

Rheology and Processing of Paints, Plastic and Elastomer based Composites
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Lecture 18 : Rheology of Fiber and Plastics

Welcome to NPTEL online certification courses on Rheology and Processing of Paints, Plastic and Elastomer-based Composites. Today we are in week 3, lecture number 6, the title Rheology of Fiber and Plastics. Once again the concepts covered today will be the polymer melt rheology. We are talking about a thermoplastics, more of it has a either crystalline or at least amorphous but stiff material it has to generally called melt rheology. So effect of molecular structure and morphology, molecular weight and its distribution I already talked about but we will try to see it at length here. So storage and lost modulus, branching, filler, blends, how does it affect the rheology in general.

The fiber rheology most importantly what you are going to learn today is elongational fluid flow that is more related to the fiber processing more or less. And for the crystalline plastics also it has lot of relevance specially for blow molding or injection molding aspects. Models for preparation of synthetic yarns and few case studies for fiber processing even though textile as such is a subject of its own. But still we will like to see very elementary process of you know textile processing is the fiber spinning, making a filament from the you know poly web in plastic material.

So that we would like to see from the rheology point of view today. The keywords for your self studies look for viscoelastic properties, complex viscosity, zero shear viscosity those are common, glass transition temperature, Newtonian, non-Newtonian, shear stress, shear rate, strain amplitude, you know storage and lost moduli and then oscillatory shear and rotational shear, extensional deformation today is important or extensional rheology rather and then time temperature superposition and of course the molecular weight distribution. So let us try to understand polymer made rheology first. So polymer made rheology aims to understand and quantify again viscous and elastic properties of a polymer. It is common for all polymers including plastic fiber.

So that the process parameter are aligned with the materials melt properties and vice versa. So that is what you must understand for any rheological characteristics how much is the viscous and elastic properties. So without any further repetition, so viscosity and elasticity by now you may having some sort of a fundamental understanding, but they are I mean characteristics of a polymer melts is that they are non-Newtonian fluids always non-Newtonian. And with viscosity decreasing with increasing shear rate, shear thinning is the best way to visualize it. Viscosity measurement can be performed either

through the direct flow measurement like I said capillary or viscometry or you can do in an oscillatory measurement techniques over the range of frequency.

I told you already I mean these two measurement techniques covers different shear rate regimes and you can have a master curve drawn I mean with certain sort of an approximation one of those are Cox-Merz transformation or Cox-Merz principle basically. That means your complex viscosity can be well I mean superimposed on the you know rotational viscosity or capillary viscosity say. So this is important from the standpoint of processing is for determining the processing energy needs that is most important. And the dynamic measurement also provides simultaneously melt elasticity. Why melt elasticity? So far I have not talked about.

So it is related to something called melt fracture something called you know, what is going to be the surface roughness of the extruded you get end of the day or finished product you get end of the day. And then when determinant of viscoelastic behavior as I told the cause of die swell I mean specially it is related to extrusion die swell is relevant to extrusion but also same thing is manifested it is the elastic effect that is manifested in the form of calendar shrinkage. It may be in the form of a mold shrinkage but it is all because of the elastic component of the fluid. So that you one must understand it. Same as all this other material I talked about for the paint say for example, adhesive say for example, but to a different tune of course.

Depending on the molecular weight, depending on the you know entanglement points, depending on the other characteristics say branching etcetera etcetera. So this I mean balance will be different. So there are two regimes of course the low shear regimes. So if you actually for an ideal polymer you look it at you can see at the very lower shear rates viscosity almost remains indifferent of that of the shear rate. You have always a lower Newtonian.

Then you have a shear thinning phenomenon. Then you have an upper Newtonian means high shear rate also then flattens out. It becomes indifferent. But most useful is the low shear one. Why say why is the high shear one? So these things ought to be captured basically as a rheologist.

You must understand importance of it. So low shear rate measurement in the melt viscosity regime is important while thermoplastic processing operation like extrusion say for example, at least 1000 s^{-1} is involved there. And then injection molding $10,000 \text{ s}^{-1}$ is involved at least. So you can understand the finish part quality or die swell is coming from the low shear regime that prediction. While the processing well flow which actually covers the high shear regime.

So both the low shear properties and high shear rheological properties are equally important one must understand. So also the testing at low enough shear rates so that measurements are in the melts linear viscoelastic regime that is also important. And the data can be linked directly to the polymers molecular structure. As I was talking of molecular weight, molecular distribution, branching that ultimately controls the polymer processability as well as the performance of it. So that is how it is important.

What is the flow aspect of it? Another aspect is this at a low shear domain. Once again you must understand one thing thermoplastic polymers or viscoelastic material and exhibit pronounced time and frequency dependence as I mentioned it to you. And for convenience thermoplastic melts are characterized by a number called material relaxation time. So λ at the ratio of the material relaxation time to those of the process time in a particular equipment say how much time the machine allows it for. And that ratio is called Deborah number De .

So this is very important number in polymer processing and rheology point of view. And a low Deborah number stands predominantly viscous behavior. A high Deborah number it invokes the more of the elastic response of the material. So that is how with a simply defining a relaxation time and if you can calculate out how much time it takes the material to flow through a particular channel or through a roll. So that ratio essentially tells you whether is material going to behave like a viscous material or it will behave like a elastic material.

So that is very very important I will invoke it again I will define another number called Weissenberg number while talking about the two roll processing also that time it will be better clarified before you. But nonetheless now stick to the Deborah number which essentially gives you ratio of relaxation time of the material to the process equipment is called Deborah number. Now very quickly it is a more or less repetition what I already told you but try to understand let us coincide it even further for coinciding your understanding practically. So most of the rheological tests are done in the shear in shear using rotational and capillary rheometer I told you already. Whereas most process flows are usually mixed flows it is not only shear but also there is elongation and particularly it is a limit when I will talk about say film blowing, blow molding, fiber spinning.

So while you are measuring only the shear viscosity of it that does not fully satisfy what it is happening in actually in blow molding condition actually it is happening in the fiber spinning cases. So you have a quite a bit of elongation polymers are coming out of its entangled network while flowing. So you have two types of viscosity at least you must understand one is called shear viscosity another is called elongational viscosity. So

in this case that is the scope. Now if you would quickly try to understand what I talked about range of shear rates which is corresponding to which you must understand one thing.

Say when I talk about entanglement polymer chain entanglement I talked about. See local molecular motion we talked about different motion know it motion can be segmental I mean short range it can be flow which is a much longer range. So local motion I am talking about fatigue properties. So all these things including the thermo forming, extrusion blow molding, blow molding, injection molding, performance impact those actually comes within the shear rate regime you can see up to 10^8 here. While the molecular structure physical as I told already molecular structure corresponds to very low shear rheological data.

So similarly physical aging long term creep those are actually it happens at extremely low shear rate. Low shear rate means longer time. It is just like a frequency you have to imagine. So similar so in the time temperature superposition principle point of view creep relaxation steady shear mode, dynamic mode, capillary rheometric mode those actually capture some. So you see the entire shear rate regimes your all this measurement is actually not capable of, and there lies the importance of time temperature superposition principle.

Then you can capture it. I mean capture it means some by the practical experimentation some by interpolation extrapolation to be very precise. So what it says the elongational viscosity of the elastic material at large deformation can deviate significantly from the shear viscosity. That is what I mean. So you know shear viscosity there is a rule that your elongational viscosity is one third of that of shear viscosity it may not hold good. It is not the you know universal law like that.

So elongational properties at large deformation correlates with the molecular structure obviously. Because it molecule has to uncoil larger the molecule longer time it will take to uncoil. Correct? So in that way the elongational viscosity as such is very sensitive indicator of long chain branching. So by shear test a long chain branch short chain branch you will not be able to discriminate that much while doing elongational test you can pretty well do it very easily. So I will come to some of the examples there.

Let us quickly try to understand I will not elaborate very very I mean each and everything here but just for your information we try to stick to the basic understanding. See this is a viscosity versus frequency or shear rate whatever. It is oscillatory then frequency if it is rotational you take it as a you know shear rate. So that way it has been plotted different molecules so from here to here I am increasing the molecular weight.

Same structure but molecular weight I am increasing.

So what is going to be reflected? See at the high shear region there is no difference. They are almost falling at the same same same position. But if you look it at low shear that means lower Newtonian part of it. See lower the molecular weight lower is the going to be the viscosity. Higher the molecular weight higher is the viscosity of it.

So this is very important from the zero shear viscosity concept and I already have given you which is terribly proportional to the molecular weight. So you can understand from this to this I am increasing the molecular weight and it is you know you can see the effect in terms of viscosity here. So this is what is the effect of molecular weight particularly on the low shear rate regimes. Zero shear close to the zero shear is the you interpolate it to where it cuts the y axis basically. So molecular weight distribution also has a lot of effect on the rheology.

Think about if I am having a broad molecular weight distribution what is going to happen? There are lot of small molecules which are very easy to swim. So as a matter of fact if you have too many large small molecules they are going to lower down the viscosity. So always always see if you increase the molecular weight distribution viscosity is going to get affected but not whole lot in the low shear rate regime but in the intermediate regime you can see it is more reflective of it. So the molecular weight distribution differences in polymer melts are easily detected by measuring the complex viscosity as a function of frequency and polymers with the broader molecular distribution tend to thin more as you increase the shear rate. So this thinning phenomena, thinning means you increase the shear rate how the viscosity is going to go down, the n value of power law index pseudo plasticity index.

So that will become less and less depending on your change in molecular weight distribution part of it. You see from this, this is your molecular weight distribution. So then you see what happens actually if you have a very very large molecules what it says I mean nanomolecular distribution each chain has on an average two entanglements and entanglement is related to viscosity. Well in a short molecule long chain it is 4 is a broad molecular distribution we are considering but for short chain only 0 to 1. So those molecules are pretty much free to swim.

So at a larger shear rate it is going to go like a flow like a water. So that is what is going to happen if you change the molecular weight distribution. So now let us try to understand again I told you even though in this particular class I am switching over rheology to dynamic mechanical sense but as I mentioned it to you it is all the OSM. It's perspective when you are considering more of a elastic material you always refer to g

prime G' double prime. When you consider is more of viscosity attributes you take it as η' and η'' not more than that.

But nonetheless I always refer to a crossover when G' dominates that means it's going towards the gel side. So this crossover there is a frequency at a frequency when your you know loss is going to, I mean storage is going to dominate that means here the crosslinking or something phenomena happening and corresponding to that frequency you call it a crossover frequency. The crossover frequency is a measure of longest relaxation time of the system and given by $1/\omega_c$. You know angular velocity ω by ω_c is the time. See inverse of angular frequency the time so longest relaxation time that way you can calculate.

All other properties of being comparable a material with higher average molecular weight can be expected to have longer λ value and consequently lower ω_c . So that you have to keep it in mind. This word exemplifies further what molecular weight has a role influencing the rheological properties in dynamic sense as well. So isothermal measurement on low of the modulus at low frequencies shows that increase in storage modulus as the distribution is broadened.

So that is also another way to look it at. So in this figure in particular the storage modulus of a broad molecular weight SBR, the rate squares are higher than that of that of narrower molecular weight SBR at lower frequency near the terminal region and also the crossover frequency you can see it. So dominance of elastic overall elastic phenomena and that is what I mentioned here the crossover phenomena. Here it is not cross linking here more or less related to the relaxation of the molecules. So that is the reflective of that. So you can understand here that the blue to red squares.

So at low to high frequency this particular changeover is reflective it is owing to the molecular weight distribution. So this distribution you can do it as I showed you earlier from you know complex rheological just viscosity measurement but also you can do it just having both the G' and G'' as a function of frequency. So branching as I said branching also can be very pretty well discriminated. So increasing the number and the size or flexibility of the branches changes the melt viscosity but if the branches are few and long enough to entangle melt viscosity will be higher at lower frequency.

So it depends what type of a branching. So long chain branching or short chain branching. So depending on that your viscosity will be different whole lot different. So you can see again SBR polymer with that example but what is interesting that as I mentioned it to you if you do the measurement in a elongational viscosity way it will be

pretty clear. I mean here some point of time very close to that you do not see much of a difference. However if you happen to do the experiment say LDPE which has a long chain branching you do it with the LLDPE which has a much shorter chain branching you see they are whole lot different at different CRI it's tested actually 0.

1 second inverse as a function of time basically. You see they are the blue and green is distinctly different and more the reason is that see the viscosity increases at large elongation strain is a characteristics of long chain branching which is much reflective you see it is upturned here it is upturned. So this is what is called strain hardening. So while monitoring the elongational viscosity it will be very obvious compared to that of course you can get a clue from here also. So you know G' and G'' and crop monitoring the crossover you get the idea of that but nonetheless you can get the same in a much distinctive way if you happen to do the test in elongation or rheology way.

I will come back what is elongational rheology again. So you know sometimes we feel it although plastics is very lightly filled unlike rubber but obviously if you have what will happen you have a filler in the system, low shear viscosity will increase at a low shear viscosity of the material will always increase. So that will be reflective again it is not only a function of filler loading but also it is a function of shape and size of the filler. Filler concentration and shape and size and its interaction among the inter-particulate interaction. So you can see the difference between neat LDPE vis a vis a filled LDPE. The filled LDPE obviously will have a here it is most more distinctive while at high shear rate regime it is coming very close although filled one is having slightly higher viscosity than that of unfilled one.

So that is what with the low aspect ratio filler L by D ratio of the filler if I consider it like a fiber chopped fiber. So L by D is high the elastic response of the filler melt is reduced with a low aspect ratio. Occasionally with the fillers of high aspect ratio may form a network with themselves and produce the high elastic response. So elastic to viscous response will be changing if you happen to have a filled system compared to the pristine one. So high filler aspect ratio of the filler such as long glass fibers as I said chopped fiber distinct features they may show you even yield stress.

At high concentration which is actually you are considering it pseudoplastic or something but it becomes a dilatant I mean dilatant fluid I mean Bingham body. So it has a yield stress basically. So filler can whole lot change the characteristic rheological properties here in this cartoon particularly figure you can see the base polymer this is the viscosity as a stress and the low aspect ratio filler. This is the low aspect ratio filler and then agglomerated filler this is the agglomerated viscosity has gone up and high aspect

ratio filler is obvious is different. I mean and that too with the stress it changes this representation is with the stress rather than you know with the shear rate basically it is a constant shear rate measurements.

Even polymer blends also you can monitor particularly so if you happen to do it in oscillatory rheology way. You can capture if you do typically the DMA or oscillatory rheology way you can see the two glass transition temperature is reflective of immiscible blends basically and their flow characteristics can be well captured. So since polymer blend is not the context of this particular lecture I am not going into the details of it I am just trying to skip it but nonetheless it is all related to the relaxation and that relaxation will obviously influence G' and G'' and obviously the tangent delta which is nothing but the ratio of it and that will be reflective. if it's a you know thermodynamically miscible blends no question of two different relaxation it will happen always in one relaxation so one single T_g will be distinctive. So I am not going into that particular details but it is a very model plastic systems in one case which is PS/PMMA blend system its dynamic rheology is shown here and while here is a SBR/PMMA which is a rubber plastic blend system.

So similar way you can see the what is the separation what is the stability of the droplet that can be well analyzed well. So now in to sum it up basically some of the factors like molecular weight always try to push the viscosity up increases whatever shear rate it is it will try to push up. So pressure pushes up filler pushes up pushes up means increases the viscosity of the system while the lubricant which actually indulges more shear I mean slip plasticizer, which actually reduces entanglement between the friction between the two chains so obviously decreases the viscosity temperature obviously decreases the viscosity. So that is what is actually happen with the plastic case a case of plastics this is what the reflection. Once again you need to have a balance in the sense you need a low good low shear viscosity for the stability point of view performance point of view and at the same time depending on type of process you are following you need a very high flow rate or low flow rate or intermediate flow rate.

So that combination is necessary for a particular processing and the properties ultimately. So that is what is the take for the plastics mostly. So I am not going into the details plastic processing is not very different from the general rheology and processing I talked about but let us try to touch upon fiber. Fibers on the contrary to plastic mostly semi-crystalline to crystalline in nature. So this as I told fiber rheology unlike the plastics I talked about paints and adhesive I talked about here fiber orientation is very important.

A plastic material like nylon if you do process it properly that means spinning and drawing it turns out to a fiber. So plastic is not a alien material only thing is that

comparatively it has a little higher molecular weight than that of a plastic which is more flowable otherwise fiber is less flowable. So fiber orientation, fiber-fiber interactions, fiber flexibility and fiber concentration matters while processing. In the unit process I am going to talk about only spinning. Spinning means you get a polymer and from the polymer to the first filament which is a primary unit you are trying to make it and that is done by two unit processes together one is called spinning followed by drawing it is a combined process only.

So in that context you can pretty well understand it is an interplay between shear rheology as well as elongational rheology plays a very very important part. See when I talk about so obviously for this case also viscosity, elasticity, stress strain relationship and other rheological properties that I talked about so far is same to same only thing is that perspective is from the point of view of spinning we will try to look it at this stage but of course in a broader way for a fiber or textiles basically making a filament is the first step. Then from the filament how do you make a yarn, yarn to cord or yarn to textiles how you make woven fabric or knitted fabric say for example. So we are not going into that you know complication at present but let us try to focus on spinning part only here. So you try to understand what happens a coiled molecule I am trying to push it through a very narrow capillary which is called spinneret.

So now a polymer molecule is not only getting sheared but also it is pretty much when it comes out after extrusion it's a kind of extrusion only to a narrow nozzle is getting elongated, it is coming out of its entanglement. So this elongation of fluid flow plays a very very important role. So let me read it out from there. As the polymer comes out of the confined channels into the open atmosphere that is extruded from the spinneret its flow behavior changes and it is said to undergo elongation also under the tensile force and not only that it gets oriented as it is very clearly understood from here but it is drawn also after a while there is a differential you know that it is getting extruded a differential speed roller is there, so that it gets oriented in the direction of the flow as well.

So these two combination. So in an elongation flow polymer fluids with uniform velocity profile perpendicular to the direction of the flow however it may accelerate or at another time decrease as it travels along the path and most of the spinning is said to occur due to the elongation flow where the fluid velocity keeps on increasing down the spinning line and resulting in unfolding of the chain. So it is getting you know coming out of the entanglement and getting little bit oriented I mean entangled also after that. So relaxation happening. So that way it is very interesting to understand and what is elongational viscosity? Same to same shear viscosity your stress is here is the tensile stress tensile notation is the elongation viscosity into the $\epsilon \dot{t}$. So I am not going into the details of you know elongational rheology but you always can go to the refer to

the elongational viscosity standalone based in trouton rule, trouton viscosity etcetera etcetera.

$$\sigma = \eta_{\text{el}} \log d\varepsilon/dt.$$

So in terms of spinning there are three distinct types of spinning. Spinning once again forcing or pumping the material through a narrow clearance and those are called spinnerets and you try to get the filament at the end. So there are three types of spinning technique one is melt spinning where the polymer is molten and then pumped to pass through the pin spinneret. Second is the wet spinning. Wet spinning is that the polymer in the form of a solution is passed through the spinneret and then you have a coagulation bath where it actually gets rid of that solvent and that solid polymer coagulates. And the third one is the dry spinning you do not use a coagulation bath while the solvent evaporates specifically and in terms of circularity of the you know if it you consider it's a like a circular channel then circularity is going to be more in case of the you know melt spinning then your wet spinning then your dry spinning.

But off course so melt spinning will give you, there are possibility of die swell is much more compared to other tube. So there are lot of things the surface roughness circularity but aesthetics of it but one thing you must understand the bottom line is that you know if you consider a spinneret through which when the polymer extrudes out the shear rate is not a uniform shear rate. At the you know wall you have the highest shear rate theoretically while in the intermediate and you at the rest of the part you have the lowest shear rate. And also if you just try to see the viscosity of the entire process the conduit through the spinneret to the dosage device and spinning pump there are different requirement of viscosity actually. And this is a typical photograph of a spinneret when multiple filaments can come out of it.

We pump it basically. In addition to that now a days another technique of spinning which is called electrospinning. So this fibers what I am talking about is more of like a millimeter or micrometer thickness. You go down to the nanometer try imagining trying to force it to the capillary. So capillary force will be so dominant that it would not come otherwise even if you try to pump it.

So in that case you can take advantage of you know voltage. So with the high voltage difference between the ground the collector you call it and spinneret head so it will try to extrude out by this process it is called electrospinning. So there also the rheology plays very important role but nonetheless I am not going into that details at this stage. Now these fibers are actually sometimes drawn sometimes in a two stage manner. So here in this particular case studies here there is a example is two stage drawn PP fiber. They try

to you know try to see how the properties how the crystallinity changes and that can be monitored in a dynamic geometric way.

It is the other way round. In this case we are not going to set up a particular process through rheology, rather rheology here is a measurement tool that how the two stage drawn fiber properties are going to be in terms of glass transition temperature, in terms of crystallinity and in terms of the damping peaks. Damping peak high means lower crystallinity more amorphous part of it damping part always refers to the you know after it melts and it is a amorphous part segmental motion basically. So that way you can I will share it with you in the long run but nonetheless again, it is a E' E'' as a function of temperature master curve and from that you will be able to perceive that what is happening I mean for a two stage drawn fiber with the change in processing condition. So I am not going into the details at this stage for that. So similar so a cotton fabric and epoxy composites you know how does orientation affects.

So you take it from different angle to the same material one at 45 degree cut one is a 0 degree cut. So you can see distinctly monitoring here it is more of like dynamic mechanical monitoring but as I said it is no different when you are considering a solidus type of a behavior you call it more of dynamic properties otherwise it is oscillatory rheology as simple as it is. So you can see it from here that 0 degree straight line and 45 degree dashed line. So you can see there is difference in terms of storage modulus, storage modulus is much higher for that when you take it from here rather than from here. So this is giving you more higher properties than that of the other but you see they are so different actually even if they are taken from the same material but all the thing is taken from different angle.

But let us try to understand another very advanced you know processing techniques which you call it 3D printing. So in this particular example a 3D printed once again I am not going to design 3D printer here, neither I am going to you know correlate rheology taking the rheological properties and design we are trying to do it other way round in this case at least. So a 3D printing of polyether is taken and that particular material at two different temperature 350 and 380 degree centigrade we monitor the complex viscosity as a function of angular frequency. And again you know complex viscosity data can always be superimposed with that of the you know other others viscometric data including the steady state data or capillary rheometric data. See what is the importance many a times while doing the measurement to capture the LVE part of it.

See in this particular example extensional stress monitored as a function of modulus that this flat part when both E' E'' is flattened out and this is the LVE linear viscoelastic region. You can ask me the question what about this there is a so

much of fluctuation this data is fluctuating data unstabilized data and after this data is a nonlinear viscoelastic data. So you must confine your measurement within that region mentioned this is the LVE range basically.

So anyway between a stress of 0.1 to 0.5 a plateau is observed as you can see here this is corresponding stresses. At the storage and loss moduli are independent of stress amplitude that is the LVE and there are stress values higher than 5 MPa higher than this onwards E' is probably decreasing it is not shown here and this is the nonlinear viscoelastic region of it. So anyway what is important here again the storage modulus and loss modulus is a function of temperature as shown for that same 3D printed objects. And what is important from this flat portion the sample is taken vice versa sample from the edge portion is also taken. So flat portion sample as you can see from this plot is going to show you higher storage modulus.

So all this characteristic after printing also fundamentally depends on, where from you are taking it depends on the flow extent of flow it depends also the extent of drying of it. So that you can monitor otherwise but again you can do other part also given a unknown polymer you try to monitor its rheological property generate its master curve try to assess the zero shear viscosity as well as you know shear rate corresponding to 3D printing and then design your machine I mean design your particular process parameter for that particular material for 3D printing better and better printing. If you want to have more gloss try to pacify the elastic part of it try to pacify the first normal force difference second normal force difference part of it and also you have to duly consider duly regard the elongational viscosity as well. So unless you do it particularly for a semi crystalline polymer it is going to be whole lot difference in terms of properties and processing basically. So that is what here storage modulus and temperature G' and G'' shows the dependence on the printing direction and in fact the moduli for the edge samples are much lower.

So this samples modulus storage modulus much lower than that this part of it that part of it. So that is what is quite quite reflective from here. So anyway I am not going into that details of it but hope you have understood the essence of it. So I briefly covered very honest with you the other part say for example you know melt fracture, die swell, it will be well taken care of in a fifth week itself but what I talked about today is more of the fundamentals which is no different from the rheology of paints you know adhesives I talked about or during the rheometry what I discussed so far. But some of the essential stuffs like effect of molecular weight, effect of you know morphology, the molecular weight distribution how does storage and loss modulus varies in terms of branching, variation of fillers, blends that we talked about. We added one thing that you must go back and read little bit more the elongational viscosity of it.

We will try to come up with more with the elongational viscosity if time permits in the long run in the maybe towards the fifth week or so. And I just showed you a case studies although I didn't go into the details of the fabrication part of it, rather after fabrication of a particular 3D printed objects I showed you how you can discriminate between a edge and you know in a flat part of it practically from the monitoring rheological properties and extends from its you know flow as well as weight actually I mean evaporates the solvent or it any its annealed basically. In the upcoming classes whatever I the basic fundamentals I talked about some equations I talked about some of the numerical problem you must exercise before we go to the next level with that thank you very much.