

## Polymers Processing and Recycling Techniques

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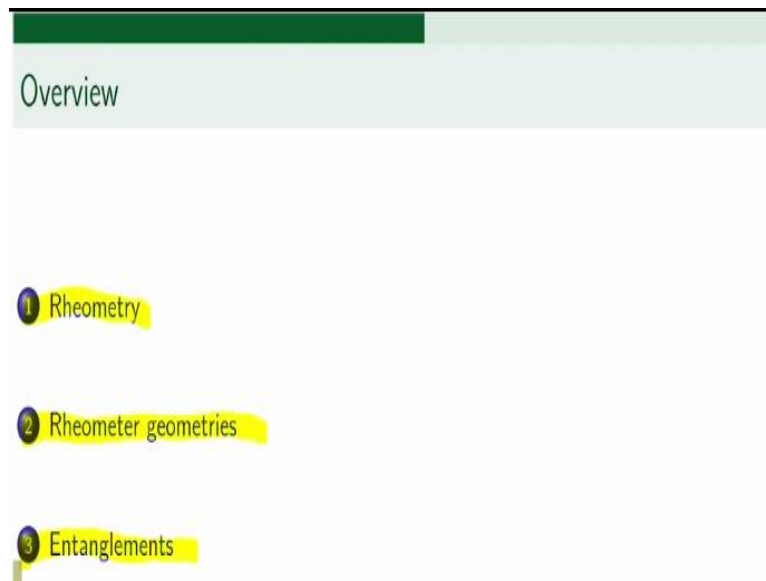
Indian Institute of Technology - Madras

### Lecture – 78

#### Rheology and Entanglement

Hello, we have transitioned into the 11th week where we are still discussing aspects of polymer processing techniques and recycling methods. Having looked at all of these techniques since we realized that the flow behavior is very important, we are spending some time discussing rheology. And in this particular lecture, we will look at how entanglement, which is a predominant mechanism of macromolecular systems in their melt state. We will look at how entanglement influences the rheological response and the focus will remain on concepts.

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We will quickly look at what is meant by rheology or measurement of rheological properties or rheometry and summarize what are the most commonly used geometry which are useful in terms of determining these rheological properties and finally the response of polymeric system in shear and extensional flow in which case the role of entanglement is very prominent.

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## Rheology: study of deformation behaviour of fluids

- Shear or extensional (shear-free)
- One-dimensional, narrow gap, ...
- Controlled variables
  - Constant strain rate
    - Steady viscosity
    - Stress growth
  - Constant stress (creep)
  - Constant strain (stress relaxation)
  - Oscillatory strain or stress

So generally, the rheology which is the study of the deformation is carried out by making certain broad set of assumptions and carrying out a very controlled set of experiments on a rheometer. So, one of the first things that we try to do is to ensure that the flow that is achieved is either shear or it is shear-free or extensional flow. So for example, this is rubbing like this is shear flow and taking fluid between two fingers and pulling is an extensional flow. So we can take fluid between two plates and we can achieve shear flow or we can try pulling the plates apart and achieve the extensional flow and if you think of water, you may think that extensional flow is difficult to achieve and you are right. But if you think of non-Newtonian fluids and especially if you think of several fluids in kitchen, then you may be able to see that if you take material between different surfaces and pull them apart very thin strands and fluids can form and in fact, the filament of fluid is quite stable and that is a consequence of in fact macromolecular network, which actually makes this fluid elastic and then it extends and achieves extensional flow like a solid like material. So therefore, given that many of the polymer processing operations, combination of shear flow and extensional flow is involved and there are several operations like film blowing or fiber spinning where extensional flow is predominantly involved, we characterize the polymer melt or polymer solution in both of these flows. The idea is to first understand them in one particular type of flow and then use this understanding to see their response in a polymer processing operation, which happens to be a combination of both types of flows. And additionally, what we do in lab while doing rheometry is try to exploit some of the controllable situation. So for example, we look at only one dimensional flow, again in a polymer processing operation in a mold filling flow can be very complex based on the geometry of the mold. But in case of rheometer we ensure that there is

only one dimensional flow, so that again analysis becomes easy. In fact, it is because of these kinds of controlled condition, we can develop a fluid mechanical theory of how the torque which is being measured and how the geometry movement can be related to each other and that's why then these flows become viscometric or rheometric, measurement of viscosity or measurement of rheological properties. So generally, we will control variables. For example, if we do a constant strain rate experiment, we can get a steady viscosity, but in the context of viscoelastic fluids even if we apply a constant strain rate, stress does not become constant. For Newtonian fluid it is true that if strain rate is constant, stress is also constant and in fact the ratio of the two is a material constant called viscosity. But in case of viscoelastic fluid even if strain rate is constant, stress can vary as a function of time before of course becoming steady eventually, so therefore, there is a stress growth that can be measured in case of a constant strain rate experiment for polymeric fluids. Then as we discussed when we were discussing the viscoelasticity in polymeric systems, one can do creep, stress relaxation or oscillatory tests, the dynamic tests to understand the viscoelasticity.

So, all the discussions that we had there regarding viscoelasticity is quite valid here also. There our focus was more related to viscoelastic solid like materials, here the emphasis will be more viscoelastic fluid like materials. One other key feature of rheometry is the narrow gap, so that the inertial forces are not significant and again analysis of fluid mechanics becomes easier for the situation. We should remind ourselves that when we are trying to do the rheology, we do not know the nature of material. Quite often it may be a new material that is being synthesized or quite often it may be a material for which flow behavior in a processing operation is not understood, and therefore we are trying to carry out rheology to understand the flow behavior in a controlled condition. So therefore, we should not be making any prejudged assumption about the material while doing this rheology. So our rheological measurements should be least dependent on the type of materials that we are using and so the measurements ought to be not contaminated or not influenced by some of these assumptions.

So therefore having very good control on deformation, one dimensionality, narrow gap, all of this is very important for us to do analysis irrespective of the material that is involved.

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## Rheometric flows

- Shear or extensional (shear-free)
- One-dimensional, narrow gap, ...
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Small perturbation from equilibrium

State of rest → equilibrium

Property at Small deformation

*Large deformation  
Non-linear rheology*

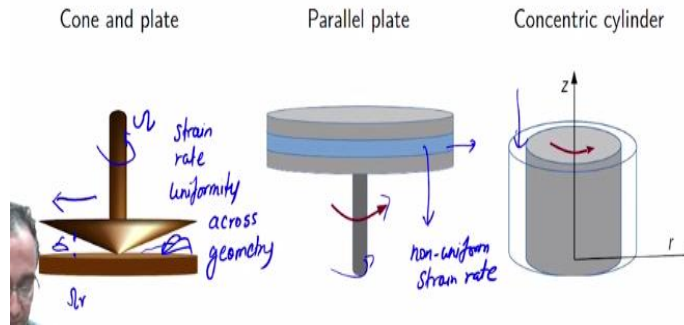
So when we do a constant strain rate experiment, we get a steady state property because we wait for steady state to occur and then so this property is not dependent on time, however, for generalized Newtonian fluid, the viscosity could depend on this strain rate. On the other hand when we do the dynamic tests, we are generally looking at small deformation and therefore this is a small perturbation. So in the context of linear viscoelastic response, what we saw is from a state of rest which is equilibrium, we perturb the material away and at small deformation still the response is pretty much determined based on the overall equilibrium structure of the material. However, in polymer processing operations, we are going to subject polymer melt to large defamations. So non-linear rheology is practically very important, by non-linear rheology we mean again rheology at very large deformations. However, since this is an introductory course on polymers, we will confine our attention to small strain behavior, especially in the context of shear response.

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Rheometer geometries (Rotational rheometer)

Capillary rheometer

Thin gaps - to minimize inertial effects:

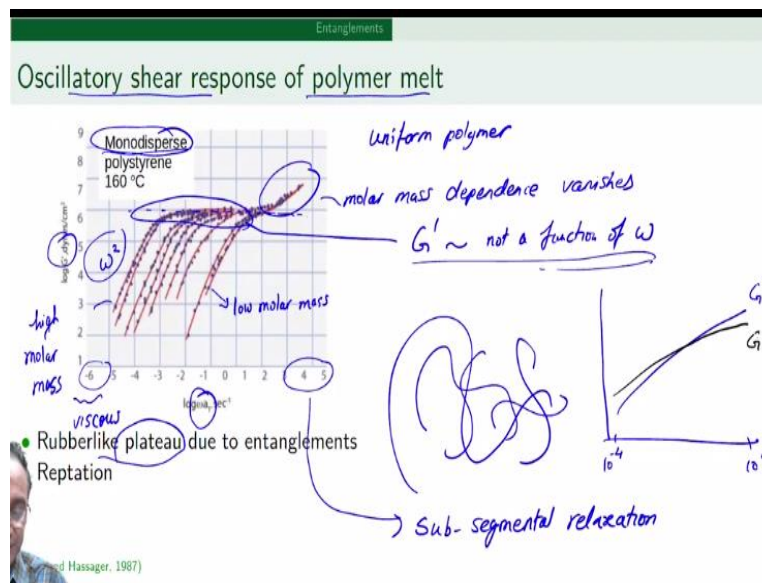


The geometries which are used are basically dependent on what type of material do we have and what type of rheological properties are of interest. These are examples of rotational rheometer and this is the most common rheometer which is used for studying rheology. For polymer melts though we also have capillary rheometer, which is an example of Poiseuille flow where a pressure gradient is generated for making the flow. In this case, either the cone is moving or one of the parallel plates is moving or the concentric cylinder the inner cylinder is moving and so these are all examples of Couette flows and so the idea in all of these is to have thin gap to minimize the inertial effects and the fluid is basically kept in the gap between the 2 cylinders, 2 parallel plates or cone and plate. Cone and plate is the best geometry in terms of assessing the rheological response of a new material because all throughout the geometry the strain rate is uniform. So strain rate uniformity across geometry. You can try to rationalize this, because effectively if you see everywhere there is a radial velocity of the cone, but the gap also is keeping on changing. So as you travel to higher and higher radius, the top point velocity keeps on increasing because if this is  $\Omega$ , then the velocity at any point will be  $\Omega$  times  $r$ , but the gap also keeps on increasing and the strain rate is actually the ratio of this velocity to the gap which is there, so therefore, it is a uniform strain rate.

In case of parallel plate, we have non-uniform strain rate. However, many cases the cone and plate gaps which are very small, 50 microns and thereabouts, we cannot use for let us say particulate systems. So then parallel plate with the gaps of about 0.5 mm or 1 mm can be used. And so parallel plates therefore are useful in terms of determining rheological properties of paste like systems. Concentric cylinders are useful for very low viscosity systems or where

torque values are lower, because the area of contact between the fluid and solid is extremely large because of being concentric cylinder. So, each of these geometries has its own advantage or disadvantage and depending on the application and the material involved, any of these can be used, but underlying the use of all of this is the fluid mechanical theory based on which the torque which is required to rotate and the motion is both measured and then related to each other through the properties such as viscosity, creep compliance, stress relaxation modulus,  $G'$ ,  $G''$  and so on.

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So let's look at a couple of examples one in shear and one in extension. Here we are looking at oscillatory shear response of a polymer melt, but this is a monodisperse polymer melt or what's called a uniform polymer, which means all the macromolecules have very similar molar masses and what you can see is at different molar mass, the response is very different. So this is low molar mass and on this side we have high molar mass and what is being presented here is storage modulus.

So the generic response is, at very low frequencies, we have basically  $G'$  being proportional to  $\Omega$  squared and this you can go back and look is a feature of viscous like response. We also see a region where molar mass becomes irrelevant and we also see a region where regardless of the molar mass, the  $G'$  seems to be constant and this is called a plateau.

In this case, it appears that  $G'$  is not a function of frequency in this particular region. So therefore, there is a plateau in  $G'$ . So the question is where does this arise from? What is the explanation for all of these observations? One other observation that you can make is the range of frequency and I am sure you would be able to recognize that time-temperature superposition is used to obtain such a large set of response. And therefore, you can see that frequencies times the shift factor which is used in the time-temperature superposition is also being plotted here.

So what we can see is, as you change the molar mass, the behavior changes and beyond a certain molar mass, all of them show this rubber like plateau and this is due to the entanglements. What happens is if you have low molar mass, then entanglements are not there and then  $G'$  pretty much increases as a function of frequency, which is more like a viscous response. However, when you have a very high molar mass, then what happens is you have these macromolecules which are all entangled with each other and if you do experiment very slowly, then because of reptation and because of the overall macromolecular motion due to reptation, the response is completely viscous. So this range, the response is viscous, which means predominantly dissipative processes and overall macromolecules can also move, it is  $10^{-5}$ ,  $10^{-3}$  frequency, so very slow shearing that is going on. So macromolecule can reptate and one macromolecule can get displaced from one position to the other, but as you start increasing the frequency, then the reptation is no longer possible. Then the points at which entanglements are there they act like crosslinks and it is only the segment between those crosslinks which can stretch, and this is a classical response of a rubber.

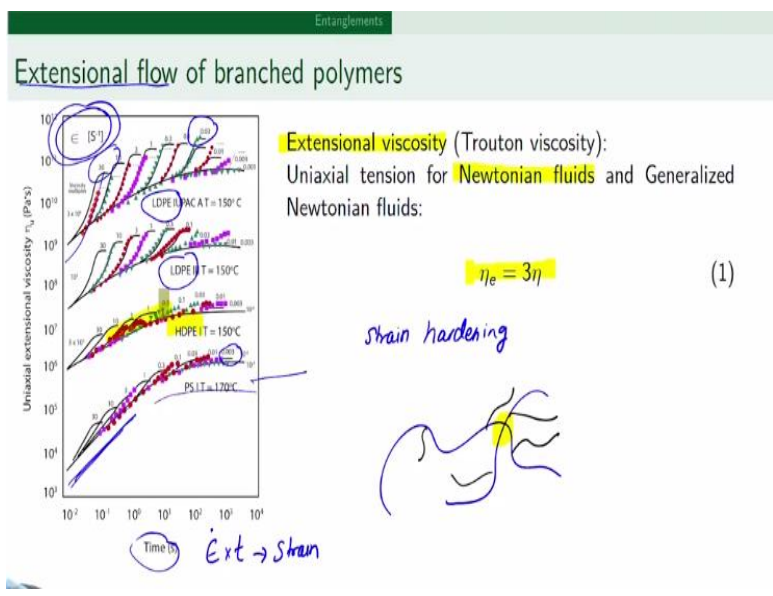
And that's why you can see that  $G'$  is not a function of frequency, which is again a feature of rubber like materials. So that's why, polymer melt which is a liquid system has this rubber like plateau at a certain range of frequency and the length of this rubber like plateau or the number of amount of frequency range in which this rubber like plateau is observed depends on the molar mass because higher the molar mass, more will be the entanglement and then more number of these segments which are between entanglement points will be available for us to observe this rubber like plateau. But as we go to further higher frequency of this range, then what happens is now the mechanical perturbation is extremely fast and so even the segments cannot really, conformational changes and segmental mobility and all of that is not possible anymore, so then what matters is much smaller or sub-segmental relaxation.

And in this case, it doesn't really matter what is the molar mass or what is the number of entanglement points because it's much smaller fragment, much smaller portion of macromolecule which is responding at these extremely high frequencies. So that's why they are called sub-segmental relaxation processes and molar mass is completely irrelevant for these sub-segmental relaxation processes. So that's why all the data for different molar mass seem to give you a similar response. So therefore, what we have seen is an example of how rheology is correlated strongly to the macromolecular structure, in this case the molar mass of the polymeric materials system.

One other feature that you can observe is if this is for commercial melt system, generally they will not be monodisperse, they will be polydisperse and there will be molar mass distribution and in that case, what is generally seen is  $G''$  and  $G'$ , again there is no rubber like plateau, because since there are molar masses of all different kinds, entanglements and the segment length between entanglements varies quite a lot and so all this average behavior basically ends up giving us gradually increased  $G''$  and gradually increasing  $G'$ . And I am showing this over again large frequency range  $10^{-4}$  all the way to  $10^4$ .

So you can look up polyethylene melt rheology data for example is classical in part of many textbooks. Even this data, which is for polystyrene is again part of all the classic texts of rheology.

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The other example that we look at is related to flow behavior in extensional case where we take a strand of fluid between let us say two plates and pull them apart. This is quite like the stress strain curve that we had discussed earlier. So extensional flow is basically like the stress strain of solid plastic sample where we pull the sample using a certain set of grips and then measure the stress as a function of strain. So these experiments are also done at a constant strain rates, and all of these are mentioned here and what we do is measure the stress that is required to maintain this strain rate and measure it as a function of time. And strain rate is constant and that into time will give us strain. So effectively, x-axis is also strain, because as time goes on strain also increases because  $\dot{\epsilon}$  is constant and so stress continues to increase.

If we do this experiment for a Newtonian fluid, we know that since strain rate is constant, stress will also be constant. If we do this for an elastic solid, then what we will see is strain will continue to increase, because strain rate is constant and of course, what we see for some set of materials is this viscoelastic response where initially stress increases or viscosity, which is the ratio of stress to the constant strain rate that increases initially and then it eventually becomes constant.

So this is expected for a very low strain rate or some materials like in this case polystyrene. But look at the response of low-density polyethylene, which is a branched polymer and what you can see is this, great increase in stress or this behavior is also called strain hardening, which we also discussed when we were looking at plasticity behavior of polymeric systems. The stress requirement is higher at progressively higher value of strain and it is much more than proportional increase and this strain hardening is very crucial in terms of film making, film blowing operations that are use.

And so to make a film from a LDPE is lot more easy compared to HDPE and this is because you have the macromolecule which are branched and when you have another macromolecule at these entanglement points, because of the branching reptation and other features are not as easy and so then in that case, the stretchability of polymer increases and at very high rates also you can process these materials and produce films which are very controlled thickness. So branched polymer is in fact added to a linear polymer to improve processability of linear polymer. Because the entanglement of branch polymer leads to an excellent extensional flow behavior in which case the stress increase leads to lot of stretching and you can achieve very high draw ratios or in other words you can achieve much finer thickness when you process

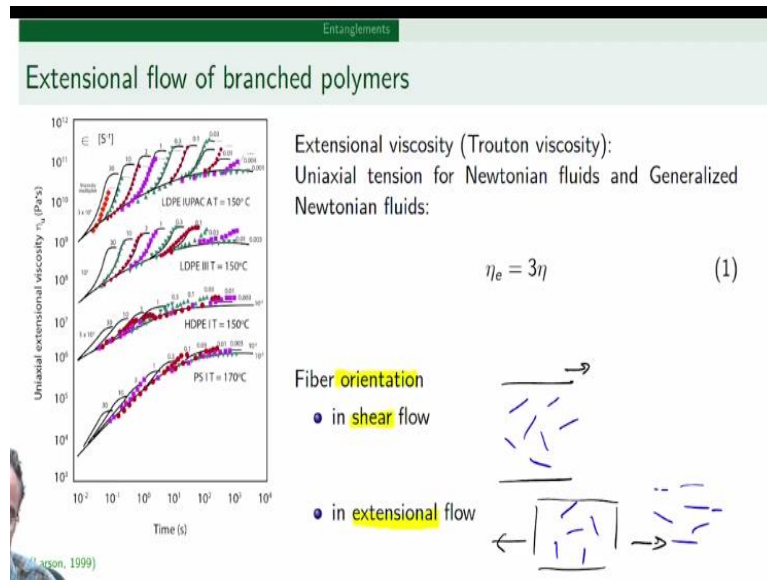
these materials and this can be done at very high rates, so that production rate of films and fibers can be very high.

So you can see that extensional flow again fundamentally related to entanglements and molecular architecture, but is a very important practical consideration as far as polymer processing is concerned. Theoretically, the extensional viscosity for a Newtonian fluid is just 3 times viscosity, so that is why in case of Newtonian fluid, characterizing viscosity as a material constant completely specifies the material response, whether it is shear flow or extensional flow. However, materials which are polymer melts can have very similar shear viscosity, but they may have very different extensional viscosity because the way the entanglement play role in case of shear and in case of extension can be very different.

$$\eta_e = 3\eta$$

So LDPE and HDPE will have similar shear thinning response as far as shear flow is concerned, but they have very different extension flow. One case significant strain hardening is observed, in HDPE the strain hardening is much less, and therefore film processing from HDPE is not easy.

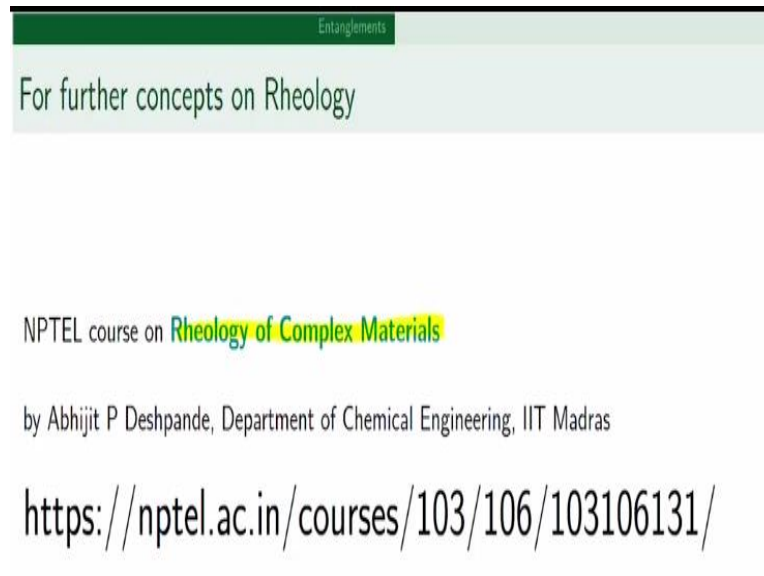
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So with this survey of sort of shear flow and extensional flow behavior, one each example, what is also important let's say in case of polymers is when we have fibers or liquid crystalline portions, which are part of macromolecular system, and how the orientation happens in shear flow and extensional flow is again very different. And quite often if let's say we have all these fibers which are randomly oriented, what we will see is if you do shear flow, there will be some

orientation of these fibers but that's marginal. But if I take the fibers and then subject it to an extensional deformation, I can get a perfect orientation of these fiber. And so achievement of orientation can again depend on what type of flow the polymeric material is being subjected to and this is true in case of solution melt or even solid-state polymers. So all of these cases, the deformation influences the overall deformation response of the material, and in case of composites even the microstructure and the fiber orientation gets influenced based on it.

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Entanglements

For further concepts on Rheology

NPTEL course on **Rheology of Complex Materials**

by Abhijit P Deshpande, Department of Chemical Engineering, IIT Madras

<https://nptel.ac.in/courses/103/106/103106131/>

So, again if you want to know further about rheology, you can look at this full-length course on the rheology of complex materials.

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Entanglements

Bird, R. and Hassager, O. (1987). *Dynamics of polymeric liquids*. Wiley.

Larson, R. (1999). *The Structure and Rheology of Complex Fluids*. Oxford University Press.

With this, we have given an overview of geological response in both shear and extension and the type of rheometer geometries which are used for rheological analysis. In the remaining couple of lectures, we will look at models which are used for rheological understanding and also look at certain features of how rheology helps in polymer processing. So with this, we will close this lecture.

Thank you.