

**Rheology and Processing of Paints, Plastic and Elastomer based Composites**  
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**Lecture 2**  
**Structure Process Correlation**

Welcome, welcome to NPTEL online certification courses. On Rheology and Processing of Paints, Plastics and Elastomer based composites. Today we are in week 1, lecture number 2. The theme of today's lecture is Structure-Process Correlation. The content we will be covering are types of bonds, bond strength, cohesive energy density, heat of dissolution because that is very very important because many of the polymers otherwise you process it in the solution stage itself. Then solubility parameter bond rotation.

Bond rotation is very very important in terms of flexibility of the products. Structure-Process Correlation, although we are every time altering structure-process correlation but of course it has a property relevance as well every now and then. Then we are going to talk about the transition temperatures and the molecular weights. As I ended up other day, I was talking about weight average, number average molecular weight.

We will try to see other average molecular weights as well. So keywords for today's lecture is the bond strength that is very very vital. Solubility parameters that is also utmost important that actually determines how much is the energy with which one polymer strand is attached to the neighboring molecules, neighboring polymeric molecules. Then we are going to talk about the little bit on thermodynamics of polymer dissolution that all together is a self-standing portion of the study, but we will just try to highlight the relevant portions. We are going to talk about the molecular weight at the end.

So these are the keywords. Now as I mentioned it to you, there are two types of bonds. One is called primary bonds, another is called secondary bonds. So secondary bonds, what there is a complete sharing of electrons between two atoms happen. It can be in the form of covalent bond.

Everyone gives its share and then shared. Ionic one gets the share maximum share of it becomes stays negative, another stays positive. It can be metallic bonds as well that means, nucleus are all around, electrons are free to move along. So these bonds actually they have a much larger strength because there is a sharing of electron in obvious reason. But there may be secondary sort of interaction, how it happened? It is not a complete exchange of electrons, it is a temporal exchange of electron cloud it may happen.

It is a very temporal exchange, transient exchange in the form of its intensity, it is of again three types. It can have a small exchange, very transient exchange, you call it London dispersion or Van der Waals sort of a force, smallest energy, quantum of energy. And by the way primary to secondary, secondary is almost one tenth or even less than that of the primary forces always. One twentieth, one fiftieth even. So dipole-dipole forces are the next one of the two.

If you have a polar molecule, they try to have a again the electron exchange. But it is more intense than Van der Waals sort. And the third category when involving hydrogen that is a one class of dipole-dipole, but since hydrogen is there suppose if you have a OH, you see the polarity delta minus and delta plus. And you have another carbon-dipole bond, oxygen for example that itself a delta negative, It is not exactly dipole-dipole, but it is called hydrogen bonding interaction and it is of larger tune. Simply speaking, as we go from rubber, plastic to fiber, based on the secondary force, type of secondary force also by and large, for rubbers it is Van der Waals type of a force, lower secondary force.

Fiber for it has to be strong, so it is a hydrogen bonding type of a force and dipole-dipole dominates in the plastics in general. Although there can be a Van der Waals port, but I mean chain is very rigid having aromatic rings say for example in the backbone, that can also be a rigid class of plastics. But higher temperature it will flow and then low temperature it will cease to flow, cease to execute any sort of a motion. Now why secondary force is so important? I already told it is very weak, then why so? As I mentioned it to you, degree of polymerization in a polymeric structure, it can be 1000 repeat unit, it can be 10,000 repeat unit. Let us take 1000 repeat unit.

So if 1000, my secondary force, so 1000 such of entities, if they have a secondary force interacting, so that it is going to be suppose if it is say 10, so 10 into 1000 is going to be 10,000. So total sum of secondary force you call it is going to be 10,000, it is even stronger than a primary force, carbon-carbon bond say for instance in the main chain backbone. So in polymer point of view, either in the form of properties or process, property means this unified structure, two molecules or multiple molecules will give you strength, because they are holding with that force. And when you try to make them flow, you have to really put sufficient kinetic energy,  $KT$  energy so that each molecules will be labile. So in that sense, secondary forces plays very very important role.

And in polymer case, always it is like a democracy, okay. I am weak, but we are strong. Secondary force is weak, but sum of secondary force decides who is going to be king, what is going to be the pivotal parameter to make them flow, to have certain properties say for example. So this is the fundamental. Now if you have a look again little precisely, metallic bonds, what is the tune in kilojoule per mole, you see Van der Waals

is even one while it is several hundreds primary forces like covalent, ionic or metallic forces.

And you can see hydrogen bonding forces is larger than dipole-dipole. And you can see carbon-carbon bond is 347, okay. Carbon double bond you add another bond pi bond on top of that you have it more, okay. You have a carbon-oxygen bond is even stronger than carbon-carbon bond. So that is how your this primary bond strength determines how strong your backbone is going to be.

So secondary force decides with which force each molecule is attached to the other, okay. So that is relevant in terms of flow as well as you know. So when you put sufficient energy, technically what is cohesive energy? Cohesive energy is a sum of secondary forces that needed to make these two molecules separated. Normally for a small molecule you can calculate from heat of vaporization, but here you calculate the total energy necessary to remove a molecule from a liquid or a solid to a position far from its neighbor, okay. So that is the sum you have to determine.

So how you determine it? By using different-different solvent because for polymer to make it a vapor you need such a kind of a kinetic energy you have to 1000 I told you 10,000 you have to overcome 10,000 by that time the backbone will break. So no way you can vaporize and try to measure the enthalpy of it. Rather you try to put in a liquid which has a similar solubility parameter or cohesive energy terms and it dissolves then they have a match of the solubility parameter or cohesive energy that way you determine, okay. So cohesive energy density technically it is a energy per unit volume of liquid required to remove a molecule from the liquid state to vapor state. But practically experimentally it is not possible because by that KTE energy your main chain backbone will shatter.

$$CED = \Delta E/V$$

$\Delta E$  - molar energy of vaporization

V- molar liquid volume

**Polymer molecules have a vanishingly small vapor pressure and we cannot compute an energy of vaporization.**

So CED is delta E molar energy of vaporization divided by molar volume, okay. So for rubber generally this cohesive energy density you see the number 231. For plastics 380 in one example say 342. So there is a distinct difference. So obviously for rubber this molecular forces holding together is much less and fiber is going to be still larger because it is hydrogen bonding and some of hydrogen bonding type of a force, okay.

Now the second question is that why rubber I need small because I need to have a carbon-carbon bond rotation in the main chain backbone that gives you the flexibility. That is a different part of the story. Plastic on the contrary in application I want it to be very high strength. So I do not want sort of a movement, okay. So that is the other part of the story.

### Heat of dissolution ( $\Delta H_m$ ):

**Also called as heat of mixing of two liquids, whose dissolution involves only dispersion force (endothermic mixing) has been expressed by Hildebrand and Scott,**

$$\Delta H_m = V_m [ (\Delta E_1/V_1)^{1/2} - (\Delta E_2/V_2)^{1/2} ]^2 \phi_1 \phi_2$$

**$H_m$  - Heat of mixing**

**$V_m$  - total volume of two liquids**

**$\Delta E_1$  and  $\Delta E_2$  - energy of vaporization of liquids 1 and 2**

**$V_1$  and  $V_2$  - molar volumes of liquids 1 and 2**

**$\phi_1$  and  $\phi_2$  - volumes fractions of liquids 1 and 2**

So actually there is a term called heat of mixing as I mentioned it to how you calculate the solubility parameter or cohesive energy. Solubility parameter is just square root of the cohesive energy density, okay. So how you determine it? From the heat of mixing, okay. And if you have a two liquids mixing each other there is a Hildebrand or Scott there is equation and with which you free energy of mixing you can calculate. I mean enthalpy of mixing you can calculate, okay.

Of course there is a entropy term involved. So that gives you ultimate Gibbs free energy of it. And that determines how whether two liquid will mix up. If you have a negative Gibbs free energy even two polymer will mix up, okay. That is again second part of the story.

## Solubility Parameter ( $\delta$ ):

Proposed by Hildebrand and Scott

$$\delta = (\text{CED})^{1/2} = (\Delta E/V)^{1/2}$$

Hildebrand reasoned that in order to dissolve a solute, one had to overcome the intermolecular attraction between the molecules in the solvent.

From the table, polyethylene has a solubility parameter of 7.9  $\text{cal}^{1/2} \text{cm}^{3/2}$ . Good solvents are likely to be diethyl ether and hexane.

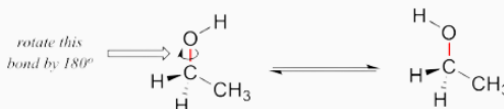
But nonetheless using this formula knowing the volume fraction, knowing the molar volumes of each you will be able to compute what is the resultant enthalpy of mixing. So similar so if I can calculate  $\Delta H$  from that process I just take a square root of it and I will be able to calculate a parameter called solubility parameter. See what solubility parameter helps us there is a thumb rule. The solubility parameter match says that you know solvent is going to be good solvent for the polymer. And similarly when I mix two polymers together they will be giving a miscible line only and then only when they have a exactly equal solubility parameter and very little difference even, okay.

As the difference goes increasing they will try to phase separate from one another like oil and water in small molecules it happens, okay. So that is the perspective. So what is the take from here is that you know solubility parameter or cohesive energy density has to be nominal and that will less amount of thermal energy will be necessary to make them strong.

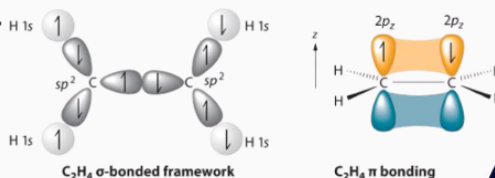
## Bond Rotation:

**Single bonds:** In organic molecules single bonds are free to rotate, due to the 'end-to-end' (sigma) nature of their orbital overlap.

**Example:** C-O bond in ethanol with a  $180^\circ$  rotation about this bond, the shape of the molecule would look quite different



**Pi bonds:** They are created from overlapping p orbitals. The lobes of the p orbitals prevent the atoms sharing pi bonds from rotating



Now let us try to see the more on the bond rotation. A single bond can undergo 360 degree bond rotation. But a pi bond where there is a lateral overlap as well sigma bond as well as pi bond that is restrained that cannot rotate. But fact of the matter is that you have a next to the double bond that single bond steric crowding is less that is more level. So you might have observed most of the diene rubbers or classical rubbers where you have a double bond. That double bond is not only to vulcanize but also make the next thing labile. And this labile is actually determines the stretch how much it comes back.

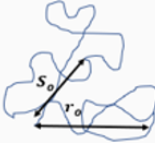
Because rubber elasticity there is a little scope here is an entropy given in plasticity. And entropy will be maximum by stretching I mean reducing entropy will be maximum if you have more labile bond rotation. So that is one of the other perspective. So obviously double bond or triple bond they themselves cannot rotate but they can make the next to that pi bond more labile. So I am not going into the details of that for the time being.

**Radius of Gyration ( $\bar{S}_o$ ):**


It is defined as the average distance between the molecular coil centre of gravity and the chain ends. This is true in case of linear polymer molecules and it is related with the end to end distance ( $r_o$ ).

$(\bar{r}_o^2)^{1/2} = \text{root mean square end-to-end distance}$

$$(\bar{r}_o^2)^{1/2} = 6(\bar{S}_o^2)^{1/2}$$



Linear



Branched

But from the flow point of view what is very important is radius of gyration. So what is the radius of gyration? It is defined as the average distance between the molecular coil because all the polymer remains in the coil or puckered form of the gravity and the chain ends. So that is how we calculate from that particular point the RMS distance. And this is true in case of linear polymer molecular and it is related to the end to end chain distance basically. Because if it is a part of in a puckered is not like that each bond you add on you get the distance that is the size of the molecule no.

Because it has a change of I mean you know configuration every now and then. And then you have a puckered structure. And rubber are more puckered by the way because it has more randomization in that sense. So this is the formula use of calculating radius of gyration. So radius of gyration is true in this case as the end to end distance can be directly calculated for linear polymer on the contrary.

Now the branch polymer as I mentioned suppose if this is the linear polymer. So this end to end distance determines. But if you have a branch polymer of same molecular weight if I confined like this only. So it is going to be all together different. The main chain backbone length gets reduced actually.

So as a result your radius of gyration actually reduces for a smaller you know polymers. But larger polymer again I will tell you in that case entanglement like octopus example I had given you earlier. So it matters. So again the radius of gyration is related to flow ease of flow. Higher radius of gyration the ease of flow will be little lesser compared to the smaller ones.

So structure process of course the property. Your processing is very good. Water flows can you make a tire out of water? Can you make a tire out of glycerin? So unit end of the day property also for polymer applications. So molecular level bonding as I mentioned covalent, secondary, bond length is very very important. So computing those you will be able to have the big picture. Monomer type, orientation, stereochemistry and reaction mechanism.

And then again based on the symmetry of the molecule the crystallinity is another part. Crystallinity determines many properties. Strength it actually determines. It determines the flowability. It determines the many other properties like thermal conductivity, electrical conductivity and what not, optical properties.

Flexibility is also related to crystallinity. Because if it is semi crystalline polymer, crystalline portion and amorphous portion they have a different reproductive index and their size is within the visible range, the domain size then it will be open. Molecular weight has lot to do. I mean because molecular weight it is a molecular size that determines the flow basically. And their distribution of course. So the thermal property, mechanical property, physical property, optical property all others say for example, permeability, chemical resistance depending on your application say butyl rubber permeability is very important.

Packaging application, permeability is very very important. While you are making a electrical insulator I mean rather than the strength of course you need certain strength, but the more determining factor is the electrical performances say for example, breakdown voltage say for example, it is you know resistance electrical resistance and so on and so forth. But obviously, when I aim for a engineering point of view not only these properties are utmost important, but also it is you know processability how it flows. So crystallinity, crystallization occurs if the intermolecular forces are strong enough like hydrogen bonding force if you have they will try to you know attract in a particular segment of it remember particular segment of it. If you have a 100 repeat unit crystallinity is going to be more because it is all probability.

Suppose if you have a lattice space two dimensional try to understand. So these are the lattice spaces where my molecules are packing. So now if I have a small molecule I can

easily put them to this you know circles I mentioned. There is a large molecule I put it here, here, here, here then I do not have. Then again that this molecule probably may come after certain while here.

So that way that this part of the molecule will remain you know unordered and that is called amorphous part of it. So when I talk about a crystallinity in a polymer you always refer to it is a percentage crystallinity rather than purely crystallinity fractional crystallinity. And again as I mentioned it you in between some molecules will have a quasi crystalline order they are not exactly amorphous. So amorphous what happens? Is they are not regular? So they have all the liberty to execute the rotation bond rotation. In the crystalline portion however you have a carbon-carbon bond that that is cis 2 execute that.

So that is the very reason why polyethylene is apparently you know plastic in nature because it has a semi crystalline polymer. So crystalline portion it cannot execute although it is  $T_g$  is minus 120 but still it is a plastic. So crystal formation occurs in two ways either the chain molecule exert very strong forces of attraction and second is they have very symmetrical structure. So polyethylene they do not have a Van der Waals force only but still they are symmetric they can crystallize.

So always remember that. So, crystallinity again is a percentage or degree of crystallinity that is what is relevant for polymer even HDPE at the best how much 60 percent, 65 percent crystalline not more than that. That gives you enough strength. LDPE, LLDPE are the tune of 50 or 40 percent crystallinity not beyond that. Polypropylene 40 percent crystallinity not beyond that but still so strong. There is another phenomena that occurs specially important for natural rubbers it is called strain induced crystallization.

Rubber in general are all amorphous in nature big molecules amorphous because it has to execute this bond rotation that will give you the entropy on the contrary. But some polymers which are not you know have a staggered methyl group as I drew it because of that they cannot crystallize but at the same time you draw it further that confirmation becomes all anti and all anti confirmation will give you a local crystallization it is called strain induced crystallization. What will happen then? If you have a strain induced crystallization provision stress versus strain if I plot it it will give you after certain elongation upturn and this upturn is because of the crystalline orientation of the molecule and that gives you a plastic type of a behavior locally. So higher strength are affordable there.

So that is very unique example of it. Crystallinity what it gives you if you have a larger



crystallinity higher the crystallinity density which going to be higher. Green temperature is going to be higher. Amorphous region will always have a low density because they are randomly packed whereas crystalline zones are very packed. So as a result if you have more crystallinity is going to be modulus or resistance to deformation will be more. And similar so you need higher temperature to make them disorder totally and then the liquid state will come then the flow will happen.

Hardness obviously will be proportional to the crystallinity. Permeability I mean packed position gases cannot escape. So impermeability will be more if you have a higher crystallinity. And heat capacity see chemical degradation takes place more easily in the amorphous region than that of you know crystalline region. So heat capacity also will change based on the crystalline segment to the amorphous segments. So I am not going into the structure property correlation in earlier NPTEL classes I have gone one by one by one by one here I wanted to give you a bird's eye view just to brush up.

Flexibility as I mentioned it to you carbon-carbon is of rotation will be more. If you have a aromatic group sitting out there a rigid group sitting out here a polar group sitting on the main chain they will have a polar-polar interaction and the resistance will be it is just like a friction parameter in a shaft. So if you have a more lubricant it will easily flow. And less lubricant less a polar group bulky group it will not move so easily. So flexibility again affect lot of properties like thermal properties because the phonon vibration flexibility mechanical properties strength wise flexible molecule will be less strength wise rubber is the lowest compared to plastics then comes your fibers.

So always always try to have the processing relevance also. Whenever I am talking about the properties here mostly altering but you try to always connect it to the flow again to make them flow each molecule should be isolated. There should not be any force whatsoever. So if you give  $kT$  energy incrementally initially it will vibrate then it will rotate and the rotation will confined to several molecules several segments and then when the rotation will be all throughout the chain molecules will flow. That is how the partition of energy happens and the highest level higher temperature it will try to flow it will have a viscous behavior. So electrical properties some of them to mention here not really that much relevance electrical resistance dielectric properties optical properties.

So those are very very important I mentioned while talking about infrared spectroscopy other time. But what is important for a semi crystalline polymer the  $T_g$  and  $T_m$ . So all polymer will give you  $T_g$  glass transition temperature. So I am not going to elaborate if I just draw quickly the modulus versus temperature I get to see amorphous polymer this type of a behavior. So at low temperature it is glassy there is no degrees of freedom of rotation only small vibration may be possible.

And you give  $kT$  energy at some point of time there will be you know tank shaft motion I mean all segment wise motion segmental motion will set in and then modulus drops down from GPa to MPa level. And this is called glassy state and this is called rubber state. Now molecules are executing this rotational motion but still they do not flow. So if you have a sufficient then number of segments involved increases then ultimately they will flow and that is what it happens here.

So viscosity is GPa here it comes to KPa or even less. So it behaves like a liquid. But for example if it is a semi crystalline polymer like polyethylene if I plot it over here it will not flow it will not see the you know rubbery plateau unless the crystalline portion is melted. So that is the difference. So typically your you know 3 by 2 factor for most of the crystalline polymer  $T_g$  and  $T_m$  you can correlate basically.

But there are some exceptions as well. So this is the master curve I was talking about starting from glassy leathery and glass transition this happens then rubbery and then finally it flows. But if you heat it further what will happen as I mentioned you cannot make the molecule separate that easily I mean if you take it to the vapour state isolated molecular state it will rather degrade. So that is what I already mentioned and I am not going to repeat it again further. So effect of crystallization during molding process is also important. So you mold it you make them flow but did not really allow sufficient time sufficient temperature they will not crystallize to that tune.

So your processing is done and that processing will not give you the property required. Even the crystal structure size type of crystals it will matter. How do you annihilate between  $T_g$  and  $T_m$  temperature? So that is also important. So when you mold it for a finished product you extrude it for a finished product whatever processing you do it but you have to make it sure that you have requisite amount of crystalline portion sustained

to have those properties.

**Molecular Weight of Polymers:**

Unlike small molecules, polymers are typically a mixture of differently sized molecules. Only an average molecular weight can be defined.

- The number average molecular weight ( $M_n$ ), which describes the lowest portion of molecular weight of the sample.

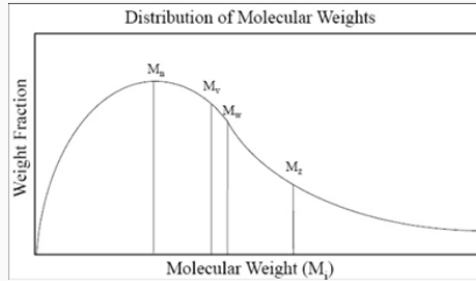
$$M_n = \frac{\sum n_i M_i}{\sum n_i}$$

- The weight average molecular weight ( $M_w$ ), which describes the average that is closest to the center of the bell curve.

$$M_w = \frac{\sum n_i M_i^2}{\sum n_i M_i}$$

- The Z average molecular weight ( $M_z$ ), which describes the highest portion of molecular weight of the sample.

$$M_z = \frac{\sum N_i M_i^3}{\sum N_i M_i^2}$$



**Molecular Weight of Polymers:**

- Viscosity average molecular weight ( $M_v$ ): The viscosity average molecular weight is obtained from the measurement of viscosity.

$$M_v = \left[ \frac{\sum w_i M_i^a}{\sum w_i} \right]^{1/a} = \left[ \frac{\sum N_i M_i^{1-a}}{\sum N_i M_i} \right]^{1/a}$$

$N_i$  - number of molecules of molecular weight  $M_i$

$\alpha$  - exponent in the Mark-Howkin-Sakurada equation,  $[\eta] = KM^\alpha$

$\eta$  - intrinsic viscosity, When  $\alpha = 1$  then  $M_v = M_w$

Generally the value of  $\alpha$  is  $0.5 < \alpha < 1$ . The value of  $\alpha$  varies with polymer, solvent and temperature systems.



That is also important. So you see structure property how close they are coming here. Last portion of it the molecular weight I am not going to repeat it you can take the average this is the different size of the molecules if I plot weight fraction and molecular weight different size you can see appears. So you can take that average with respect to number this is the formula. The next number average comes over here viscosity average and then next is weight average and next is Z average.

So practically they have a different formula you can see. See normally speaking viscosity average comes in between what weight average and number average and viscosity average is very close to weight average because as I mentioned it to you viscosity is related to flow. Flow is related to the size of the molecule because weight average takes care of gives weight average more to the larger fractions rather than the smaller

fraction that is important. Another parameter as I mentioned it to you  $M_w$  bar by  $M_n$  bar that gives you the spread of it. Molecular weight distribution of that curve this is a Poisson distribution type and that actually gives you clue broader the molecular weight distribution flow consistency will be there because you have a different segment small, medium, larger.

So small will flow faster wherever there is a gap it will make it up. So you have a flow consistency that way set in. So always keep it in mind if you have a broader molecular weight distribution from processing point of view they are better, but from the strength point of view more uniform the distribution larger is the molecular weight property is going to be good. So if you compare Imolsan SBR which is made by Imolsan process as a broader molecular weight distribution that is easier to process whereas, solution SBR which is made by anionic polymerization process which has a narrow molecular distribution is difficult to process, but it has a higher properties strength you know other dynamic properties as well. So there lies the beauty of it. So this is the viscosity average molecular weight and that is determined from viscometry.

**Molecular Weight of Polymers:**

**Degree of polymerization (DP):**

DP represents the average number of monomer units in the polymer chain and is an alternate way of expressing average chain size of the polymer. Both number average ( $DP_n$ ) and weight average ( $DP_w$ ) degree of polymerization are defined as,

$DP_n = M_n/M_0$

$DP_w = M_w/M_0$

**Polydispersity Index(PDI):**

Index of polydispersity or PDI is used as a measure of molecular weight distribution and is defined as

$PDI = M_w/M_n$

In case of monodisperse system (natural polymers and synthetic polymers made by anionic polymerization),  $PDI= 1$ , Since,  $M_n= M_w$ ; and for other cases,  $PDI>1$  or  $M_w$  is used as a measure of molecular weight distribution and is defined as-  $M_w>M_n$ .

Normally from the solution viscosity following Mark Howink equation you can always calculate the intrinsic viscosity in a Oswald viscometer depict as and when required and based on this parameters of nature of the you know molecules we can always calculate the viscosity average molecular weight as I mentioned it comes very very close to weight average molecular weight, but of course, precisely the viscosity is directly related to viscosity average molecular weight. Degree of polymerization is nothing, but the number of repeat units PDI as I mentioned it to already of natural polymer like your DNA as a PDI of one because all molecules of same size, but that you cannot even if best of best polymerization technique like leaving polymerization anionic polymerization control radical polymerization also you cannot make you can at the best make it 1.0 or

1.00 something, but not exactly I remember this. So this is what about then LDPE, HDPE the basic difference such linear molecule HDPE and there is a branching molecule.

So, there will be change in crystallinity change in radius of gyration that will be reflected to the process ability flow ability and what not whatever I talked about you can easily correlate it what I told so far about the correlation. There are more to talk more is written in this books given here. So, you can refer to any other books. I have just included another very interesting book very small book by bright son some of the flow property I will cover a great deal of you know flow ability flow through channels you know even the viscometry like specifically the capillary viscometry from that book. So, quickly to conclude what I talked about the relevance of bond strength cohesive energy as well as the solubility parameter crystallinity flexibility molecular weight how it affects properties ultimately also the flow.

So, it is a triangle structure property processing. So, you have to optimize on this you know triangle ultimately. So, next lecture I am going to talk about the basics on rheology. So far so forth I was talking about the elementary introduction to polymers now we will be focusing more on the keyword rheology, till then. Thank you very much.