Rheology and Processing of Paints, Plastic and Elastomer based Composites

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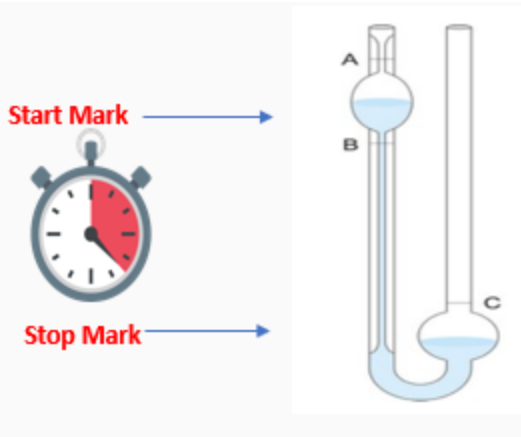
Lecture 09
Ostwald Viscometer, Brookfield Viscometer, Falling Piston Viscometers,

Welcome to NPTEL online certification courses on Rheology and processing of paints, plastics and elastomer based composites. Today we are in week 2 lecture number 2.3 and the content is Ostwald viscometer, Brookfield viscometer, falling piston viscometer, falling ball viscometer, MFI, plastometers and Mooney viscometers. So, today we will be grossly covering the concepts on Ostwald viscometer, then bubble viscometer, then Brookfield viscometer, falling piston viscometer, falling ball viscometers, melt flow index which is abbreviated as MFI, Mooney viscometer and of course, the plastometers. Again if you try to have a you know have a look into this topics grossly. Some of the keywords given here U-tube viscometer, then Poiseuille's law, BYK Gardner bubble viscometers, kinematic viscosity, shear stress, shear rate, Norcross viscometer, thixotropic liquids, viscous drag force, buoyant force, gravitational force, Reynolds number, terminal velocity, thermal plastics, melt flow rate, delta Mooney test, cost time and shear rate index.

So, let us start from the Ostwald viscometer which is a very rudimentary viscometer you might have used it some form or other during your undergrads ok. And even in the secondary school level also somewhere you might have seen the demonstration of it. So, Ostwald viscometer is actually a class of U- Tube viscometer or capillary viscometer and which is a device to measure the viscosity of the liquid with a known density ok. So, if you know the density of the fluid and of course, normally it is compared with a viscosity of a fluid whose viscosity is well known, we can call it a standard basically.



Normally water is used as a standard in many cases. So, the method of determining viscosity with this instrument consists of measuring the time. So, time is the only variable because density you know. So, for a known volume of the liquid the volume contained between two marks as you can see, from the cartoon right side there is a start mark and there is a end mark. So, within that the fluid has to flow through a capillary under the gravity basically ok, and you record the time.

So, the instrument must first be you know calibrated with a material of known viscosity like normally as I said pure deionized water is used ok. And knowing the value of the viscosity of one liquid one can easily calculate the viscosity of the unknown liquid of course, density must be known. So, if eta 1 is the viscosity you want to determine and eta 2 is the standard liquids you know viscosity and rho 1 and rho 2 are the you know density of you know two liquids and t1 and t2 are the time, t1 is the time for the liquid you want to really estimate the viscosity and t2 is the of course, the liquid whole viscosity and density of course, are known. So, this is the formula you do it. So, if you go back how do I get this formula of calculating it originates from originally Poiseuille equation, Poiseuille law ok.

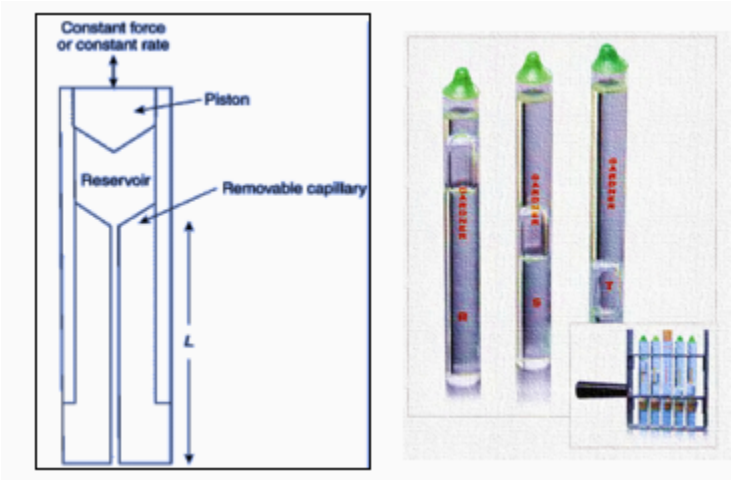
$$\eta_1 = \eta_2 \cdot \rho_1 t_1 / \rho_2 t_2$$

$$\eta = \frac{\rho g t}{8 l \pi r^4}$$

So, from Poiseuille law you can very easily calculate out the viscosity that is absolute viscosity basically. So, eta equals to rho*g*t by 8*L*pi*r to the power 4 where eta is the viscosity of the liquid you want to measure, rho is the density of the fluid or liquid ok, g is the acceleration due to the gravity, t is the time taken to flow through a definite you know length of the capillary, L is that length of the capillary and r is the radius of the capillary. So, not only that that Ostwald will always measure the relative viscosity or otherwise one viscosity is known with reference to that you calculate you can pretty well

calculate the absolute viscosity of the fluid you want to do it, fluid means which is flowable it can be liquid it can be gas ok. So, this is what is the concepts of Ostwald viscometer, I am not going into lot of other who will hold other form of you know U-tube viscometers, but the essence is to get rid of any sort of a air pressure by all means or any sort of a drag basically ok. So, these things are pretty well used the Ostwald viscometer to calculate out the intrinsic viscosity of the liquid following Mark-Howink equation and which can be well correlated with the molecular weight of that.

So, that has been taught to you or otherwise those are the very basics you can refer to Mark-Howink equation, how to calculate the specific viscosity, relative viscosity and of course the intrinsic viscosity ok. So, this is the Ostwald viscometer the essence of it. So, there is another type of viscometers which is called bubble viscometer. See obviously all of you have seen if you have you beat it and try to create a bubble ok if you have a fluid of definite level the bubble will form you will try to climb up or else if a bubble can be gone from up to down by some extra pressure differences ok. So, the movement of the bubble across the fluid depends on the viscosity of the fluid.



So, if the viscosity of fluid is high and high this movement will be sluggish that is the essence of it ok. So, following that there is a viscometer which is called bubble viscometer which is normally from the I mean inception it has been practiced for resin and varnishes which are of low viscosity material relative ok. Those are used to use by this process called bubble viscometer. So, BYK Gardner bubble viscometer are used to quick determination of kinematic viscosity. I already defined the kinematic viscosity before you and absolute viscosity essence of it.

Of no liquids such as resin and varnishes ok. So, they are used to measure the viscosity of a fluid by absorbing the flow rate of the bubbles through the capillary tube or a porous medium basically ok. And these viscometers are based on the principle of flow rate of

the bubbles as it is influenced by viscosity of the liquids. So, this is the conception of it ok. And the time required for the air bubble to raise or rise in is directly proportional to the viscosity of the liquid ok.

And the faster the bubble rises the lower is the viscosity as simple as it is. So, this viscometer comes with the different types of capillaries ranging the size marked size from like as you can see from here A5 to Z10 different types. So, 4 different tube sets covering the viscosity range see very low viscosity 0.05 strokes to 1000 strokes that is the viscosity range all these different types of tubes will cover. So, it is specified which grade of tube you must choose of capillary.

And the basic let us have a look into the basic design of the you know viscometer here. It consists of a glass or transparent tube of capillary section and with a large reservoir this is the reservoir here. And with that you know constant force here you the piston with that you try to make some you know bubble here and that bubble you proceed to flow through the capillary. So, that is how entire the distance of the capillary here to here the length is specified how much time it really spends to bubble to cover up. So, the capillary section is narrower than the reservoir as always and creating a pressure difference that drives the bubbles down there.

And to measure the viscosity using a bubble viscometer the fluid is introduced into the reservoir section a constant pressure or a constant flow of gas typically air is applied to the system. And the pressure difference causes the bubbles to form and flow through the capillary. And the flow rate of the bubbles is measured by observing the time it takes for certain number of bubbles to pass a predetermined point that is what I told essentially. So, there these are the different types of you know capillary combinations you can see it. So, this is one of the ways, but once again this particular viscometer is practiced for resins and varnishes.

Next is Brookfield viscometer and essentially Brookfield viscometer measures the torque required to rotate you know a rotor inside a you know fluid. So, think about you all of have probably done that experiment to do some reaction in a beaker or round bottom flask. So, what you have you use a mechanical you know stirrer instead of you just imagine you are using a stirrer physically that does not have a motor wear. So, you have to literally rotate it inside the fluid. So, if you happen to rotate it depending on the viscosity higher the viscosity you need to give more and more torque to make them rotate at the fixed RPM.

So, that is the principle of it. So, a spindle is rotating inside a fluid at a constant RPM and you try to measure the torque of a selected spindle. And this value as I mentioned

the torque value here is directly proportional to the viscosity of the fluid. So, this is the principle of it. So, the viscosity of the fluid can be described as the internal friction of the fluid and the friction is apparent when the layer of the fluid is made to move with respect to each other.

So, that means there is definite shearing happening. And if you look it at from the processing point of view this shear force is essential for say for example, pouring a fluid, spreading a fluid you are applying a paint on a wall say, you spraying a fluid, mixing etcetera etcetera. So, this particular you know understanding shear force is very very important. Now, thing is that how do I calculate the viscosity using the Brookfield viscometer you have to go back to the Newton's law of viscosity which says that viscosity is actually equal to the shear stress that means force divided by area divided by the rate of shear that is dv by dx which is essentially a velocity gradient between the fluid layers. So, if you really try to calculate the torque I mean a torque with automatically the rotor will measure it.

The equation below was developed by Newton is used to calculate the viscosity of a fluid:

$$\eta = \frac{\tau}{\dot{\gamma}} = \frac{F/A}{\frac{dv}{dx}} = \frac{\text{shear stress}}{\text{shear rate}}$$

F/A - force per unit area
dv/dx - change in speed at which the intermediate layers move with respect to each other.

The following equations can be used to calculate the shear stress and shear rate:

Shear Stress

$$\tau = \frac{M}{2\pi R_b^2 L}$$

M - torque input
R_b - radius of the spindle
L - effective length of the spindle

Shear Rate for Small Sample Adapter

$$\dot{\gamma} = \frac{2\omega R_c^2}{R_c^2 - R_b^2}$$

Shear Rate for all other spindles

$$\dot{\gamma} = \frac{2\omega R_c^2 R_b^2}{x^2(R_c^2 - R_b^2)}$$

ω - angular velocity
Rc - radius of the container
x -radius at which the shear rate
***Rc should not exceed 2R_b for a well-defined shear rate.**

So, if the torque is m then shear stress can be easily calculated m by 2 pi rb square by L, rb is the radius of the spindle, L is the effective length inside the fluid of that particular spindle. Again from small to large adapter depending on the viscosity of the you know fluid under consideration the equation little bit gets modified if you look it at for a small adapter equation is of you know shear rate I mean so far I was talking about shear stress. So, shear rate equals to 2 omega into rc square by rc square minus rb square, omega is the angular velocity of the you know rotor here and rc is the radius of the container, x is the radius you can measure at different point vertically if you try to think up. For the other spindles the equation little bit gets modified. So, that is how you get that so this x factor is comes into that picture.

So, only one constraint is that that this rc that means radius of the container if this is the container the rotor radius I mean this rc should not exceed 2 rb. If it is more the liquid vortex will form more and more and your you know your evaluation of the viscosity will be more and more erroneous in that essence. And you can always refer the particular internet site is given here and you can refer back for more details. Okay. But nonetheless possibly the principle is clear to you, you are measuring the torque you know that at a given angular velocity you are doing from the torque you are getting the shear stress from the angular velocity and other geometric parameter you are calculating out the gamma dot which is the rate of shear.

So, you can have a you know shear stress versus shear rate across a range of you know shear rate you will be able to estimate. So, that is what the principle of this viscometer is. So, now there is another viscometer is a very precise viscometer which is falling piston viscometer. So, far we are talking about bubble. So, here is in this case again through the liquid one piston will you know move and from that movement a resistance to that movement in other word will give you the clue for the viscosity, Okay.

And this viscometer is called I mean the founder is Austen Norcross viscometer. So, this viscometer is also known as Norcross viscometer as well. The principle of the viscosity measurement is based on the piston and cylinder combination. Okay. The viscometer is a durable sensitive industrial device and very robust.

This is largely practiced in the paints and adhesive industries as well. The substance being measured is pulled through a clearance that is a gap okay between the piston and the cylinder wall into the space below the piston and as it is regularly lifted by the air lifting mechanism. Okay. So, as you can see from this cartoon okay there is the fluid the blue colour one and above that you have a you know piston and that gives you the motion once it goes in through the capillary you know the fluid passes through and you essentially measure that while it passes through the resistance it encounters. The assembly is held up briefly before falling to the shear of the liquid being measured and the viscometer is sensitive enough even see while it passing through time is a variable.

So, time dependent viscosity also you can monitor. Say for example, for a thixotropic fluid also you will be able to measure pretty well. So, such sensitivity this sort of a viscometer is having. So, the duration of the fall is used to compute the viscosity from the piston cylinder clearances and the viscosity controller determines the viscosity from the fall time okay. And the controller can set the time of fall to you know centipoise or cup seconds also known as the efflux cups basically.

So, quickly what are the advantages of this kind of a viscometer that means falling

piston viscometer. This instrument is common for industrial application since it is easy to repeat requires no upkeep and is unaffected by flow rate and the operating concept is very flexible, adaptable and perfect for environments involving process controls. So, that way this viscometer is very unique.

Gravity	:	$F_G = -\frac{\pi}{6}\rho_p d_p^3 g$
Buoyancy	:	$F_B = +\frac{\pi}{6}\rho_f d_p^3 g$
Fluid Drag	:	$F_D = \frac{\pi}{8}\rho_f V_p^2 d_p^2 C_D$

Where ρ_P is the density of the solid sphere
ρ_F - density of the fluid
dp - diameter of the solid sphere,
g - gravitational acceleration (9.8 $m|s^2$),
Vp - velocity of the sphere, and
C_D - drag coefficient.

As a corollary of falling piston there is another methodology it is called falling ball viscometer okay. Only thing is that you can understand the geometry of the monitoring device which is falling through the fluid is changing here okay.

The principle of viscometer is to determine the falling time of a sphere with known density and diameter within a fluid field inside glass tube. And the viscosity of the fluid sample is related to the time taken by the sphere to pass between the two specified lines on the cylindrical tube. So, it is looks like this okay. This is the cylinder and if you can see the force balance okay you can see there are three distinctly three types of force are acting on the you know sphere or ball here. What are the forces? FD is the viscous drag force, B is the buoyancy force and FG is the gravity okay.

So, gravity obviously acting downward if it is coming from there and then in the upward you have the buoyancy force as well as the drag force acting okay. So, net flow is net you know translation is because of the balance between this force okay. And the viscosity of the sphere which is falling through the tube is dependent on the viscosity of the fluid okay. So, the velocity is dependent on the viscosity of the fluid rather. When the sphere is placed in an infinitely incompressible Newtonian fluid it initially accelerates due to gravity as it obvious.

After a, B transient point okay a steady state will be reached. So, steady settling velocity at that or a constant terminal velocity will reach okay. And that is the point for the velocity to be steady that means no change in linear momentum happens. And the Newton's second law requires that the net force acting on the spheres that means because of the gravity in the opposite to that buoyancy and drag will equal to be 0, okay.

$$F_G - F_B - F_D = 0.$$

$$Re = \frac{\rho V_p d_p}{\mu}$$

So, that is the steady state condition. So, under that condition you have cruise on this three forces obviously what is going to be Fg what is Fb and what is Fd that means gravity buoyancy and you know drag forces. And finally, these are the parameters I do not need to you all know rho we consider the you know rho p is the density of the solid sphere rho f is the density of the fluid through which it is you know traversing and d p is the diameter of the solid sphere and g is the gravitational acceleration you know 9.8 meter per second square is the value and is the velocity of the sphere and c d is the drag coefficient that is very very important here. So, based upon that if we impose the steady state conditions in that case, Fg minus Fb minus F equals to 0 and that is where your streamline velocity you can consider laminar velocity you can consider that condition. So, drag force acts upwards and is expressed in terms of dimensionless drag coefficient and the drag coefficient is the function of dimension of Reynolds number again the Reynolds number because it is a laminar flow condition we are assuming okay.

So, Reynolds number can be interpreted as the ratio of the inertial force to viscous force as simple as it is okay. For a sphere setting in a in the viscous fluid the Reynolds number can be modified as Re equals to rho vd divided by mu okay. And then where mu is the viscosity of the fluid if the drag coefficient as a function of Reynolds number is known as terminal velocity can be calculated okay. So, drag coefficient as a function of Reynolds number if it is known the terminal velocity that is the vp can be calculated from there. And for the strokes regime Re less than 1 the drag coefficient can be determined analytically as this.

$$V_p = \frac{g d_p^2 (\rho_p - \rho_f)}{18\mu}$$

$$\mu = \frac{g d_p^2 (\rho_p - \rho_f) t_p}{18L}$$

So, CD is nothing but 24 by Re, Re is the Reynolds number okay. So, you can pretty well following that you can calculate out from these equations for Reynolds number and drag coefficient you can easily calculate out vp equals to g into dp by rho p minus rho f by 18 mu that is the equation you can easily I am not going into the detail derivation of it, but you one can very easily do from the force balance basically and invoking the Reynolds number into the picture. And the following work viscometer requires measurement of you know spheres terminal velocity usually by measuring the time

required the sphere for a given fall. So, ultimately the time factor is the most important factor here. So, if we measure the piston position of the sphere as a function of time and determine the steady state settling velocity for this we can calculate the viscosity from the equation given below.

That means nu essentially boils down in the condition Re less than 1 okay that is the strokes condition we imposed already into the system that equals to g into dp square into rho p minus rho f into tp divided by 18 L. So, that is the final expression and this is the this is how you determine knowing the other parameters you can pretty well calculate the viscosity. Another important viscometry is normally used for plastics and thermoplastics is melt flow index or MFI there is a definite ASTM standard ASTM D 1238. So, melt flow index what it is once again you have a capillary you put that in the reservoir your material under molten condition put certain weight and over a specified time normally the you know 10 minute time how much weight of the fluid is extruding out of the capillary. Of course, depending on the type of fluid you are handling say you if you do LDPE say for example, HDPE I2 is normally used it is close to 2 kg less than 2 kg 1.

8 some kg dead load is applied. For nylon say for example, you do it at even higher temperature like 190 degree centigrade, 210 degree centigrade and you try to use I5 that means you need more weight there. So, that is the standard says you refer to the standard. So, as you can understand it gives you a quick. So, lower the viscosity of the material more will be flow under a specified time 10 minute time. So, as simple as it is, but these days MFI machines are good enough where it can constantly vary the load and load means actually it is related to the you know shear stress.

So, shear stress and shear rate that lot you can generate with today's MFI machines. Those are the I will talk about more when I will talk about the capillary viscometer in details. So, essentially MFI is a rudimentary capillary rheometer none other than that and normally practiced from the inception for the plastics. Wherever you try to maintain a quality of a plastic you refer to what is the MFI. You have more molecular weight that means MFI is going to be smaller, more branching is going to be smaller, more straight lower molecular weight MFI is going to be you know higher and higher that means flow will be high.

I mean it is ultimately higher the flow you know lower the viscosity that is where it boils down. So, disadvantage of MFI it is a list it is also the least accurate method to obtain accurate and meaningful viscosity data in conjunction with MFI of course, you have to do capillary rheometer or cone and plate or cone and parallel plate geometry if you do it for. But as I told you today's MFI machines are much much good very close to your you know capillary rheometers it functions. And again I already told these are the

relations is again written what I told already and this is the machine looks. Here a thermometer bob where you can measure the temperature set the temperature meter control is there and then you apply a specified load to the piston and then through the capillary it extrudes out and over 10 minute wait you cut it and wait with a balance and that gives you the MFI.

So, melt flow rate is a indirect measure of molecular weight with a high flow rate corresponding to a low weight. So, that is the essence in plastics is mostly plastics and thermoplastics is used. See if I give you a fluid of high viscosity how do you check it? You try to apply tap it pressurize it and see how much it is deforming. And principally this tap is amount of force you are using for compressing the material if you can quantify and that is the that is what the viscometry or is called plastometers. And this is the first generation rheometer which mankind has ever discovered.

So, as I can you can understand you have to put a material inside two plates and try to apply a definite load at a given temperature you try to monitor what is the initial thickness and what is the final thickness after certain specified duration. And that indirectly gives you the clue for the plasticity or flowability at in opposed to the viscosity basically. So, the work of Williams led to the first parallel plate instrument you know parallel plate plastometer rather here. So, as I as you can understand it is a very simple and rudimentary technique. And remember one thing when you are compressing a material it actually is giving a very low shear rate operation like 0.

1 second inverse. But remember rubber you know plastics, fibres all even adhesive spends are pseudo plastic. So, it will be more relevant to higher shear rate when you process it say you do a you know transfer molding, you do a injection molding, extrusion something around you know 100 on, 100 to injection molding 10,000 second inverse. So, this machine does not really give you that clue what it is exactly going to happen at a high shear rate. And it is a very rudimentary in there in that essence and the very first type of first generation rheometer you can call it. So, I am not going into that details, but I can of course, show you there are two methods one is disc type test another is a plate type of test.

Only difference between a disc type of test that once you pressurize it since area remains constant there will be bulging on the pressure you know material and the pressure drops. While there is a plate type of material you have enough space the material bulges even if bulges it will it will fall under the pressurized zone basically. So, there are two varieties of it. So, I am not going into that details, but of course, there are as I mentioned there are compression zone and where you have a parabolic sort of a protrusion and you call it like a compression zone there. So, I am not going into that details of it, but nonetheless this is

the first generation you know rheometer mankind has ever discovered and measuring the force required to compress a test specimen to a given thickness at a given time as I mentioned it to you.

And of course, that force is directly proportional to the viscosity of the material. The next generation that means second generation rheometer that is the monoviscometer. So, so far so forth we are talking about when we are talking about a you know Brookfield rheometry we are talking about a fluid of low viscosity. Now, what we are talking about plastometer and this is a viscoelastic fluid we are talking about. So, that means, what it has a higher viscosity like something around 10 Pascal second or so.

So, in that case the first one was compression and second one was of course, you know applying the torsional force rotation. So, you have to embed your rotor inside the solid material you heat it out make it to a fluidic thing and try to rotate this you know rotor and try measuring amount of force required to maintain the same you know RPM of it and that is what the principle of this torque rheometer and muni viscometer which is by and large used in the rubber industries. So, this is what the viscometer looks like one of the cartoon one of the company manufacture monotex this days you will get it there and it measures a torque it is not a viscosity although it is called muni viscometer ultimately output of the machine is a torque and what is the torque value either 1 muni unit means 0.

735 pound force inch the torque or 0.083 Newton meter or 0.48 848 kg centimeter that is a torque of 1 muni unit. So, for raw material quality control always refer to what is the muni value and muni how you measure it? It normally measured as ML 1 plus 4. What is 1? You put a material and then try to wait for 1 minute for conditioning temperature equilibration then again you will allow it for 4 another minute 1 plus 4 at 100 degree centigrade measure how much the torque equilibrium torque you are getting. So, that is what the designation ML 1 plus 4 what is M? M for muni viscometer L for large rotor again there are there is a catch L for large rotor S for small rotor and depending on the viscosity of the material if your viscosity is way too high then you try to use a small rotor otherwise large rotor is a convention.

So, this is what is a muni viscometer. So, do not get afraid in rubber terminology rubber language of rubber when I talk about muni viscosity what it is? It is not actually the viscosity of it, but under a specified time a equilibrated torque that needs to rotate a rotor of a specific dimension of course, estimates specifies the dimension to maintain a constant rotational speed there. So, ML 1, 1 is the initial time of temperature equilibration then 4 after that 4 minute you wait till you get the final reading of it. So, that is what is ML 1 plus 4 significance and I told you the difference between small and

large rotor I am not going into that details about what the dimension, but you understood in inside a cavity which has a heating arrangement rotor will be embedded top and bottom it will cover the rubber will cover it and try to measure the torque value after 1 plus 4 basically. See this muni viscometer is also a rudimentary viscometer you do not get much of a viscosity versus shear rate neither you get a result of die well, but most importantly since it is a rotation inside a matrix once rubber gets cured cross linked there will be slippage. So, you get the data up to the time when rubber is just scorched or before scorching before vulcanization, but of course, so you calculate a delta muni which is a empirical parameter so that gives you idea about the muni value between two specified time and that gives you the ease of processing of that material.

Of course, you can calculate muni scotch that means, a rubber you put it in a muni viscometer at 100 degree centigrade you try measuring and you try to see after how much time 5 unit of Mooney value initial value it is raised up and that means, your rubber has just started cross linking and up to 35 unit it gives you idea about the cure time up to 35, I mean unit of rise of it, but after that what happened whether it is a reversion plateau or it is whether it decreases further remains stay flat or increases that clue you do not get it from Mooney viscometer and that invokes the third generation geometer which I will depict in the next class basically. So, let me read it out some of the stuffs the delta muni is a extension of muni used for empirical grounds as a general indication of the processability of a non-pigmented oil extended you know SBR elastomers. It quantifies the changes that occurs in the Mooney viscosity you know with time as a difference between the viscosities is recorded to specified time normally 1.5 and 15 minutes within that how much is the change happening. So, the difference between this minimum and maximum viscosity is delta Mooney and it is taken as a measure of the processability of the rubber higher the value of this difference better processability that is the bottom line as I mentioned cost time you can determine even the cure time also you can determine.

But there is one convention for butyl rubber instead of taking 4 minute you take it 8 minute because you know butyl rubber is a damping type of a rubber. So, get a steady state value it takes little more time. If EPDM rubber which has a plastic character instead of doing at 100 degree centigrade you rather do it at 125 degree centigrade that is the basic difference as you can understand muni viscosity. Once again I will say it is a very very rudimentary second generation viscometer to have more details more variants of it next generation variant of it please stay tuned up to the second classes. Next class we will elaborate on now what is the third generation, fourth generation counterparts of it.

So, these are the references I already told you. Again to conclude what I talked about today is the Oswald viscometer, bubble viscometer, Brookfield viscometer, falling piston

rheometer, falling ball rheometer, MFI, plastometer and its principle advantages disadvantages, Mooney viscometer, some how to express like ML 1 plus 4 at 100 degree centigrade or 125 degree centigrade. ML 1 plus 8 for mutual rubber. So, M again is a torque that you have to whatever measurement value you are getting. So, in the next class we are going to talk about ODR although I did not go into the details unit versus time graph I will elaborate it again when I will talk about some of the disadvantage why the next generation oscillatory rheometer came into the prominence that means ODR followed by MDA and MDR and you know RPA a little bit on the capillary rheometer we will try to show light on that. Thank you very much.