

Polymers Processing and Recycling Techniques

Prof. Abhijit P Deshpande

Department of Chemical Engineering

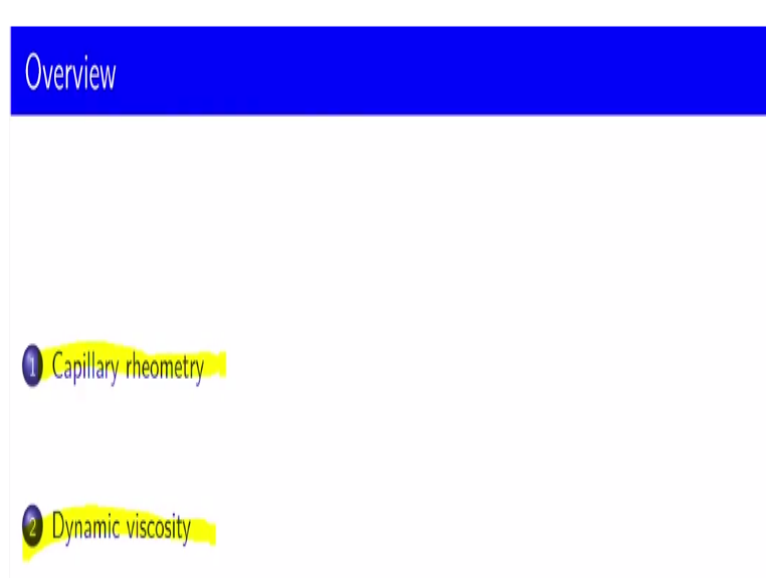
Indian Institute of Technology - Madras

Lecture – 83

Viscosity for Polymer Processing

Hello, welcome to this course on polymers. In the couple of weeks, we have been discussing polymer processing and recycling techniques and this is the last of the lectures which will focus on viscosity exclusively for polymer processing as one of the applications in mind and so the focus will remain on viscosity as a property for characterization in polymer processing.

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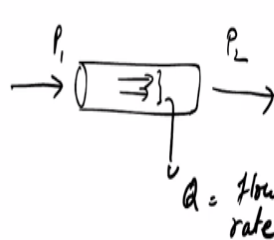
Capillary rheometry is used. The rotational rheometers have become quite common, but from a polymer processing point of view capillary rheometry is very important because of the high shear rates that can be achieved and as we have seen in case of injection molding or several other polymer processing operation, high shear rates are always present while in a rotational rheometer such high shear rates may not be always possible. The viscosity that is measured using oscillatory measurements is also quite commonly used. So we will look at both of these in this lecture.

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Capillary rheometry

For Newtonian fluid, Hagen-Poiseuille equation

$$Q = \frac{\pi R^4 (\Delta P)}{8\mu L} = \frac{\pi D^4 (\Delta P)}{128\mu L} \quad (1)$$



$$\frac{\Delta P}{L} = \frac{P_1 - P_2}{L}$$

pressure drop

So capillary rheometry is nothing but basically taking the fluid in a capillary or a tube and basically forcing it to flow through using a pump or any other arrangement. In this case, therefore the pressure at the entry is higher than the pressure at outlet and so fluid gets pushed through a capillary and so this $\Delta P/L$ or $(P_1 - P_2)/L$ is the pressure drop and what we can do is we can measure the amount of fluid through the flow rate and so if this were to be a Newtonian fluid, then the relation between the flow rate and $\Delta P/L$ is well known through this Hagen-Poiseuille's equation which is always studied in the first course on fluid mechanics. So, if we know the capillary size, the radius or the diameter and if we know the length of the tube and how much is the pressure drop that is there and the flow rate we measure, then we can in fact determine the viscosity of the fluid.

So that's how capillary geometry can be used to measure the viscosity of the fluid and in case of Newtonian fluid, this is straight forward. But in case of an unknown fluid, the viscosity is not just known, even the relationship between flow rate and pressure drop is not given by Hagen-Poiseuille equation and we cannot solve and get this equation because we do not even know what's the relation between stress and strain rate for that particular material. We do not even know whether we can approximate it as a shear thinning material, should we approximate it using a PTT model or should we use a Giesekus model, so none of those are known. We don't even know what is this material like. In such cases, how do we do?

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Capillary rheometry

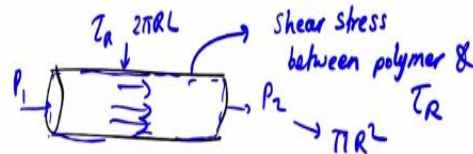
For Newtonian fluid, Hagen-Poiseuille equation

$$Q = \frac{\pi R^4 (\Delta P)}{8\mu L} = \frac{\pi D^4 (\Delta P)}{128\mu L}$$

For a viscoelastic fluid, equation of motion (balance of linear momentum),

$$\tau_{rz} = \frac{r\tau_R}{R}; \quad \tau_R = \frac{R \Delta P}{2 L}$$

$\tau_R \rightarrow$ the stress at the wall



And so again knowing overall force balance, we can actually still continue to use capillary rheometry for a general fluid by focusing on the wall of the material. If you for example look at this capillary and do a force balance given that now we have this polymer which is flowing, what we have is we can do a force balance by looking at a control volume which is basically the cylinder itself and at the wall we have shear stress between polymer which is being forced to move and the wall. This we will call τ_R , and in the entry and exit we have P_1 and P_2 pressure. So P_1 and P_2 are acting on πR^2 which is the cross-sectional area and the τ_R is acting on this surface area which is $2\pi RL$. So if you do a force balance between these two, you can show that τ_R is related to $\Delta P/L$ regardless of the fluid that is available. Similarly, you can do also linear momentum balance on such a material where you do not know what the material type is, but you can still show that the overall stress in the material is a linear function of the stress at the wall. So when $r = R$, the shear stress at the wall τ_R is present and at the center where r is 0 the stress falls to 0.

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Capillary rheometry

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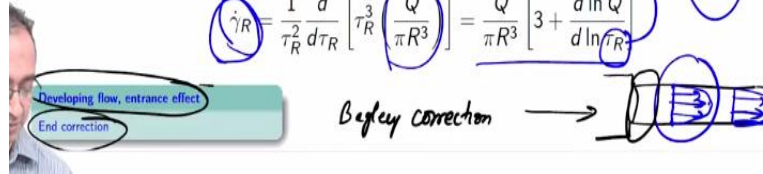
For a viscoelastic fluid, equation of motion (balance of linear momentum),

$$\tau_{rz} = \frac{r\tau_R}{R}; \quad \tau_R = \frac{R \Delta P}{2L}$$

$\tau_R \rightarrow$ the stress at the wall

Weissenberg-Rabinowitsch equation

$$\dot{\gamma}_R = \frac{1}{\tau_R^2} \frac{d}{d\tau_R} \left[\tau_R^3 \left(\frac{Q}{\pi R^3} \right) \right] = \frac{Q}{\pi R^3} \left[3 + \frac{d \ln Q}{d \ln \tau_R} \right]$$



So with this knowledge, then we can start developing and which is done using what is called a Weissenberg-Rabinowitsch equation where the strain rate at the wall is also related to the flow rate that's there in the material and it is written in couple of different ways, but you can see that if you measure the flow rate and if you measure the τ_R by knowing, we can calculate what's the $\dot{\gamma}_R$ at the wall. So if you know τ_R and if you know $\dot{\gamma}_R$, then you can get the viscosity. So see in this process we do not know what the fluid type is, but we do not need to know, we do not have an expression like the Hagen-Poiseuille equation, but by suitable manipulations of variables and by doing force balances and getting to know the variables whatever we know and whatever we can measure, we can get an estimate of the viscosity.

$$\dot{\gamma}_R = \frac{1}{\tau_R^2} \frac{d}{d\tau_R} \left[\tau_R^3 \left(\frac{Q}{\pi R^3} \right) \right] = \frac{Q}{\pi R^3} \left[3 + (d \ln Q) / (d \ln \tau_R) \right]$$

So that's why capillary rheometry is very commonly used for a polymer processing operation. By increasing the pressure drop, you can achieve very high flow rates and remember that in all of these cases the tube flow implies that there is basically a velocity profile where the velocity is 0 at the wall and then it is maximum in the center, and so the shear rate that the polymer is seeing next to the wall is very high and that is what we are estimating and then we are also estimating the wall shear stress and the ratio of these two can give us estimate of the viscosity of the material.

Now one of the things that when you draw velocity profile like this, it implies that ah you know it's the same when you travel along the pipe. Then this relation that we have talked about are

valid, but generally what will happen is this capillary is being connected to some reservoir through which fluid comes in. So there will be some entrance effect and so developing flow or entrance effects will require some end corrections, and given that capillary geometry is a very common technique, we also have something called the Bagley correction or there are other corrections which are far more modern in terms of their usage by practitioners, so we can get very good estimates of viscosity using this capillary rheometry.

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Maxwell model: viscosity

$$\dot{\gamma} = \dot{\gamma}^0 \sin \omega t$$

$$\sigma = \sigma^0 \sin(\omega t + \delta) \quad (4)$$

$$G^* = G' + iG''$$

$$\eta^* = \eta' - i\eta''$$

strain rate $\dot{\gamma}$
 σ and ϵ
 G^* : G' (in-phase storage elastic modulus), G'' (out-of-phase loss viscous modulus)
 η^* : η' (in-phase with input strain rate loss dissipation/loss viscosity), η'' (out-of-phase storage elastic viscosity)

Let's look at the dynamic viscosity now. Dynamic viscosity is obtained by subjecting the material to a sinusoidal strain rate. If you recall, earlier we had talked about subjecting the material to a strain, sinusoidal strain, and then we looked at the stress that is generated in the material and then we realized also for viscoelastic material there will be a phase lag. So now similarly, we are subjecting the material to a strain rate because our interest is in calculating viscosity and viscosity is a parameter which relates stress to strain rate. So the result will be again a stress but with the phase angle again and now using these two, we can then calculate what are the in-phase and out-of-phase component because we know $\sin(a + b) = \sin a \cos b + \cos a \sin b$. So we can expand this and we can have some factor multiplied by $\sin(\omega t)$ and some factor multiplied by $\cos(\omega t)$. So you can see this portion is in-phase with input strain rate and we have the out-of-phase portion, also this is the out-of-phase. So we will define this as η'' and we define the in-phase portion as η' and so this is very similar to our earlier definitions where we had defined G^* as $G' + iG''$ and this was in-phase or storage and this was out-of-phase and loss, but remember here the relation was between stress and strain. In this case, we have relation between stress and strain rate. So this is the loss or

dissipation while this is the storage or elastic. So just the way we had viscous modulus earlier and we had elastic modulus, now we have elastic viscosity or we have loss viscosity.

So oscillatory test again like earlier can be used to split the overall input output relations in trying to ascertain which are the energy dissipative contributions and energy storage contributions or elastic contributions and viscous contributions. So therefore, η^* which is the complex viscosity is related to η' and η'' and so η^* which is called the dynamic viscosity is characterized for polymeric system quite often and let us look at how does this look for a simplest possible model which is the Maxwell model.

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Maxwell model: viscosity

$$\dot{\gamma} = \dot{\gamma}^0 \sin \omega t \quad (4)$$

Solution for Maxwell model PoCoPUS-Lecture-48

$$\tau(t) = \dot{\gamma}^0 \left[\left(\frac{\eta}{1 + \omega^2 \lambda^2} \right) \sin \omega t - \left(\frac{\eta \omega \lambda}{1 + \omega^2 \lambda^2} \right) \cos \omega t \right] \quad (5)$$

First term \rightarrow the viscous contribution to stress, as it is in-phase with strain rate
 Second term \rightarrow the elastic contribution

$$\eta' = \frac{\eta}{1 + \omega^2 \lambda^2} ; \eta'' = \frac{\eta \omega \lambda}{1 + \omega^2 \lambda^2}$$

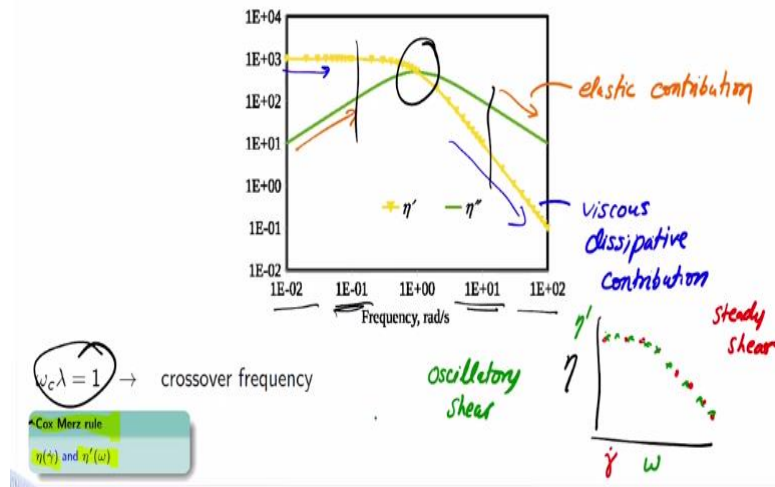
$\omega \rightarrow 0, \eta' = \eta$ $\omega \rightarrow \infty, \eta' \sim 0$ $\eta'' \sim \frac{1}{\omega} \quad \omega \rightarrow \infty$ $\eta'' \sim \omega$ (6)

So for Maxwell model using the ordinary differential equation if we input this strain, we can get the solution for stress as a function of time and it will have an in-phase component and it will also have an out-of-phase component and so therefore this is η'' or the elastic part of the viscosity and this is η' the loss or the usual viscous viscosity. So the first term is the viscous contribution to the stress and the second term is the elastic contribution.

Let us look at how do these variables vary as a function of frequency. I am sure you can look at it and you can see that when ω is very large, this factor will be very large and therefore what you will find is η'' is $1/\omega$, as ω tends to very large values. When ω is very small value, then η'' will be proportional to ω . Similarly, on the other side as ω is very large, then η' will basically be $1/\omega^2$ or it will go to 0 because ω is very large and if ω is very small then η' will be a constant.

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Maxwell model response in oscillatory shear: viscosity



So, this is what is depicted here graphically that at low frequencies η' is constant and then at high frequencies η' keeps on decreasing and this is remember is the viscous or dissipative contribution. On the other hand, η'' increases initially and then decreases and this is the elastic contribution and this is based on by the way Maxwell model. So general polymeric melts will have a far more complicated response compared to this.

$$\eta' = \frac{\eta}{1 + \omega^2 \lambda^2} ; \quad \eta'' = \frac{\eta \omega \lambda}{1 + \omega^2 \lambda^2}$$

As we have seen in case of G' and G'' and any other oscillatory property whether it's in terms of the compliance or J' and any of those will have similar properties. Similarly creep or stress relaxation also, the response will be far more complicated than what is usually indicated by simple models like Maxwell or standard linear solid model.

One of the things that you can notice here is that there is a crossover frequency and this again is where $\omega \lambda = 1$. And you can see that when you go for two orders of magnitude, so -1 to +1 you already see that the responses go from predominantly viscous to predominantly elastic. So when we are subjecting the material to very slow frequencies, very low frequencies or very slow rates, polymer molecules behave like a viscous material and therefore η' is constant. This is like saying zero shear viscosity if strain rate is very low in case of steady shear.

When we go to higher frequencies, now we are subjecting the material at very fast rates and

segments cannot relax, the entanglements become basically permanent junction points, so material behaves more and more elastic and so with this kind of a feature you can try to explain behavior of polymeric melts which are practically very useful. One of the empirical observations and which has been justified theoretically also is called the Cox-Merz rule, where you can compare the viscosity measurement from either rotational rheometer or a capillary rheometer in steady shear, where strain rate is constant. So you can plot η as a function of $\dot{\gamma}$ and that is the steady shear measurements. So, let's say several shear rates the data measurement is done and we usually observe the Newtonian plateau followed by shear thinning response.

Now the same measurement on the material can be carried out by looking at the dynamic viscosity and so therefore we can do what is called the oscillatory shear and we can measure now η' as a function of ω and then plot it and if both of these superimpose on each other, then that's called that Cox-Merz rule is being obeyed which says that as long as $\dot{\gamma}$ and ω are same then η and η' will be same. So this is observed for some of the polymeric melts and whenever this is observed we know that the structure of polymeric melt is not as complex, but whenever we have filled polymer melts, when there are fibers there or there are liquid crystalline portions, so any structural complications then more often than not this Cox-Merz rule is not observed. So this is a good way to understand what is the structure of polymeric material while it is flowing and it can be useful for looking at the practical polymeric systems.

So with this, we will close our overall discussion related to polymer processing and recycling techniques. We have seen the practical techniques which are used, we have seen the underlying requirements of sustainability to be able to reprocess or recover the materials. We have also seen the rheological response which is very important to determine the overall processing quality and the effectiveness and robustness of these processing and recycling operations. So with this, we will close this lecture. Thank you.