the salvation energy, salvation energy that salvation energy breaks this molar cohesion cohesive forces, cohesive bonds present in solid.

Once it breaks this molar cohesive forces in solids, then it helps the moving off, moving out, moving apart from each other that is the role of solvent is to break this cohesive forces between intermolecular cohesive forces, it should break then only individual spaces individual molecules can separate each other, can move from move away from each other, here is the salvation energy of that thing.

Now, this water molecule cannot do this cannot break this cohesive force present in ethylene because it is a non polar system, water is a polar system, polythene is a non polar system. So, you are putting a non polar system in a polar system, it cannot break. So, it cannot dissolve, it cannot act as a solvent then, what should you do? You should select a non polar solvent, what are those non polar solvents did you give me a example of one non polar solvent.

Student: (( ))

THF, who told THF who told, who told THF why you said THF is that a non polar solvent, THF these are fundamentals, these are fundamentals you always ignore these fundamentals, if you do not know these fundamentals you would not understand this subject. THF is not a non polar solvent, it is a polar solvent, dimethylformamide is a polar solvent, alcohols, ethanol's, methanol's are polar solvent. Benzene is polar solvent?

Student: (( ))

Benzene is non polar solvent because it is hydrocarbon. So, you have to take the hydrocarbon solvent, you take benzene, toluene, xylene, hexane, heptanes, aliphatic or aromatic compounds or aromatic or aliphatic solvents. So, you take this polyethylene put in heptanes, no it will not dissolve. Although it is non polar, you put in benzene no it will not dissolve, put in toluene no again not, you put in xylene no it will not go. There are certain reasons that to find out the reasons although by theory.

As I told it is suppose to be a good solvent for polyethylene these benzene, toluene, xylene yes it is so it is suppose to go into solution, but it cannot. Then what is done, you have to you have to heat the system, you put polyethylene in toluene see LPDE in toluene and rise the temperature of that toluene, till its boiling point once it is starts boiling. What is the boiling point of the toluene is 109 or 110 degree celsius temperature boiling point of toluene. So, when it starts boiling polyethylene starts going into solution, there are reasons, there are reasons because these polyethylene are crystalline in nature, semi crystalline polymer.

Now, those crystalline has to broken by that thermal energy, once these crystalline are broken then only these toluene molecules, can penetrate in between the polyethylene molecules, and it can separate these molecules from each other by placing solvent molecules in between the solvents, are you getting the concept. Then you cool once again you cool that system, polyethylene will precipitate out will come out of phase soluble phase, polyethylene will come out of soluble phase, solution phase it will again it will solidify that is exceptional cases, but the normal thing is if you add some put this polymer in a suitable solvent, then it goes into solution I mean to say that the concept of like dissolves like.

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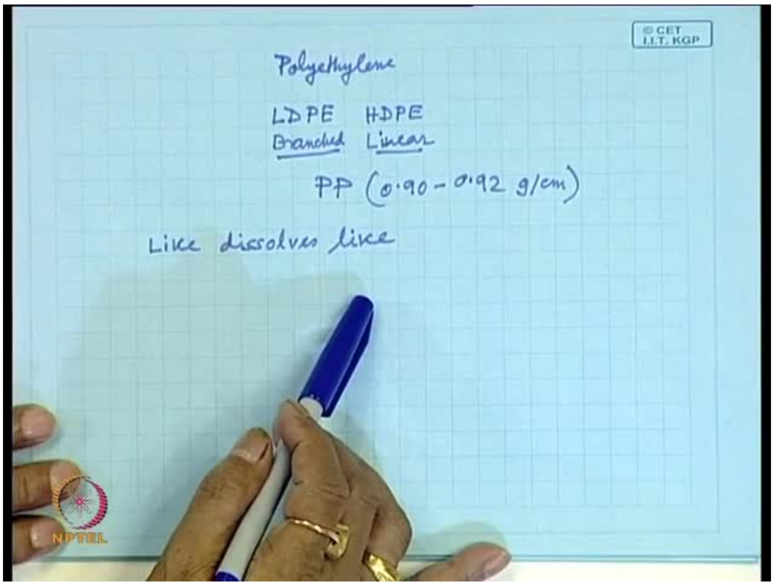

Polyethylene

LDPE HDPE

Branched Linear

PP (0·90 - 0·92 g/cm)

Like dissolves like

Similar things, if you want to live in a room, you have a selectivity for your partner don't you have? Can you allow anybody to live with you in your room answer me. No, that is right otherwise, your compatible to that extent or you can allow anybody, even you can live with a poisonous snakes or even you can live with tigers, those are exceptional cases. Yes, there are person who live with tigers I have seen in the news, there are people who live with poisonous snakes also, those are exceptional cases then it is not you have a selectivity to select your partners, here also this solubility concept or miscibility concept phenomena comes from this theory.

And then I am giving you another example, you take some nylon put in water, water is a polar solvent nylon is also a polar material. Can it be a solvent for nylon? No, there are certain reasons, you have to find out the reason. You take a dilute solution of hydrochloric acid, aqueous solution of hydrochloric acid put nylon immediately it goes into solution probably, few of you can have experience in the laboratory of course, if you have done your lab classes in a serious way, then you could have noticed it otherwise not that is the brasses you use with nylon bristles for cleaning glassware, nylon bristles, brasses containing nylon bristle for cleaning glassware.

Sometimes you use that with a acid that means, your glassware is dirty you put some acid then you want to rub also with the help of a brass and eventually, you find it becomes a sticky and it goes away or this entire brass is damaged that is due to the solubility of nylon in that acid. So, sometime acid is a solvent for some polymer. Nylon is a polymer is a polyamide CONH functional group is there. Now, that CONH functional group is attacked by this acid because the intermolecular forces of the interaction in nylon occurs through the hydrogen bonding between CONH, CONH of one polymer with the other polymer, I will show. So, these are the things solubility concept and the mechanical properties. So, all these things are related to this molar cohesion polarity as well as the crystallanity.

So, I have explained with the help of simple examples how this molar cohesion, how this crystallinity, how this polarity comes into play in the attack of solvents to those polymers or their mechanical properties extra. This crystallanity also adds on to the mechanical properties. Amorphous character is also another kind of mechanical properties because the elastomers amorphous, rubbery amorphous whereas, polyethylene and other solid plastics they are crystalline, the effect of temperature how it behaves if the temperature is increased if the temperature is decreased because you have seen in the winter, your cycle seat cover becomes hot, I do not know whether you have noticed it or not.

If you take some bags made of pvc made of pvc it becomes hard in winter and in hot summer or if it is exposed to sun, direct sunlight the seat cover of your vehicles becomes very soft why it is so, at low temperature it behaves like stiff and rigid structure. Whereas at elevated temperature it becomes flexible that means, the effect of temperature also there and again there is a limit of temperature above which, beyond which it becomes unstable it degrades starts degradation or it decomposites or it can be flexible.

Deformation behavior in the amorphous state, say deformation behavior in the amorphous state means, the elastomers, elastomers they are amorphous they deform easily that is why we can get the comfort of riding a car using elastomer tyre that is flexible, that can absorb the vibration that provide damping action, it minimize the your vibrational energy, there as due to absorption of that vibrational energy.

Who wants to travel in goods car say goods train in goods train, if you ask you want to go to Delhi goods train is your getting accommodation in as these in your passengers trains well, this empty crate, empty bug is going from you are some your goods train is going with enough space go, would you go no because you would not get that kind of comfort this is because of the vibration damping effect. Even if a train runs at a very high speed in the passenger train, that too in AC class there is a difference between AC class and sleeper class, travelling in AC class and sleeper class more damping effect is absorbed is available in AC class rather than in sleeper class.

Again there is a difference between AC class in normal train, and AC class in Rajdhani more damping effect and again bogies meant for ministers are far and far better than the bogies are meant for common people like us, poor people like us that is the dampening effect. So, those dampening effects made by spin action which can absorb the vibration that can be available from a polymer.

You will see, when you will understand will you read this viscoelastic nature or viscoelastic properties with the help of mechanical models, you will see that mechanical models are combination of springs and dust parts in series and in parallel. You will see how this damping effect is available polymer is a very good material for that this polymer molecule provides that kind of thing artificial springs. Then transitions and rubbery regions is a glass transition or multi transition and the property demand and for polymer end use. So, these are few points I will cover, I will cover try to understand if you want learn polymer, you have to put attention to this chapter.

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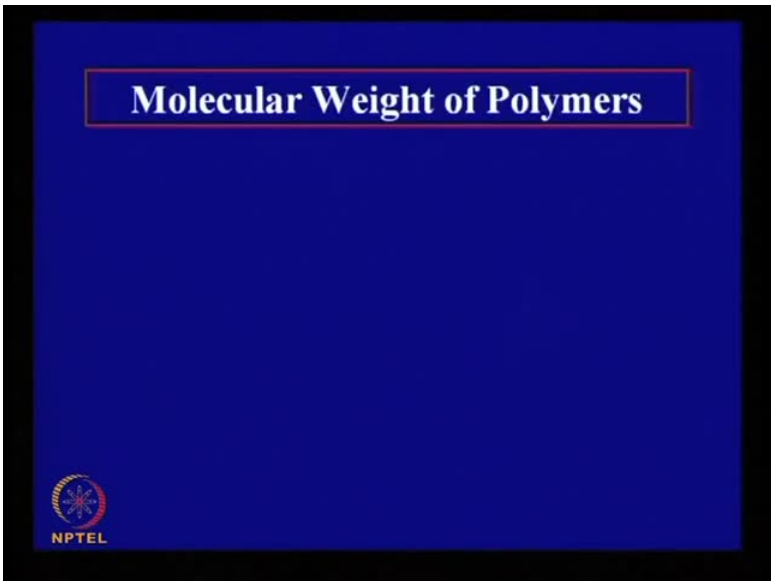

Molecular Weight of Polymers

Now, let us come to molecular weight of polymers. And molecular weight of polymers how to calculate you know, for condensation polymers molecular weight is calculated by calculating the molecular weight of the residual (( )) into number average or degree of polymerization plus mass of the n groups, from there you can calculate the molecular weight. Similarly, for additions chain polymers if you know the molecular weight of the monomer, and if you know the number of units linked in a polymer a molecule known as degree of polymerization then, multiplying the monomer weight by the degree of polymerization, you can calculate this molecular weight.

So, these are simple theoretical calculation how to get the molecular weight value and how to know, we need some data. That means, you have to determine the molecular weight, you have to measure the molecular weight, how to measure the molecular weight. For the simple molecule, what are the techniques known to us for determination of molecular weight.

So, think of sodium chloride or think of methanol, think of benzene, how to determine the molecular weight there are certain techniques. Now, you can say sir that is that necessary if we know the structure, we know the formula so we can calculate the molecular weight, but there must be some method, experimental method by which one can evaluate or one can develop, one can get this molecular weight, one can measure the molecular weight that is necessary extensively for this polymers.

How to measure the molecular weight very difficult, very difficult because these polymers are again i told you is very complicated, molecule is very complicated until and unless you cannot, you can you cannot isolate a separate polymer molecule, how can you distribute this is molecular weight. So, you have to isolate the polymer molecule once you isolate the polymer molecule then, you can estimate the size then how does this techniques once, the molecular is determined. For example, say by colligative properties measurement, can you tell me one colligative property.

Student: (( ))

Defreezer freezing point, osmotic pressure, elevation of boiling point.

Student: (( ))

Discretion of freezing point. So, these are the properties of materials so, these basic fundamental properties of materials are exploited in measurement of this molecular weight of this polymers. And there are other techniques also if the molecular weight of a species increases in a solution, then the viscosity of the viscosity of the of that solution varies, more concentration more viscosity will be. So, as well as molecular size molecular size bigger the molecular size bigger the size of the solute, bigger the size of the solute when it is dissolve in solvent then it will be more viscous, you understand. The viscosity of water is you can measure the viscosity with the help of flow time.

You take a thin capillary allow this liquid or water to flow through this capillary. So, by measuring the flow time of this liquid through capillary, we can calculate the viscosity that you have already done in your lab classes. So, once some solute is dissolved in that liquid the viscosity changes. So, you measure the flow time of the solution of that solute in that particular solvent. So, the difference from this flow times you can calculate the viscosity.

The same concept can also be extended to this polymer here, you dissolve a polymer in a solvent before that you take the flow time of the pure solvent, then you dissolve the polymer in the solvent, measure the flow time it will differ flow time will be more. Now, you start thinking, you start thinking how it takes more time to flow, when some solute is dissolved over there. That means, what is the viscosity? It is resistance to flow, it hindrance to flow it resists the flow of that liquid.

If you take imaginary plains, imaginary layers in a fluid system flowing through a pipe or flowing through a tube, if you imagine infinite numbers of layers the resistance offered by one layer towards the other is the measure of viscosity understand. So, if the molecular is bushy if the molecule is bushy in nature, it will offer more resistance. If molecular is smooth molecular nature is smooth, viscosity will be less these are the basic fundamental concept, let us see.

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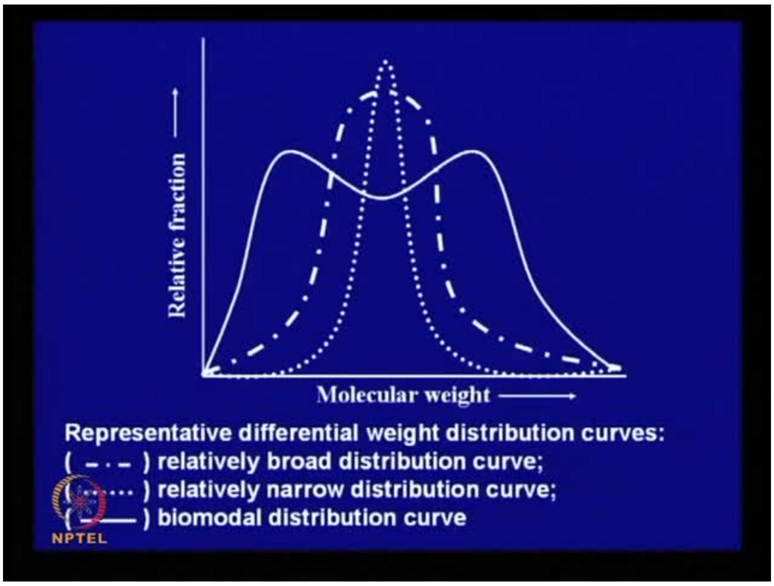

Representative differential weight distribution curves:
(– · –) relatively broad distribution curve;
(······) relatively narrow distribution curve;
(——) biomodal distribution curve

Now, this is a diagram showing distribution of molecular sizes, various distributions of molecular sizes. How this is obtained? Suppose, you take a sample of material say in our case it is polymer, it dissolve in a good solvent I mean good solvent, I mean that it can dissolve the polymer, it is a very good solvent for the polymer. That means, solubility of the polymer in that solvent is excellent at in a particular temperature again, the solubility of that polymer in that solvent at any specific temperature depends on the friendship between the solvent and the polymer.

Here both are like human entities or both are like both are goats lambs, but not a goat and a tiger. So, the units solvent and the polymer are friendly to each other, one likes the other. So, they have likeliness with each other. A solvent can act as a friend to that polymer, polymer can also a friend to that solvent then only it can be a good solvent. Why? If the force filled surrounding the solute and the solvent are equivalent or close to equivalent, then only a solvent can be a very good solvent. There you are putting the polymer that polymer samples contain molecules of the different lengths.

So, if you are asked to develop a distribution curve distribution curve molecular distribution curve, this axis defines the molecular weight, this axis defines the fraction. So, to develop a distribution to draw a distribution curve, what you have to do. So, you have added this polymer to that solvent, it is dissolved then what you have to do, you have to fractionate it you have to fractionate it.

Means, you have to separate different fractions having different molecular sizes how to do you can do with the help of solubility property only then, you take a mixture of solvents where higher molecule will be insoluble. Whereas, lower molecular will be soluble, this way you choose two solvents mix those two solvents in different proportions, this way you can have containers 1, 2 say 20 numbers say you have 20 containers in those 20 containers, you take 10 containers you take say 10 cc of one solvent and 90 cc of other solvent then 10, 90, 20, 80, 30, 70, 40, 60, 50, 50, 40, 50, 40 60.

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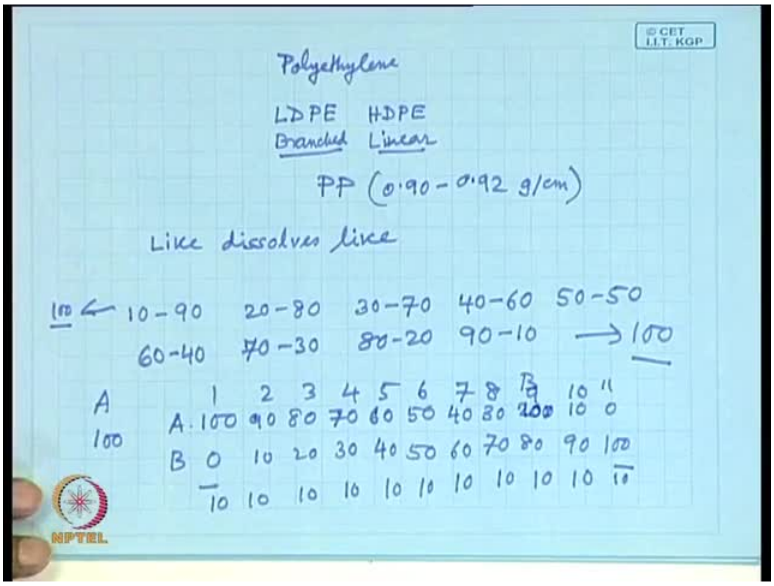

Polyethylene

LDPE HDPE

Branched Linear

PP (0.90 - 0.92 g/cm)

Like dissolves like

100 ← 10-90 20-80 30-70 40-60 50-50

60-40 70-30 80-20 90-10 → 100

A

100

	1	2	3	4	5	6	7	8	9	10	11
A.	100	90	80	70	60	50	40	30	20	10	0
B	0	10	20	30	40	50	60	70	80	90	100
	10	10	10	10	10	10	10	10	10	10	10

So, this way you can have 10, 90, 20, 80, 30, 70, 40, 60, 50, 50 and then 60, 40, 70, 30, 80, 20, 90, 10 and 100 percent one side and another is 100 percent pure solvent, this is pure solvent this is pure solvent. That means, if you take A and B 100, 100 here B is 0 or if you write this way A and B here it will be 100 here 0 like this, way 90, 10, 80, 20, 70, 30, 60, 40, 50, 50 then 40, 60, 30, 70, 20, 80, 10, 90, 0, 100.

So, we are having 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 containers pure solvent, pure solvent an intermediate compositions. So, put a stock solution master solution with a same quantity to certain volume for this compositions, take 10 milliliter each everywhere the composition is like this everywhere, take 10 milliliter there you add, there you add say 1 cc of that concentrated solution, you will find certain fractions of solid has come out and you filter it, wash it by (( )) you get the fractions of that solutes you have got.

Then you plot those fractions you have got, then by with the help of other technique like once you have got certain quantity of one fraction, you measure by you measure its molecular weight by certain techniques by some absolute techniques by some absolute techniques and after measuring the molecular weight, you have a data of fractions different fractions say 11 fractions or 10 fractions of different molecular weight, or 11 fractions of different molecular weight, and then you plot make a plot and after plotting you can get either this type of distribution curve, or this type of distribution curve or this type of distribution curve.

Now, this curve this curve can be designated as a broad distribution curve, distribution is broad. Means, it is having this distribution source species or portions or fractions of low molecular weight along with very high molecular weight of which the middle fraction, or some fraction highest fraction is obtained for medium molecular weight. So, it is a mixture of low molecular weight with high molecular weight, and medium molecular weight. So, distribution is broad.

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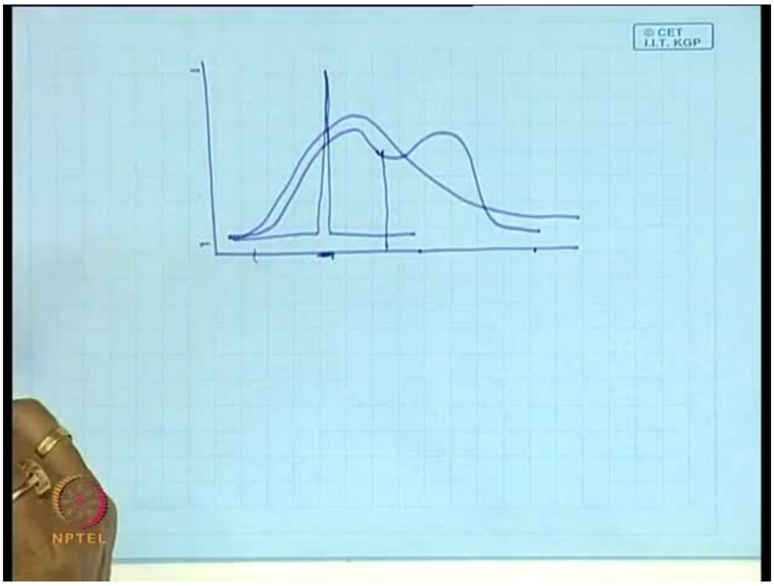

Now, this distribution is narrow or it can be further narrow, it can be further narrow if this distribution looks like this. You can say this distribution is monodisperse distribution means, it contains this up to this fraction, this fraction it contains only molecules of this size this space is very narrow this is known as monodisperse specimens. Whereas, if it gives the distribution like this, this distribution is broad this distribution can be anything depending on the method of manufacture extra.

Now, here you have seen one curve is here who looks like this distribution, bi-modal distribution. That means, certain portion certain fraction has this molecular weight, and certain other fraction has this molecular weight that means, it is a mixture of equal amount of low molecular weight with the high molecular weight polymer. So, that has profound effect on the processing and fabrication of the polymer, that melt be viscosity melt behaviors solution behaviors, all those properties are controlled by this thing.

Now, for a film grade polymer LDPE low density poly ethylene is a very good material for film making film. Whereas, HDPE is difficult to convert it to a film whereas, you can make pipes or rigid structural items from high density polyethylene, but the low density polyethylene can be used for making films, not only that during processing what happens it needs heating of the polymer to increase its flow behavior or flow characteristics, for which it needs to be heated to very high temperature.

Now, if the melting point of say HDPE is melting temperature of HDPE is say 130 degree celsius, then the polymer needs to be heated up to say 160, 170 then heating this polymer to that high temperature provides adequate fluidity, fluidity flow behavior of that polymer or rheology of the polymer so, that it can be excluded in the form of pipe or it can be used for the induction moldings of items like chairs or buckets like this. So, that flow behavior flow characteristics all this things depends on the molecular weight distribution

Now, if there are small molecular fragments fractions present in a sample of polymer along with high molecular sample, high molecular molecules contribute to the strength properties and low molecular weight fractions, contributes to the processing characteristic. So, here this portion amounts present in the lower side of low molecular weight that adds to that contributes, during processing characteristics of the polymer.

Whereas, high molecular fractions that contributes to the mechanical properties, thermal properties all those properties. So, this shows there is a need of a broad distribution of polymers for certain applications. Whereas, there is also a need of polydisperse sorry mono disperse polymers means, very close molecular weight dispersity is less low, will see gradually.

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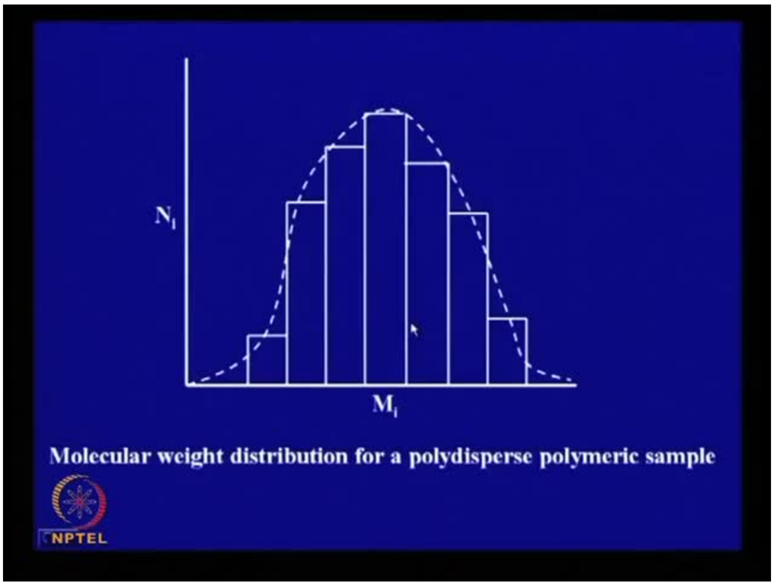

Molecular weight distribution for a polydisperse polymeric sample

Now, you see this is again another distribution curve based on number counts number of molecules of different species, high species with their molecular weight. So, this is a distribution curve, how it can be evaluated for a poly disperse sample.

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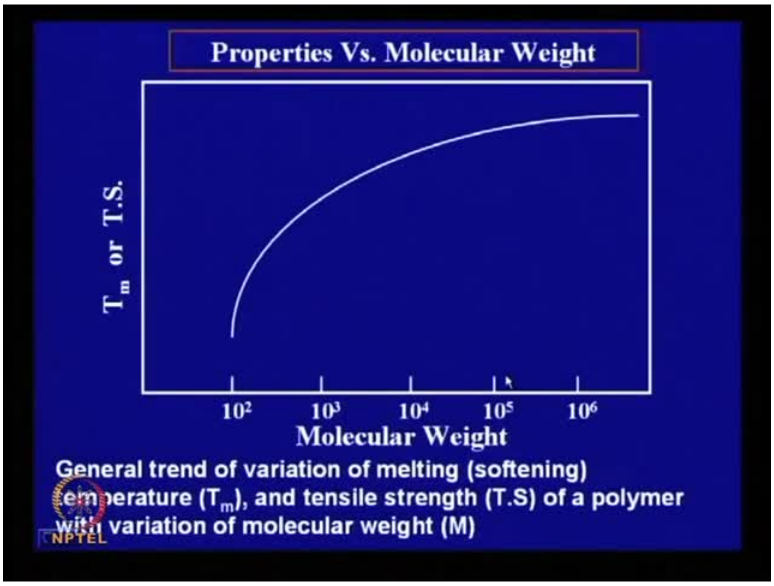

Properties Vs. Molecular Weight

General trend of variation of melting (softening) temperature (T_m), and tensile strength (T.S) of a polymer with variation of molecular weight (M)

Now, let us look into because we will again come across about the molecular weight relations and the distributions. Now, let us see I am talking so much, but you are not getting, how it is influencing or how it is related to the properties of this polymers. This is a schematic representation here, this axis shows the increase in molecular weight molecular weight increases in this direction and this axis shows the properties, properties may be thermal properties may be mechanical properties or other properties. Now, this kind of curve addition of this properties with this molecular weight. So, there is some minimum properties for a minimum molecular weight then, gradually this property increases with the increase in molecular weight.

Beyond certain value of that molecular weight, then that increase of those properties are not very high, not very pronounced. What does it indicate? Suppose, you have developed a polymer you have synthesized a polymer, you want to use as a film or you want to use as making a molded item, will it be that strong, can it be can it provide film characteristics, can it bear huge load.

So, these questions comes so, that is related to molecular weight. What the molecular weight of that polymer you have prepared so, you evaluate that molecular weight if you find that molecular weight of your polymer is only 1000 see that properties, here if the molecular weight is 10000 properties higher than this molecular weight, up to 1000 if the molecular weight is 100000, the properties increases to this value. So, this can be taken mechanically more stable, mechanically bearable this polymer as compare to this one. So, this indicates there is a threshold value of molecular weight.

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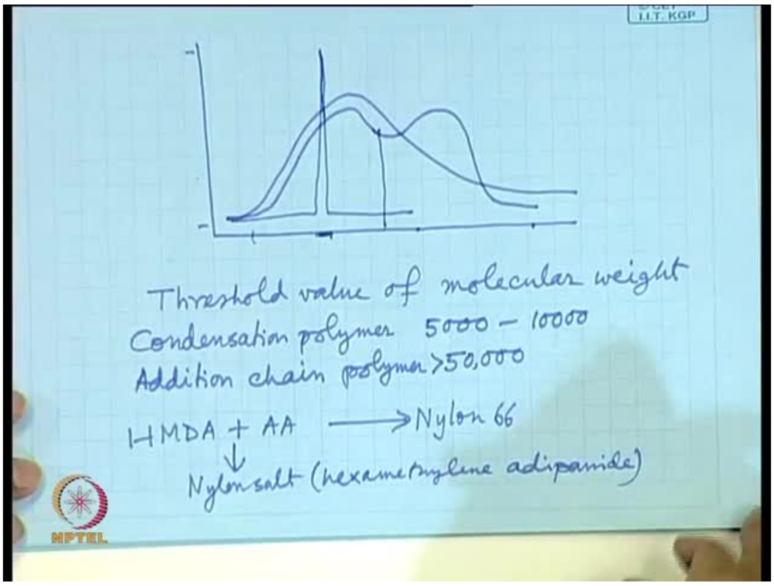

Threshold value of molecular weight
Condensation polymer 5000 – 10000
Addition chain polymer >50,000
HMDA + AA ⟶ Nylon 66
↓
Nylon salt (hexamethylene adipamide)

What is this threshold value? The minimum molecular weight so, that it can be used as a polymer it can behave like a polymer, what is this threshold value for condensation polymer, this threshold value can be 5000 to 10000. Whereas, for addition chain polymer, this threshold value can be 50000 higher than 50000 greater than 50000. Look at the difference. Why is it so? Suppose, you are synthesizing nylon. How nylon is synthesized? See take see for example, nylon 6, 6, nylon 6, 6 is made from?

Student: (( ))

HMDA plus adipic acid initially for nylon synthesis what is done, a nylon salt is made when these two are dissolved in a solvent, when these solutions two solutions are mixed immediately eventually, it will form a salt and that will that will precipitate out. So, if you mix a solution of HMDA and AA in water, when you mix this two solutions immediately the nylon salt HMDA and adipic acid salt, hexamethylene adipamide that is known as hexamethylene adipamide that hexamethylene adipamide salt in insoluble in water it precipitates out you filter it.

It is got advantage that this HMDA and AA when they are polymerized, you see if it is polymerized in one is to one molar ratio, then only you can get a polymer high molecular weight polymer one is to one molar ratio. Otherwise this (( )) control becomes a problem in nylon synthesis a nylon 6, 6 synthesis because somehow by weighing, you can take little difference you can just deviate from stoichiometry during weighing, there may be certain mistakes. So, it is difficult to take this same weight so, in order to avoid that you dissolve these two and mix these two solutions, and salt will be precipitated out and that salt will be form in one is to one molar ratio.

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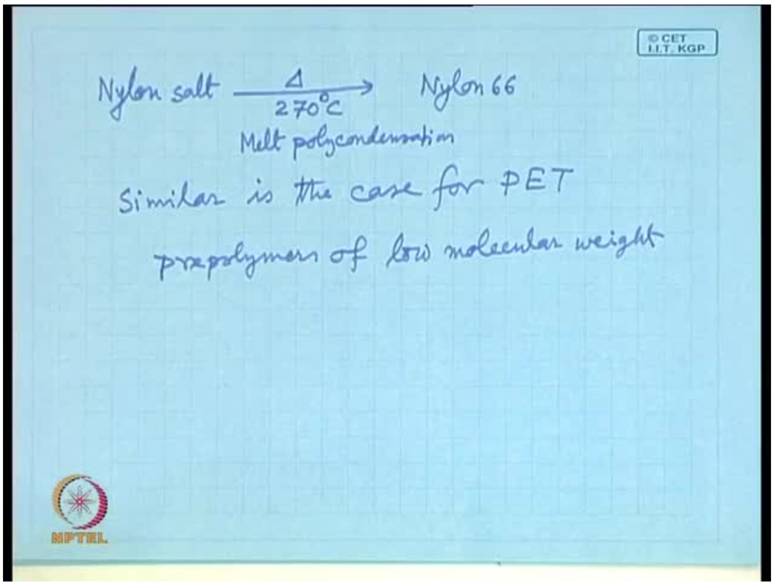

Nylon salt $\xrightarrow[270^{\circ}C]{\Delta}$ Nylon 66

Melt polycondensation

Similar is the case for PET

prepolymers of low molecular weight

So, this nylon salt hexamethylene adipamide when that is heated, temperature is around 270 degree celsius, this nylon salt melts forming nylon 6, 6. Now, this nylon salt is highly viscous nylon salt when its melted, it is become viscous due to condensation to increase the molecular weight. So, you have to maintain that high temperature otherwise, the fluidity will not be there and your growth will not be adequate high molecular formation will not be adequate.

Here you understand in order to synthesize a very high molecular weight, in condensation polymerization is very difficult. Similarly, the synthesis of similar is the case for polyethylene terephthalate that is also produced by (( )) because once this oligomers, higher oligomers. Higher oligomers means, more than say 6000, 7000 molecular weight oligomers are formed there melting point is quite high. So, you have to heat at a very high temperature then only it will permit otherwise, one will be in liquid phase and other will be in solid phase, heterogeneous phase will be there polymer growth will not be there.

So, both of this reactants should be kept in the same phase not heterogeneous phase rather in the homogeneous phase and that is possible only, if you carry over this polymerization in at very high temperature polyethylene terephthalate and nylon. And even doing that you cannot get very high molecular weight. For nylon it is for poly ethylene terephthalate it is you can get few lakhs of molecular weight, but for phenol poly amide and other polymers it is very difficult to get high molecular weight.

So, sometimes pre-polymers are made, this pre-polymers of low molecular weight then those prepolymers are further converted to high polymers, high molecular rate polymers at later stages. So, this gives you the concept of threshold molecular weight of a polymer for getting or for making useful product out of that threshold molecular weight, molecular size polymer do you understand. So, it is 5 to 10000 are condensation polymer it is beyond 50000 for addition chain polymers, and that is indicated from this schematic presentation schematic curve.

Yes, please

Student: Sir this property we get is beyond the saturated level.

Yes, almost saturates that means, if you go further say 10 to the power 7 you cannot go you cannot get tensile strength beyond this value, but it is not too rigid for each and every polymer systems, there is some exceptions.

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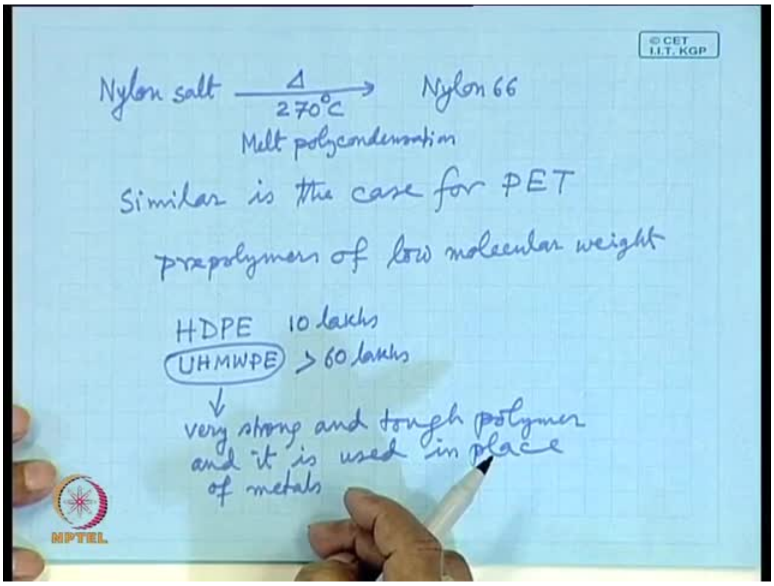

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Nylon salt $\xrightarrow[270^{\circ}C]{\Delta}$ Nylon 66

Melt polycondensation

Similar is the case for PET

prepolymers of low molecular weight

HDPE 10 lakhs

UHMWPE > 60 lakhs

↓

very strong and tough polymer and it is used in place of metals

Say for example, polyethylene, HDPE what is the molecular weight of this HDPE, say it may be of course, it depends on the branching in linear polymer. So, HDPE molecular sets about 10000 rigid polymer, but ultra high molecular weight polyethylene it is greater than 6000000, 7000000, 8000000 like that. Now, this ultra high molecular weight polyethylene, very strong and tuff polymer and it is used in place of metals. In substitute of metals its very strong polymer and that strength comes from this high molecular weight, and it is difficult to process also of course, this ultra high molecular weight polymer is processed by centering not by this conventional polymer processing techniques, polymer processing machineries, ultra high molecular weight.

So, there you see is a exceptional case going or increasing the molecular weight, you can increase the mechanical properties mechanical strength, but not always because it levels up properties will levels up beyond a molecular weight. So, there is necessity of manufacturing or synthesizing, very high molecular weight because that will be difficult to process is not it. If you take a very high molecular weight product it neither you will be able to melt it, nor it will go into solution in a suitable solvent. So, to find out a suitable solvent or to find out a suitable temperature of processing is very difficult, for high molecular weight. So, you must leave it at some molecular weight so, that it can be easily processable.

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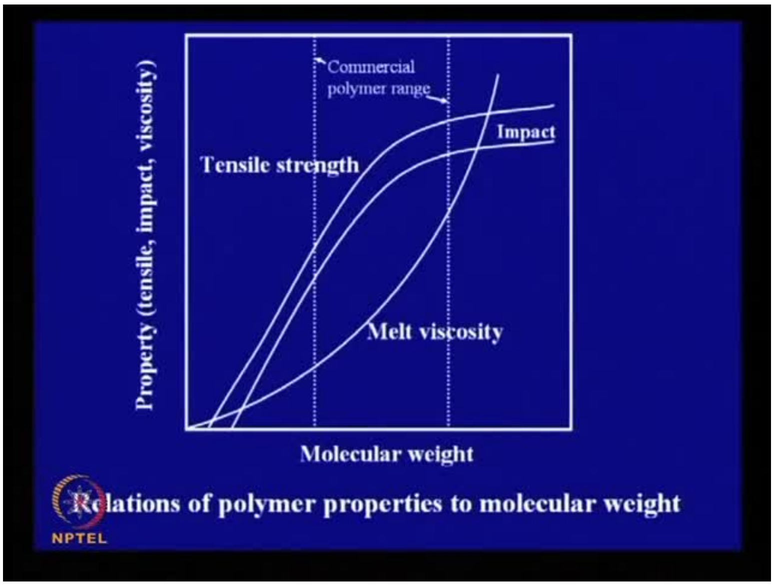

Relations of polymer properties to molecular weight

In other way look relations of polymer properties to molecular weight, you see here you think of this impact properties sorry think of melt viscosity. Melt viscosity increases in this fashion with molecular weight whereas, tensile strength it increases in this fashion beyond certain threshold value increase is not so much, as this the case in lower molecular weight species. Look at the impact property again, it is like the tensile strength impact property also levels up beyond certain molecular weight.

Now, this is a range of molecular weight between this range of molecular weight, where you can have intermediate properties, this is known as commercial polymer range here the axis is not defined axis is not defined. So, the hypothetical range, hypothetical molecular weight range where you can get adequate tensile properties, adequate impact properties, adequate processability that is, you have to have a compromise, you have to archive the compromise between the processing as well as the properties.

If you want only high molecular weight, if you want only very high molecular weight, but you would not be able to process it, if you are unable to process it, if you cannot make a product that is useless. So, you have to make a suitable product so, it should match with processing machinery. That means, the machinery you have say one extruder you have or one induction molding machine you have. So, if you get a polymer which is not of which cannot give you a molded product or extruder pipe, then it is useless this is the range of molecular weight is known as commercial polymer range, where it process well through existing machinery, as well as it gives a balance of properties.

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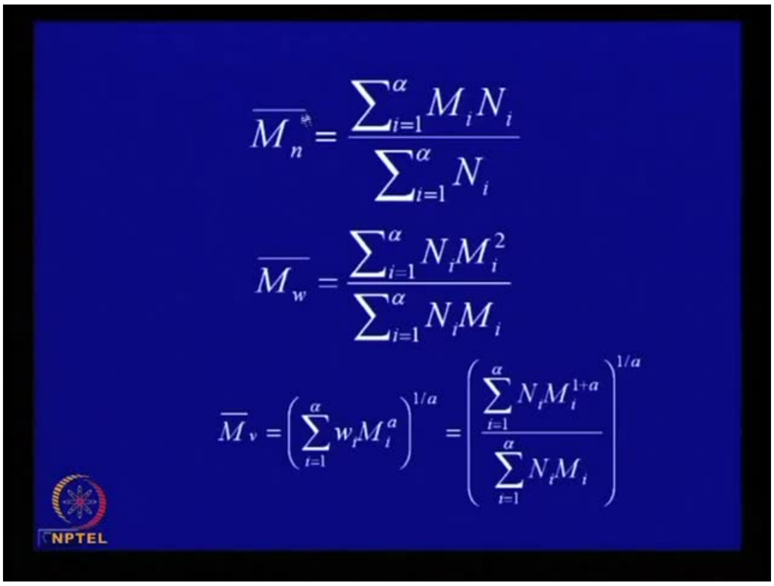

$$\overline{M_n} = \frac{\sum_{i=1}^{\alpha} M_i N_i}{\sum_{i=1}^{\alpha} N_i}$$

$$\overline{M_w} = \frac{\sum_{i=1}^{\alpha} N_i M_i^2}{\sum_{i=1}^{\alpha} N_i M_i}$$

$$\overline{M}_v = \left(\sum_{i=1}^{\alpha} w_i M_i^a \right)^{1/a} = \left(\frac{\sum_{i=1}^{\alpha} N_i M_i^{1+a}}{\sum_{i=1}^{\alpha} N_i M_i} \right)^{1/a}$$

Now, here you see some averages number average molecular weight.

Thank you.