Rheology and Processing of Paints, Plastic and Elastomer based Composites
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Lecture 3
Basic Rheology

Welcome to NPTEL online certification courses on Rheology and processing of paints, plastic and elastomer-based composites. Today we are in week 1, lecture number 3 where we will be just giving a brief about the basic rheology. So quickly the concepts that will be covered today includes some definition, essential definitions related to rheology. Rheology and processing, understanding rheology how we can go for processing and then deformation little bit on shear stress, shear strain, I mean shear rate we will start from the basic conception point of view. And then we will talk about the constitutive equation because we will be dealing with this constitutive equation later on again and again. Then one of the very important properties that makes polymer rheology little complicated which is actually normal stress differences, we will realize that essence of it.

Then hooky end, non-hooky end but off and on we will switch from solid to liquid, liquid to solid sort of a behavior because polymers are all viscoelastic in nature. So whenever you are making them flown at higher temperature it has a maybe more liquid like properties but it has some solid behavior embedded into that. So when you are around at lower temperature when you try to monitor the dynamic properties it is mostly solid as behavior but it has some liquid also in it. So that way hooky end and non-hooky end solid behavior understanding is necessary.

Then little bit on viscoelasticity that means creep and stress relaxation because DMA will be covering separately later on. DMA and the concepts of oscillatory rheology actually. Then we will talk about a Newtonian fluid which is considered to be a classical fluid basically. And your polymer fluid will obviously give deviation from there. And then bit on rheological models, model in the sense again I mean it is a spring and dashboard models in the last courses also I talked about.

But here we will take all this I mean in relevance to rheology basically. So very quickly the keywords that you can search it for book although I am giving you some bibliography but again the teaching learning is a continuous process. So you can always give a search on this keywords and figure it out from the computer resources and all. So the keywords are rheology, deformation, shear stress, shear strain, shear rate, bit on viscous elastic and viscoelastic discriminating all these three because we are ultimately dealing with the viscoelastic behavior of it. Then as I said Hookean and non-Hookean and then Newtonian Newton's law of viscosity or Newtonian fluid how it those fluid that will obey Newton's law obviously call it Newtonian fluid.

And similarly some rheological models basically that you can search for. So coming to the very basic let us start from the very basic to a lay person what rheology means. So rheology say for example is essentially science of deformation and flow. And let me give you some example then things will be clear to you. Mayonnaise I am sure all of you get a mionese specially making a burger or making something.

So mionese does not flow even under the stress for a long time but you see honey till the bottle I mean at a room temperature I am talking about not putting in the refrigerator. So it flows continuously. You might have seen your toothpaste also to take it from the toothpaste from the nozzle you have to really press it then only it will flow. Siliputti as I mentioned it already is a silicon based borax cured system sold for that as a toys for kids playing with nowadays that is embedded with lot of LEDs and all it mounts us. It is elastic but you keep under load for whole night even a book you can put it on that that spherical things will deform heavily overnight.

So dilute floor water solution you can easily work with but once you make a dough you know you see how to make a chapati out of it. So you have to really make it like do the processing then you have to give it a you know circular shape and then you have to put it in the tawa and all you get it in the form of a roti finished roti actually. So similar so corn starch and water can display strange behavior I mean here you see here is the example of mayonnaise the bottle for your representation if you by chance do not use mayonnaise and then you see the second example here is of the siliputti. So siliputti is a bouncing ball that you keep it under the that see the kid will obviously not like that that ball is deform overnight it flown. And then you see this chapati or dough you make it out of floor and that once you make it how you processes I am sure everyday you are seeing that but there is very strange behavior you get it from corn starch solution.

See you hit it, it bounces actually you cannot your but you if you deform it very slowly then you see it hits. But once you poke your finger in you see it is a strange way it goes very easily not only that you poke the whole five fingers you see something is trying to coming out actually as it sees from here. So definitely this starch is nothing but a polymer solution it has some strange behavior compared to normal fluid everyday you deal with say water say oil say glycerin. So definitely it is a very interesting science to understand the flow and deformation behavior of polymer in the molten stage as well as polymer in the form of solutions. So that is what we are going to learn eventually.

Again going to classical definition of rheology as the word says rheo means flow, logos means science it is a flow of science of course the deformation also. So rheology is a science of flow and deformation as you can see with the red you know wording of matter at that distance the interrelation between force deformation and time. Force deformation you may be understanding if I put a force the material is going to deform force is enough but point is that for viscoelastic material time is important. So for a rheologist actually everything is flow and you can I can quote a word mountain flows before the god. So if you allow really really very very long time even a mountain can flow as well.

So science of rheology is actually is at its youth actually I will say it is not that old it is 70 years old only since that you know it formalized in the scientific way and it was found by two scientists professor Renard and professor Bingham. So you can see there is a fluid dedicated by the name of professor Bingham meeting in the late 20s and finding out having the same need for describing the fluid flow. So it is very very necessary first understanding to flow and Greek philosopher you know Heraclitus described the rheology means everything flows that I mentioned translated into rheological terms by Renard again that everything flows you just wait enough time like I said mountain flows in front of god. So that is what it is so time is also important factor that is what I wanted to emphasize here. Not only the force apparently with the force it is not flowing but if you allow sufficient time ultimately it flows.

So you have to understand the time as well. So rheology and processing two complementary terms so you have to understand the rheology a sense of rheology science of rheology quantify the terms and then you try to translate it so that you can manufacture the product. So that is how in every engineering with every material understanding rheology is a first stage. So rheology is the science related to the study of interrelationship between flow and deformation of matter and the factors causing the controlling the flow and deformation unless you understand the factors and even the factors how they are interrelated they are interrelated or they are independent variables that is also very necessary. So you see here some of the fluids apparently you do not see honey you see this is a honey. I am sorry this is not coming exactly what we put it here but it is a honey flows very easily you all know like a solidus type of a character also it has little bit but you see this material which is a magnetic putty that same silly putty you have a magnetic material you see how it dances basically and you see the example of the dough.

So all are basically kind of a polymeric fluid whose behavior is not exactly same as you can understand or see for a Newtonian fluids say for water oil etcetera etcetera so this is essential. Now how the rheology I can translate where to the process inside. Processing means like you are riding on a tire how the tread pattern is designed how the side wall is designed how it is fitting that big part where it fits with the rim is designed and then how you assemble it the whole story of manufacturing it tire is actually a one one unit operation you can call it like a processing. So similarly so if you want to make a chair plastic chair say for example that plastic chair has to be made by certain processes maybe injection molding say. So you make a thin sheet of plastic packaging material you go for blow molding say for example make a bottle out of it for a paint point of view you are trying to make a paint and that paint you really have to paint on by the help of a brush or a spray on a well and you are making sure that it does not really sag before I mean all solvent goes out and then it has to be permanent and it has to be aesthetically also good otherwise nobody will buy your fence.

You make a material apparently you given a shape that shape is apparently comes up but it has lot of surface roughness would you buy that material question is no. Now from a engineering point of view what I have to understand what we have to understand we have to understand what is the factor that is giving the me the surface defects surface roughness and that if I can take care in the design of the processing apparatus and the parameters like temperature pressure etcetera etcetera or the design of the die or screw we can really manufacture a product which is flawless and a glittering shining surface so obviously it will be sold out it will have a industrial value. As you can see here in the cartoon that that some of the things are getting manufactured by injection process here this thing you cut it after that you get the product. So same is that case most of the cases polymers are not pristine before manufacturing it has lot of ingredients in it. So for example it has a filler it has a pigment it has a antioxidants they are in different states some are in liquid state some are in the solid state and some are of course inorganic in nature some are organic in nature some are even in the gaseous state.

Suppose if you are manufacturing a foam or sponge you have gaseous gaseous embedded into the solid also. So to that you have to do the mixing properly you have make the maintain the homogeneity otherwise point to point there will be you know there will be difference in terms of you know its property attributes its finishing its forming and many of the material like thermosetting material that includes, thermosetting resin as well as rubbers that needs after doing the final assembling after the unit operation assembling it to a given product safe that you cure it you have to really put it under pressure and temperature to manufacture that product example as I mentioned it to tire. And this is typically giving a calendar machine where you make a continuous heating profiles. So ultimately what it is happening your polymer either in the solid state or, in the solution state textile you are making you have to spin it to make a you know unit fiber from fiber you make a yarn to make a rope or a textile material say. So that basic material is manufactured by a process called spinning.

While spinning you can do solution spinning or you can do melt spinning also. So rheology or flow of the material in the nozzle while spin in the spinneret is very very important. So that is why these two things rheology and processing are not in isolation they are combined. As you understand rheology you cannot process it you process it you want to do the betterment you have to go back again understand the rheology fine tune and do the you know processing of operation purified change your machine design maybe change the parameters come up with a more purified product. So that is the essence of it.

So now very very quickly, let us try to understand the process of deformation and quickly try to see the classification of flow. See deformation I can make it on a solid we can have a elastic deformation and that can be again very very transient or instantaneous or it can be reversible deformation. So based upon that I can categorize it Hookean, non Hookean. Hookean stress is proportional to strain. So I am not going to that at present because at present context will be flow not the deformation in the solid state.

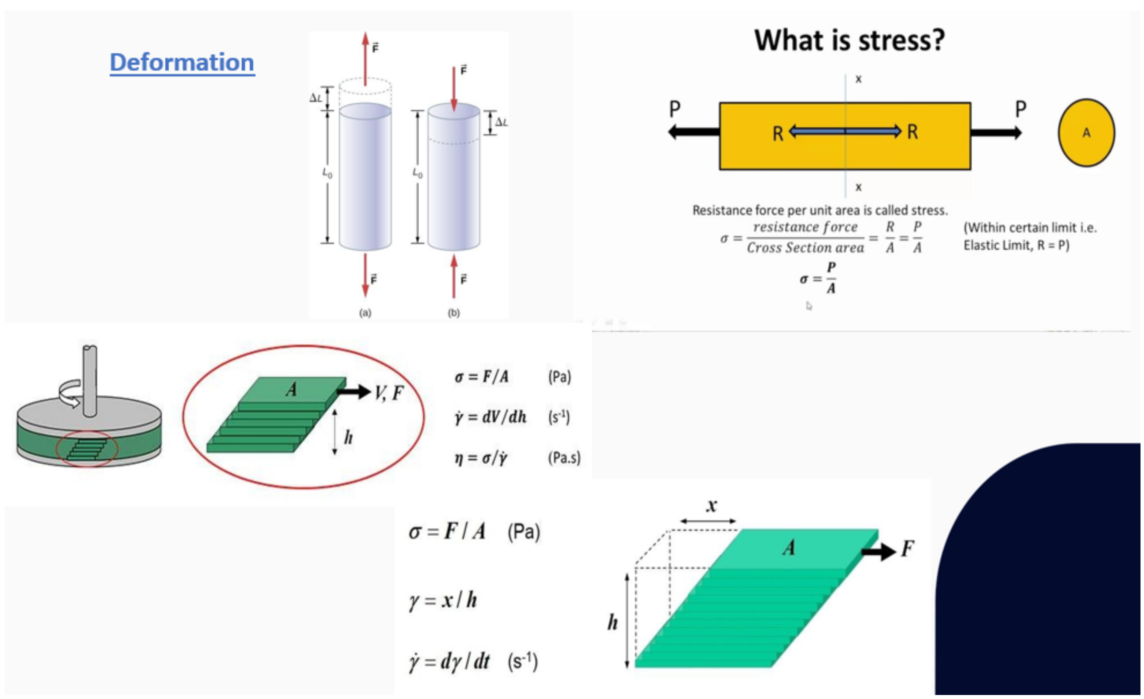
So in the flow again it can be irreversible and permanent deformation. So you can understand while the deformation was part of it most of it was reversible recoverable in solid state say rubber in the solid form but rubber before curing in the molten form it is if you flow it its flow is going to be most of it is you know irreversible deformation is irreversible. So based on that the fluid I can categorize into two, one is Newtonian another is non- Newtonian. Again Newtonian is a is a ideal gas like ideal situation. So most of the fluids realistic fluids are like including polymer solutions suspension those are all non Newtonian.

So non Newtonian again can be viscoelastic that means it has elastic property embedded maybe less but little elastic property is there it still has a memory effect. But another can be non viscoelastic but again viscoelastic material if you look it at from there you can have a further classification in terms of time dependency directly it can be you know time dependent like rheopectic or thixotropic and time independent class there are lot of but two prominent ones are pseudo plastic and dilatant. So there is another fluid called Bingham fluid there are some fluids which are called Senn-Wenant type of a fluid I will classify I will show you how it behaves. But nonetheless this is the tree how you classify the flow of a polymeric material in general. Now let us first I was talking about deformation deformation deformation.

So let us quickly try to understand various types of deformation. So let us take a block cylindrical block here I can put it from up and down the force. So it is called compression. I can do this arrow you can arrow mark where I am trying to extend it you call it like So I get a block I am putting force like this side wise you call it shear. You get it just followed by this pen I am giving a torque here.

It is a torsion. I have a beam I am trying to put load here supported here and it is called bending. So you see this point this force direction just try to follow you understand all different modes of deformation starting from compression, tension, shear, torsion as well as bending deformation. So maybe there they can happen they can be there in the combination forms also. Say for example you are trying to measure a shear rheology your fluid is getting extended as well. So it is called extensional viscosity I will come down there I mean shear viscosity as well as extensional viscosity.

So anyway viscosity is resistance to flow by the way. So if you look it at the deformation it is typically different modes of deformation you see is a little bit of torsion here. But ultimately if you try to understand this particular green color as a material you can divide it into certain layers and upon application of this shear force here. See this is getting this large if it is a stack of card just put that force it is going to get bit dislodged. So now some of the parameters let me alter sigma which is stress is a force if you know the how much force you are putting in force by area.



So always stress is force upon area and then there is a strain rate it is actually velocity gradient dv/dh, h is this direction thickness direction wise. This is called you know gamma dot, gamma is for the strain per time. So you can define viscosity as a this shear stress divided by rate of shear. Obviously the unit will be Pascal second, because sigma is a unit of Pascal Newton per meter square. So you can see all this definition even gamma what I call it as a strain which is nothing but this x, this is the x the deformation you make it divided by h.

So this is called shear strain. Even if this symbols I have used 'sigma', sigma generally used for tension notation actually is a 'tau' in shear way. So when I talk about a shear stress so stress always notation in shear it is 'tau' in tension it is 'sigma'. And when I talk about strain is gamma is a strain and then sorry shear stress is shear 'gamma' yes and in tension it will be 'epsilon'. So likewise is a general notation that is followed but nonetheless you can use either way can do it exchange rate all means all the way same sigma or tau is always for stress and gamma and epsilon is always for strain.

So this is how we define stress. So only one thing you must understand here you know the quantity as a scalar vector and tension stress or strain is a tension because area is involved scalar it has only the value no direction vector as a value and its direction, tension value direction at area involved basically. So shear when I talk about its involving area so you can think about a 3 by 3 matrix I will elaborate later.

Flow and Deformation Parameters:
Shear Stress, Shear Strain, Shear Rate

✓ **Shear Stress:** **Force per unit area.**

- **Symbol: τ Unit: Pa (SI)**

✓ **Shear Strain:** **Relative deformation in shear.**

- **Symbol: γ Unit: Unitless**

✓ **Shear Rate or Strain Rate:** **Change of shear strain per unit time.**

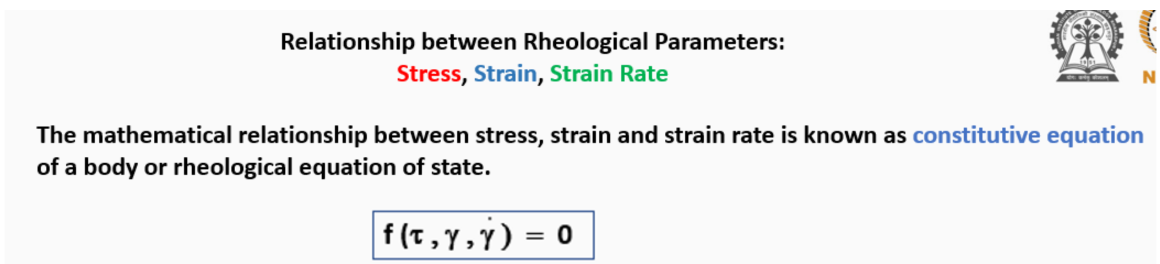
- **Symbol: $\dot{\gamma}$ Unit: [1/s] = s^{-1}**

So again very very quickly the notations and units symbol tau here it is corrected this is false shear gamma for strain gamma dot is for rate of shear rate of deformation. So similarly if I put it again to clarify you here I will put in place of tau will be sigma remember when I am talking about tension mode is mode of deformation is tension here.

I will put epsilon here and rather than gamma dot I will put gamma dot.

Gamma dot is nothing but d gamma dt is the d epsilon dt. So obviously strain does not have a unit so its unit is second inverse this is unit less as I mentioned strain and stress is always in SI unit if you think about Newton per millimeter square obviously in CGS unit its dyne per centimeter square so that is the unit conception of it. So three important parameters again as a recap stress it can be shear or tension as you can alter it whatever mode of deformation you chosen. See it is shear which is chosen here in this slide so I call it shear stress I call it shear strain I call it shear rate. So this should be clear you should not have any confusion about this so far.

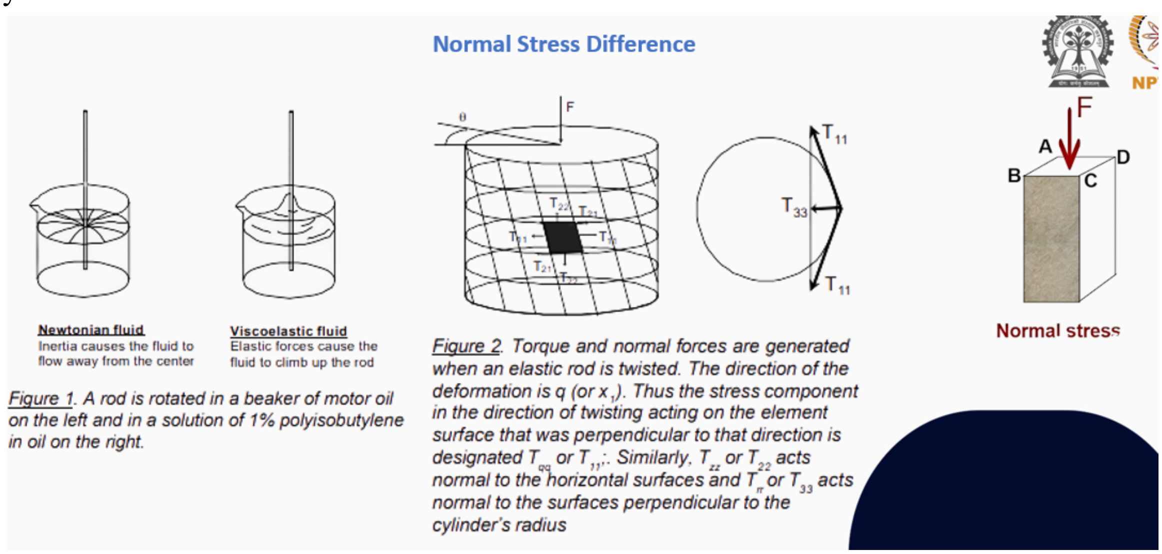
So there is some equation some relations which you call constitutive relation that you must understand because we will be using them whole lot towards the end. So it is a function mathematical function that deals with again shear stress, strain and strain rate. So that kind of equation is called constitutive equation that you should not forget. So the science of rheology is developed on this. So how it is done? You get experimental results experimentation is in rheology called rheometry we will elaborate on that.



So experimental data to develop empirical correlation that is one of the ways or theoretical analysis of the response of the system to applied stimuli. So then you can really isolate what are all parameter involved and try to formulate your constitutive equation basically there. And then theoretical analysis involves the relationship between stress, strain and strain rate tensors against tensors all are tensors not vector anymore. And then they are highly complex generalized equation I am not going into that much of mathematical rigor in this particular course I am telling you. I only will cover whatever is bare minimum necessary those mathematics will be dealing here and we will try to see the application of it.

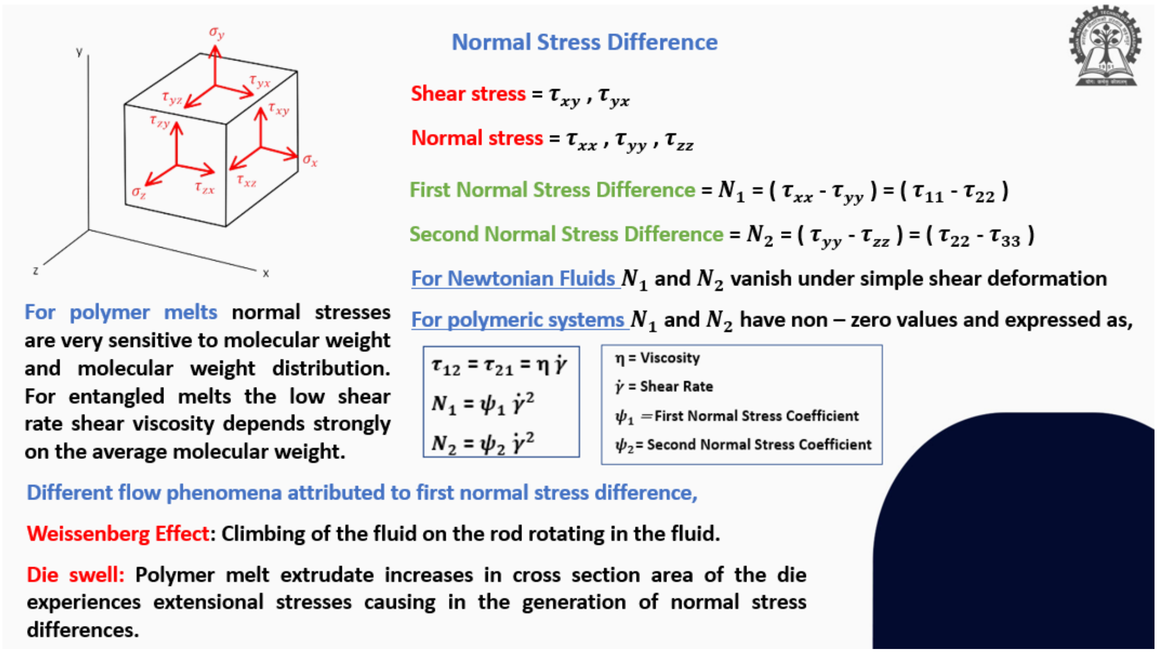
That is our goal of this course in particular as I mentioned in the introductory session also I mentioned that there are some of the rheological class which has lot of mathematical rigor that particular things we are trying to avoid here. So that a beginner with 10 plus 2 standard of knowledge will be able to understand or start a beginner can start from this course particularly on rheology that is our motto here. Then the equations give better insight into the combined effects of different types of stresses and corresponding response. So you can look it at different forms of stresses different types of tensor form of it in plane stresses so like that you can realize different form of stresses how the flow or deformation behavior is happening in a material. The experimental approach results in simple applicable equations containing few material parameter and constants.

So that is where ultimately we will be boiling down from our experimentation and they are highly important in finite element analysis. So these things actually these results after getting a rheometric results will try to come up with a constitutive equation and that constitutive equation will be borrowed in the simulation platform and we give the accordingly different boundary condition it can be flow boundary condition like the rheological boundary condition it can be thermal boundary condition and then we will try to see the solution. So that way we will be designing the components of the processing equipments like a die, a mold that design part will try to do at the end. At this stage one must understand what is so different polymer solution or you know polymer melts which is called normal stress difference. See a simple experiment you can do in a beaker you put water and try to put a rod stirring, rod let us start with a mechanical stir you will see vertical down vortex for water.



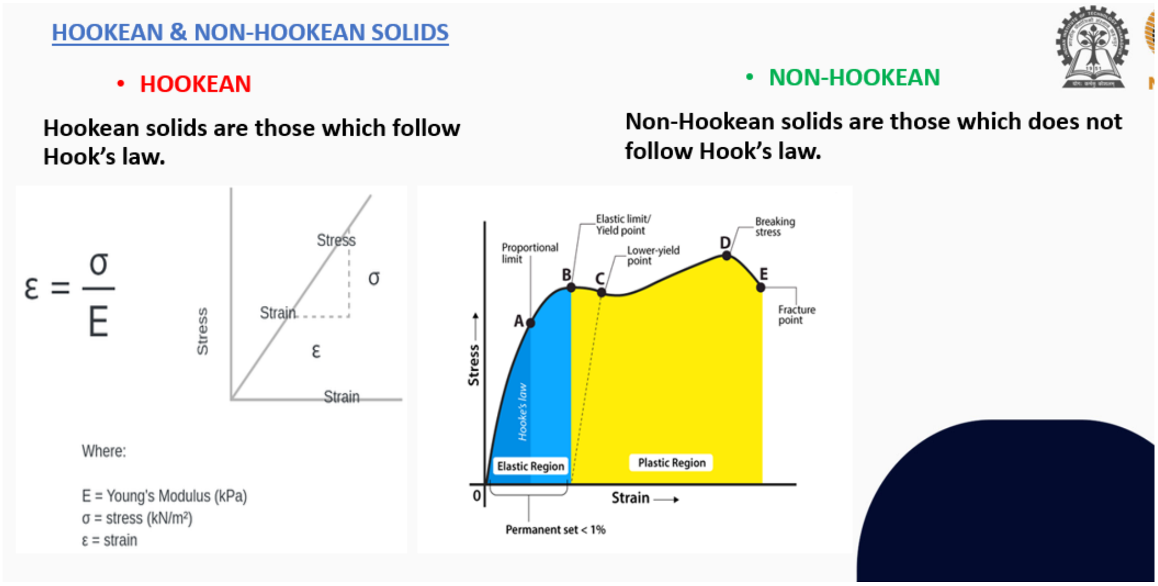
However if you do it in a polymer solution or polymer melt you will see rod climbing effect and that effect is happens with all viscoelastic fluids basically. You can do the theoretical analysis layer by layer the tensor form of it and you will able to see the finally this what is giving you the lift off what is the component of it. So you can easily actually take this problem of it is called generally the weisenberg effect basically and you can see it very easily that the normal stress. So you are deforming in one direction xy plane the z direction there will be some sort of a force that will be generating that is why it is climbing up. So same thing if you extrude a polymer through a small oriface of die we will try to see after it extrudes it try to swell it is called die swell.

If you calendar a rubber sheet or plastic sheet you will see after it extrude the width wise it will try to shrink it is called calendar shrinkage. All these things happen because of this normal force difference I will elaborate little bit on further. So now again this is the normal stress. Since here stress is cross x y y x so if you consider a matrix involving this tensors.



So this actually stress components basically. So this normal component is in the matrix form the diagonal component of it and that is what it is called you know tau xx tau yy tau tau zz. Now difference between tau xx and yy is called first normal force difference and difference between tau yy and tau zz which is also abbreviated tau 22 minus tau 33 is called second normal force difference. For Newtonian fluids n1 n2 vanishes simply for polymeric fluids they are non zero and actually this tau 12 n1 and n2 can be calculated if you know the shear you know shear rate and that depends with the function psi and shear rate square basically. And actually I will talk about later how you actually calculate out this normal force I mean this is called stress first normal stress coefficient. So psi 1 and psi 2 there first and second respectively basically eta is obviously the viscosity of it.

So that is what is the bottom line. So again this Weisenberg effect what I told you it is called otherwise rod climbing effect also and die swell I already elaborated specially in the time of extrusion the swelling that it happens for all polymers including plastic rubber it is little bit more you call it die swell. And the second normal force difference actually gives the surface roughness that I elaborated. So if you have a you know hold on how much is my second normal force difference and how I can take care of it. So if I can effectively reduce that difference second normal force difference and obviously I will not have much of surface roughness like a what a what except it goes the surface goes very very smoothly that does not happen in case of polymers. So this is what I told already for polymer mills or polymer solutions it happens.



Again quickly to Hookean and non-Hookean again it is not our subject matter here but you can see I mean stress by you know strain which is called modulus is always linear for While for a non-Hookean it happens in the plastics and most of the polymeric materials you do not get a linear behavior that you may get it from you know classical elastic material like steel or ceramics you get something called elastic limit proportional limit yielding and then it breaks finally for a plastic say for example. So those you categorize where the linearity is gone stress versus strain you call it non-linear. So I am not going into the details of it for the timing. But try understanding a Newtonian fluid like what are it obeys. Newtonian fluid is defined as one of the constant viscosity with zero shear rate at zero shear stress that is shear rate is directly proportional to shear stress that means viscosity tau equals I mean shear stress equals to viscosity multiplied by du/dy, du/dy is nothing but is a gamma dot as I defined.

Newtonian Fluids

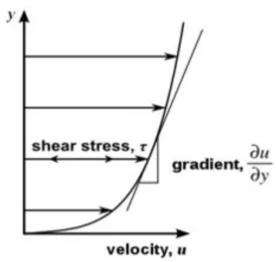
When a fixed and constant stress is applied to a liquid or fluid body, it undergoes continuously increasing amount of strain or deformation which is non – recoverable on withdrawal of the stress.

A Newtonian fluid is defined as one with constant viscosity, with zero shear rate at zero shear stress, that is, the shear rate is directly proportional to the shear stress.

A liquid is thus a material of zero yield value in which the strain is a function of stress as well as time i.e,

strain = f(stress, time) or $\gamma = f(\tau, t)$

Newton's law of viscosity:



Viscosity, $\tau = \mu \frac{du}{dy}$

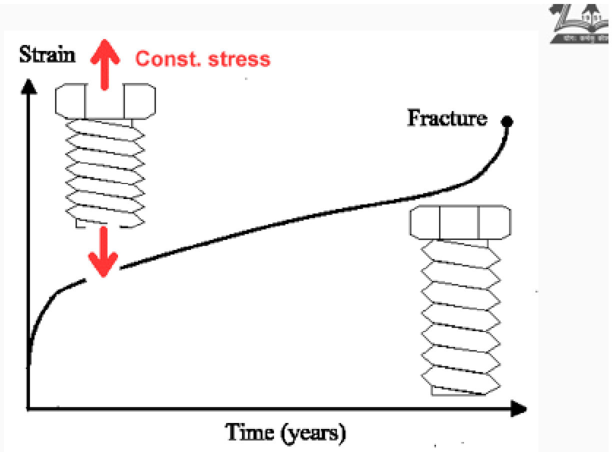
Where,

μ = Dynamic viscosity

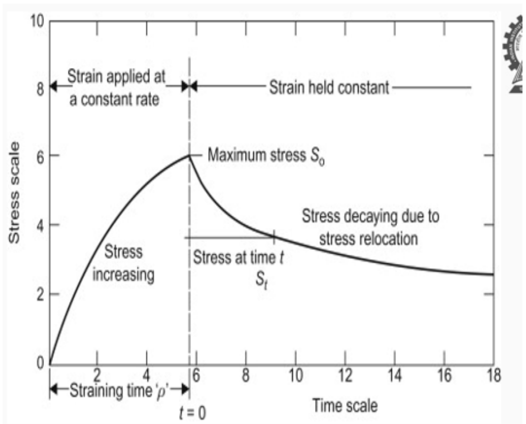
τ = Shear stress= F/A

$\frac{du}{dy}$ = Rate of shear deformation

How you get it? You see a fluid you can think about a layer by layer and through velocity gradient you can get it from here by plotting with the velocity and from there you can have it the shear rate i.e rate of shear and simply speaking if I plot viscosity with shear rate it does not change. So that is that if I plot shear stress say gamma, tau versus gamma dot is going to give you a straight line behavior and that is a typical of a Newtonian fluid. Creep I am not going into the details of it for the timing.

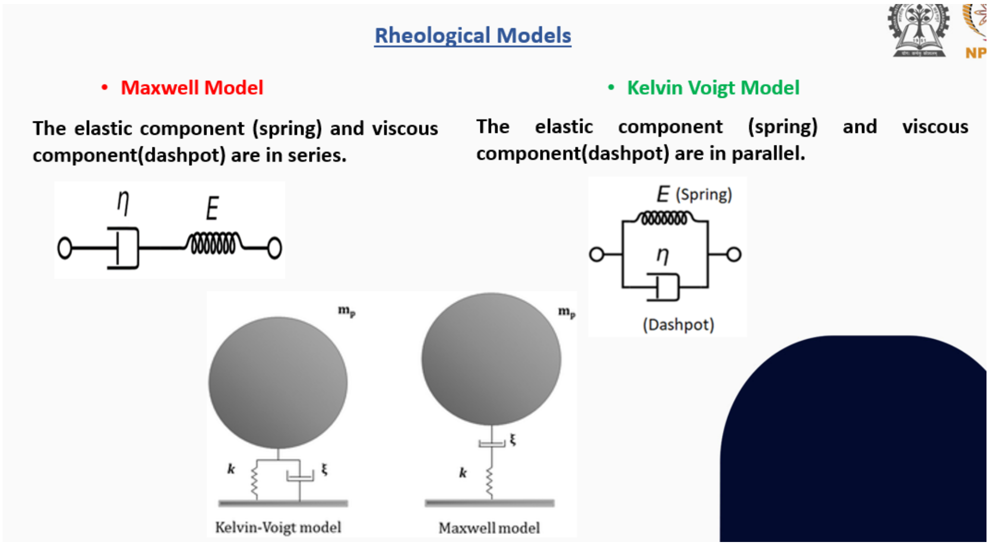


Creep and stress relaxation are two viscoelastic properties. See for as I said for Hookean solid 'E' is a constant, modulus is a constant it is independent of time but for a viscoelastic fluid 'E' is a function of time. If 'E' is a function of time, 'E' is what? modulus is what? Stress upon strain. So I write E as a function of time equals to stress which is a function of time by strain which is also a strain. So I can do some experiment where I can keep either one constant of time. So let us apply a shear stress very instantaneously or other way round Ican apply shear strain very instantaneously.

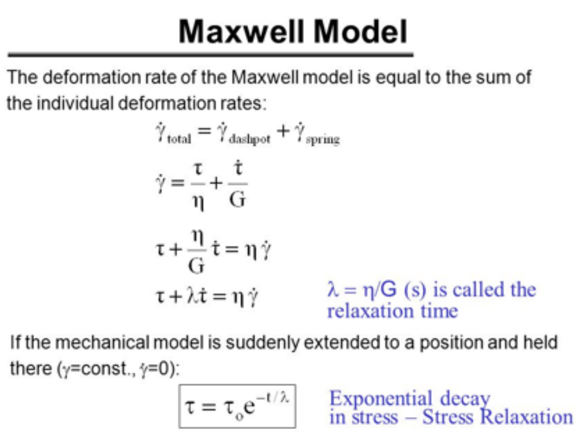


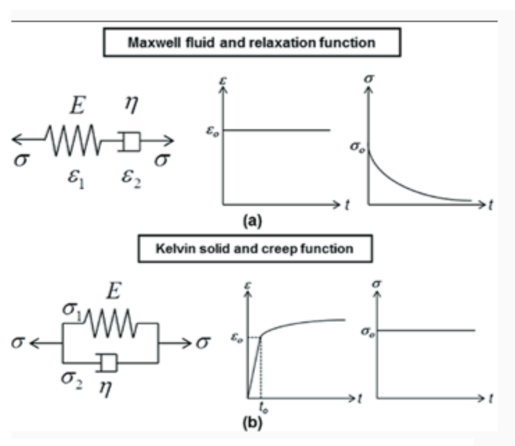
So one is called if you apply shear strain instantaneously that means then shear strain is that means I can write is a gamma 0 independent of time and that experiment is called stress relaxation experiment. If you do it other way round that means if you make it like tau 0 independent of time and try to see if formation as a function of time you call it creep experiment. So these two experiment actually are very very essential understanding the viscosity of a polymer. And actually they bear certain relation I will talk about as and when required actually they are related together in a different space. Laplace transformation of J is called compliance it is inverse of modulus that way is a modulus shear modulus equals to 1 by p square.

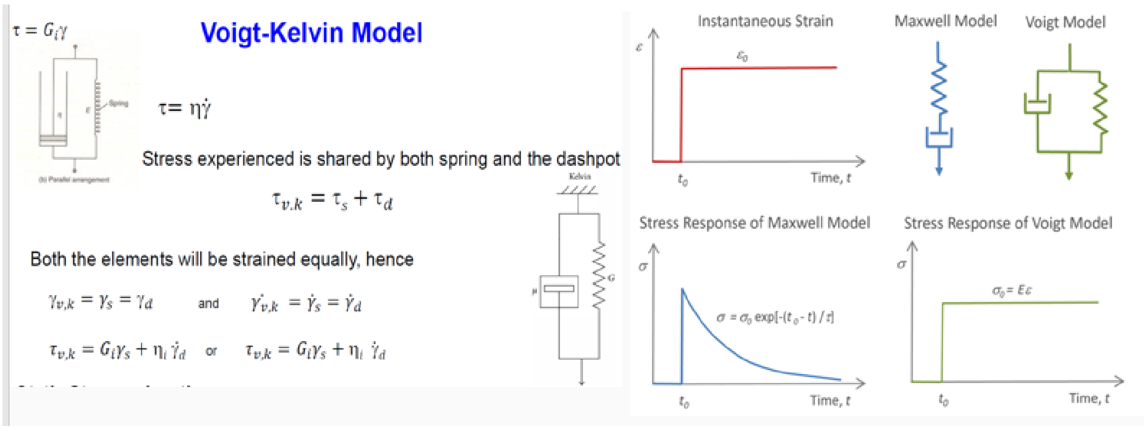
So they are related in Laplace space. So I am not going into the act complication presently but you understand one thing I am trying to make intentionally one time independent one and I am trying to see one I mean out of stress and strain and trying to understand it. So stress relaxation as I mentioned it to just other way round in this case you make strain independent stress as a function of time and you try to see the how it behaves. So I am not going into the details for the timing just to I mean give you some idea about it because it has lot of relevance to flow both the cases flow of the molecules obviously in the solidus behaviour in the solid state basically. So again you can understand there are two properties in one hand your polymer behaves like a fluid that means it is irreversibly flows and another case it has a elasticity that means flows but it is recoverable. So you are getting a viscoelastic property which is combination of those classical example is your motorbike soccer.



See what it has actually you have a spring and you have a dash pot which is nothing but in a piston you have a fluid and with in which the piston goes on up and down and this represent liquid behaviour this represents the solid behaviour and your final property is a is a collate of solid and liquid behavior at room temperature or lower temperature solidus behaviour dominates, at higher temperature liquid like behaviour dominates, but after all it is always viscoelasticity.







So, viscoelasticity is a property of a material that exhibit both viscous and elastic characteristics when undergoing deformation and viscoelastic materials have elements of both of these properties such as exhibit time dependent strain whenever time dependency is coming into picture and that is why the fluid type of is embedded, because this element flows as a function of time this is classically Hookean solid it is independent of time. So that way viscoelastic material exhibits both of these properties and polymer, biopolymer, metals at very high temperature are the classical example of those. Quickly into the models as I mentioned it to you spring and dash pot they may be in a serial combination you call it a Maxwell model and spring and dash pot in a parallel combination you call it a Voigt model. So with that viscoelastic behaviour at a first place as a beginner you can understand.

So I am not going into that details that for but again if you just try to solve the I mean try to see the relation between the shear rate, stress and shear rate I mean strain you end up having a relationship which is called constitutive equation. So similar so viscoelastic I mean Voigt model also you end up having a relation which is called you know constitutive equation corresponding to Voigt model and with that you will be able to if you now perform the creep experiment or you perform the stress relaxation experiment you can get those based on this model what is going to be the predicted response of it. Nonetheless, let us understand up to this today because we are not going to go that far from here because our motto is not to teach you viscoelasticity at this stage at greater length what I am going to teach about a basic idea about how what is the origin of solidus behaviour coming because this component this is the spring component out here and that is going to give you actually that solidus behaviour embedded and that is why when it comes out unlike a water molecule it tries to shrink, as it shrinks it will try to increase swelling in the you know diameter of it and die swell happens as simple as it is.

So, we will try to look into details but for today up to this there are lot of good books classical books available so you can consult the applied rheology in polymer processing by Professor Gupta our Professor here from Rubber Technology Centre, ex Professor.

Plastic materials and flow properties of polymer melts by J.A. Brydson. In the next class we will introduce you some more fundamental books on rheology. Till then let us conclude very quickly, rheology is a science of flow and deformation of matter and describes interrelations between these two parameter once again force, deformation and time and that is what constitute the constitutive equation basically and processing how it is related to the geology I try to give you some glimpse of it just introduction of it for a Newtonian fluid you see viscosity mu or sometimes designated by eta also is shear stress is proportional to the g u g y which is nothing but gamma dot. So this was Newton's law of viscosity Hookean solid conception I elaborated little bit definition of modulus also I have given of course creep and stress relaxation very briefly I introduced those keywords just remember the keywords and try to go back read little bit on Maxwell and Voigt models that is what you have to do it after this class and then Maxwell and Voigt model we talked about. Now we will go into the details of the fluids and its model particularly for complex fluids like non Newtonian fluids that we are going to talk about till then wait for it. Thank you very much.