Polymers Processing and Recycling Techniques
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Lecture – 75
PolCoPUS: Flow Behaviour - Rheology

Hello, welcome to the course on exploration of properties, uses and concepts and sustainability related to polymers. We have been discussing techniques which are related to how to fabricate parts out of polymers how to process them. We have also spent significant amount of time looking at recycling or opportunities in terms of improving the sustainability of these polymeric materials, and all throughout this discussion we have raised issues related to the flow behaviour of polymeric materials.

So, we will spend some time looking at the rheology which implies study of deformation of matter in this week and in this lecture as well as three more subsequent lectures. So our focus overall is on processing and recycling of polymeric materials and we will look at conceptual information related to rheology and then see how rheology can help us understand the flow behavior in a better manner.

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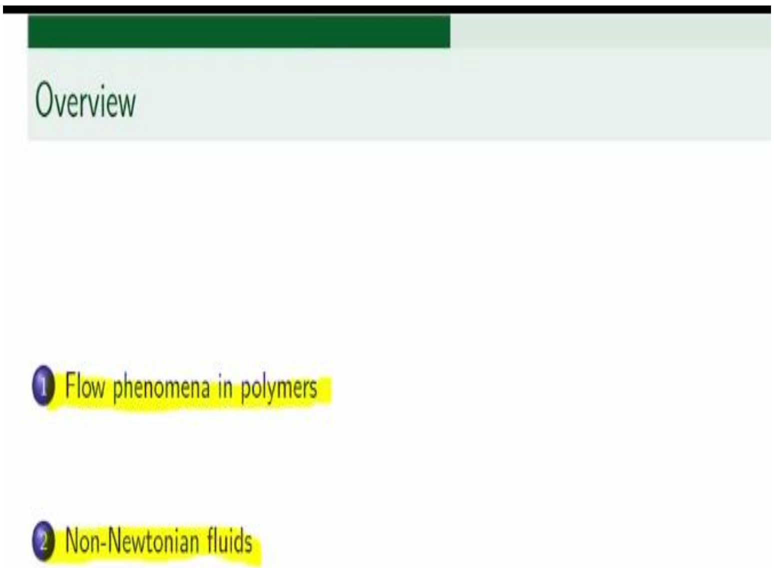

So, let us first look at the flow phenomena and summarize what we have been discussing in the context of structure of polymers as well as the processing techniques and then we will begin the discussion related to non-Newtonian fluids which most of the polymeric materials are.

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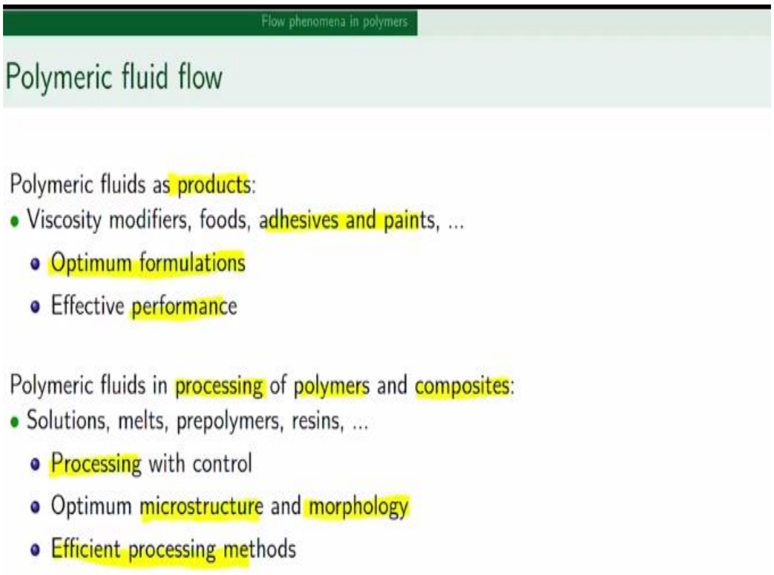

So where is the fluid flow of polymers involved? So, it could be where macromolecular systems are there as a product itself. So shampoo or foods, cold creams, adhesives and paints, so various such products are there where during the performance of the product flow behavior is very important. So how does a cold cream spread on our hands as well as on our screen skin. When we are painting how is the flow and spreading happening.

So all of these cases, the flow behavior during the performance of the product is extremely important. So, in these cases if we understand rheology, if we understand flow behavior of these polymeric systems, we could achieve optimum formulations so that we do precisely what the material is supposed to do. Example of course that can be given is ketchup or many of the sauces which are used.

They tend to flow out of the bottle very easily so that when we are trying to pour them, we expect the pouring process to be a smooth process instead of trying to shake too much or have to put spoon inside and then take it out. So, we want pouring capability from the sauce, but once it comes on the plate or on a slice of bread we do not want it to be running all over, we do not want it to be too fluid like.

So therefore, we have expectations of flow or not much flow from the same product. So, therefore in such cases the flow behavior has to be manipulated or controlled very precisely. So, we could do that if we understand what makes this kind of flow. So what is it in case of ketchup that when we are trying to pour it out it seems to flow out very easily and what we will see in technical terms is actually shear rates are higher when we try to pour.

And so at high shear rates it seems to have a low viscosity, but when we see it stationary in a plate or on a slice of bread then it has higher viscosity. So, this shear thinning nature which components in the formulation enhance that which type of macromolecules will bring better control on this shear thinning property. So, for a jam for example we want it to be almost solid like, but when we put a spoon and try spreading it we want it to spread very easily.

So again, we seem to have different requirements of flow behavior depending on the context and so all of this can be done if we understand rheology appropriately. So, effective performance will be obtained if we optimize the formulations and so we should be able to understand the flow behavior in a much better manner where we know the role of each and every component and in case of macromolecules the molecular architecture, how is it influencing the interactions of macromolecules.

And whatever other factors that we have been discussing in terms of segmental mobility. So, whatever structural features of macromolecular systems how do they influence the flow behavior. The other context in which flow behavior is extremely important is when we are processing these materials and we have seen several examples of techniques such as resin transfer molding in the case of composites, injection molding or extrusion in case of polymeric materials.

All of these cases polymer flow either melt or resin or solution is extremely important. And so in all of these cases we would like to do processing with a required degree of control so that we get the final part which is successful in terms of least number of defects and it is the shape that we had designed for and so while we are making that part the other feature that we want is microstructure to be appropriate so that a semicrystalline polymer should have the required amount of crystallinity.

If you are looking at an oriented microstructure, then the macromolecules have to orient to the required amount so that we get required mechanical properties. So therefore, optimum microstructure and morphology is required during processing itself and eventually what we would want are efficient processing methods, methods which require less cost and energy to produce a polymeric part with given microstructure and morphology with a good robust control. So, that is the overall goal of trying to know the flow behavior so that we can achieve these goals.

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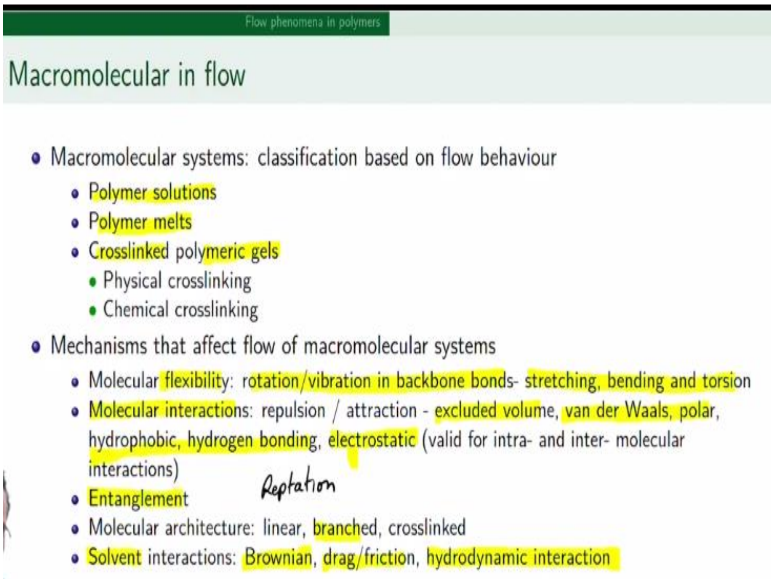

So, what is it about macromolecules that makes them so interesting in case of their flow behavior and we can look at basically these macromolecular systems in few broad classes. So if we use the macromolecules in a solvent, then we have the solution and we have seen that you can have dilute, semi-dilute or concentrated solutions. For example in dilute case, the polymers are very far separated from each other.

So polymer-polymer interactions from one macromolecule to another are not important. Of course given that macromolecule is a giant molecule, intramolecular interactions are always important in case of polymers except if it is an ideal chain behavior. So, polymer solution is one class of materials. Polymer melts where we have entangled set of macromolecules are another class which is very important from processing point of view.

Polymer solutions are also used in several processing operations, for example fiber spinning there is wet spinning processes and dry spinning processes and wet spinning processes imply the use of a solvent which then we use the thermodynamics of mixture between solvent polymer and maybe a non-solvent to try to achieve good morphology for the polymer. There are several polymeric materials where either during processing for case of thermoset and rubber like rubber materials we have crosslinking and gelling, the phenomenon of gelation, or we have products themselves which are gels. So, in both, we have physical as well as chemical crosslinking and the class of behavior is demarcated between solution and melts and gels because gels are far more elastic and far more solid like features, while melts are somewhere in between, while solutions have more fluid like features.

This will also become apparent when we look at rheological response of some of these materials. The underlying mechanisms from a microscopic and molecular standpoint which define the overall flow behavior are what we have been discussing throughout the course. Paramount importance is there to the segmental mobility. Therefore, the rotation, vibration in bonds; stretching, bending and torsion of bonds which allows conformational changes to happen in a macromolecule.

Of course, the molecular level interactions which could be either excluded volume or secondary interactions that we have been discussing throughout the course, some of these are long range for example electrostatic, some of them are much more short range like the repulsive interactions. However, they make the overall macromolecular interactions quite complex depending on the macromolecule of interest.

Entanglement is a very important feature which determines the melt behavior. Given that macromolecules are entangled with each other, they cannot really move because there is another macromolecule preventing it, but they can move like a snake and what is called the mechanism of reptation. So this was a historically important mechanism that was identified which could explain behavior of concentrated polymeric solutions as well as melts.

And this is very important in terms of recognizing how deformation in polymeric systems which are melt or concentrated solutions happen. Of course, given that this entanglement and reptation, all of this would be influenced by what kind of molecular architecture do we have, whether we have a branch system or not. So therefore, processing behavior of linear low-density polyethylene LLDPE in terms of making bag will be very different compared to LDPE which is quite heavily branched or HDPE which is hardly branched.

So therefore, branching influences the rheological response a lot and therefore also the processing behavior. In case of solutions, we also have the interactions between the solvent and the polymer which could be in terms of a thermal force that the solvent molecules impose on macromolecule or it could be relative motion between macromolecule and solvent which leads to a friction between the macromolecule and the solvent or it could also be the two parts of polymer chains which are interacting with each other because the solvent is there.

So when one part moves, it disturbs the solvent and this disturbed flow of solvent is what is seen by this part. So, therefore these two are interacting with each other, two portions of macromolecule are interacting with each other through this solvent. So, therefore we have solvent mediated hydrodynamic interactions. Again, the hydrodynamic interactions are over long distances while the drag friction or the Brownian motion is just confined to the macromolecular group itself or the smaller portion of the macromolecule itself.

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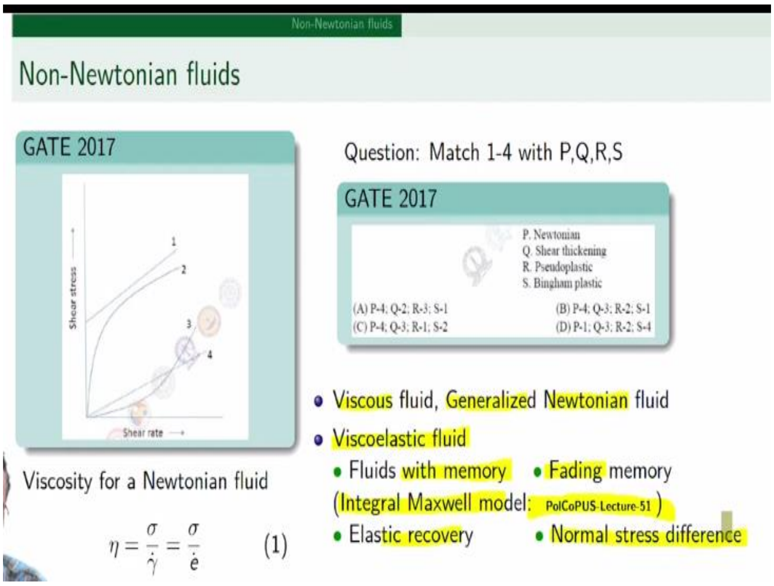

So, given all these complicated interactions which are spanning of course multiple time scales and length scales the behavior of polymeric materials is often non-Newtonian and again this is a very common first concept to be learnt in terms of what are different classes of non-Newtonian fluid. So this we have already discussed once. So, I will leave you to look at the question and try arriving at the answer which should be relatively straightforward if you have already looked at these different classes.

A Newtonian fluid of course is defined based on a material constant which is viscosity and once we specify viscosity, then problems related to fluid flow behavior of that particular fluid can be solved using let us say for a Newtonian incompressible fluid using Navier-Stokes equations and the only coefficient that we need to specify the behavior is the viscosity. Viscosity is of course function of temperature, but other than that no other information is necessary.

In case of non-Newtonian fluids, this is not the case and we still try to use the analysis based on viscosity by measuring stress and strain rate. So we measure stress and strain rate and then try to look at the variation of how does stress vary as a function of strain rate or how does strain rate vary as a function of stress and so even non-Newtonian fluids are analyzed using the same behavior.

However, this is only an incomplete picture. While discussing viscoelasticity of polymeric systems, we had seen that how there are different ways of looking at viscoelasticity in the polymers. You can look at creep behavior, stress relaxation behavior, oscillatory response. So same thing is true also when we analyze the flow behavior of polymeric systems. So, therefore viscosity is only one parameter.

And in case of non-Newtonian fluids the viscosity is also not a constant, but it varies as a function of shear rate and that is what is being depicted in a picture like this and so generally the polymeric materials as non-Newtonian fluids, we will look at them under two broad categories. One set of fluids where viscous dissipation is the feature and there is no elasticity in the material and these are called generalized Newtonian fluids.

So pseudoplasticity or shear thickening or power law fluid, these are some of the examples of saying that we will still look at predominantly shear stress versus shear rate or stress versus strain rate behavior and the ratio of these will define in terms of a viscosity, we realize that this is not a material constant, it is a function of shear rate itself, so therefore it is a material function.

However, with that limitation, we have generalized the concept of Newtonian fluid to a fluid where viscosity is a function and not a constant, but broadly speaking the overall method that is used for Newtonian fluid can still be used here and mechanism wise it is still a perfectly dissipative material like what Newtonian fluid is. On the other hand, of course, given the entanglement, the segmental flexibility and the ability of segment to come back after getting stretched.

So all these elastic features that are inbuilt into macromolecular systems, macromolecular systems will generally tend to have some memory, they will recover to what was the earlier state. We do see that the memory will also fade away with time. The deformation which was immediate in the past will influence the behavior at present time lot more compared to deformation which was further in the past.

This we saw in the 51st lecture where we discussed while discussing the concepts related to time temperature superposition and viscoelasticity, we saw that when we look at Boltzmann superposition principle the integral Maxwell model can be visualized as current state of stress being dependent on past deformation multiplied with relaxation modulus and the relaxation modulus keeps on decreasing as we go further back in time.

So we have elements of elastic recovery and an important concept related to flow behavior of polymeric materials is normal stress differences. So we will see that if I carry out a shear flow of Newtonian fluid, I only need to apply force in the direction to apply shear, but in case of polymeric fluids and other fluids with elasticity or viscoelastic fluids, in addition to applying a horizontal force I will also need to keep a vertical force so that the gap between the two plates is maintained.

And so this is a consequence of normal stresses which are the diagonal components in stress tensor and so viscoelastic fluids have normal stress differences when they are subjected to shear flow.

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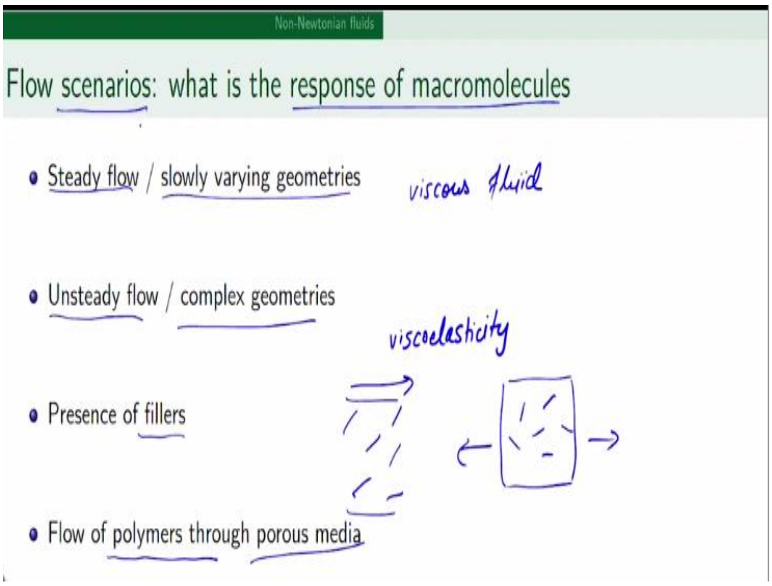

So, the importance of knowing all the mechanisms of macromolecular microstructure and this overall classification in terms of flow behavior is important because the overall fluid flow of macromolecules can be different depending on what scenario it is being subjected to. So, for example if we have a steady flow which means the same strain rate is being applied for a long amount of time, this could be a scenario let us say in a pumping of the fluid.

So pumping of over long distances ah generally the cross-sectional area of the pipe is constant and once we start pumping the flow rate would also be maintained constant. So, in these kind of situation with slowly varying geometries, it is okay to consider polymeric material as largely a viscous fluid. Given that it has fading memory, given that the immediate past deformations are important, but if this is a steady flow then that means that same deformation has been going on for long amount of time.

And so in that case polymer fluid will flow and largely viscous dissipation will be the predominant feature and therefore elasticity of fluid is not very important. But we saw that whether its injection molding or extrusion or stretching or extensional flow for let us say in film blowing, all of these are extremely unsteady flows and which are occurring through complex geometries. So, necessarily macromolecules respond to time change, rate of change of stresses, rate of change of strains.

And also the fact that there are corners, sharp corners, not so sharp corners through which the macromolecules have to go. So, the conformational changes and stretching and recovery of macromolecule goes on and so viscoelasticity is extremely important for all of the processing operation, but if you look at work in 70s and a lot of engineering applications that happened, the assumption of viscous fluid along with lot of empiricism was used to actually manipulate the processing operations.

So, the cost of ignoring the elasticity is in terms of just adding more factor of safety as well as lot more empiricism and so that was possible, but now given the computational power and given controlling strategies that we have and the understanding between the microstructure and molecular structure and rheology and processing behavior, we are far more into looking at viscoelasticity in much more detail and that is why we saw that in flow simulations, we can choose viscoelastic fluid flow models also in addition to just using viscous fluid models.

The other complication in case of composite processing is the fact that there are fillers. So if you have let us say fibers and then if they are in shear flow or let us say these fibers which are randomly oriented but then they are in extensional flow, how these fibers orient will be very different and that is of interest for the final product. So, therefore behavior of macromolecular systems along with fillers is a very important field.

Similarly, when we have composite processing where there are already fabrics and reinforcements there and then polymeric resin or prepolymer or polymer melt is flowing through these porous media, again it is very complex geometry and what happens to macromolecular conformations through such narrow pores, widening out, again becoming narrow this is very important. So, depending on the scenario we may have to look at rheological behavior of a certain kind or another and this is what we will see in the remaining lecture related to rheology.

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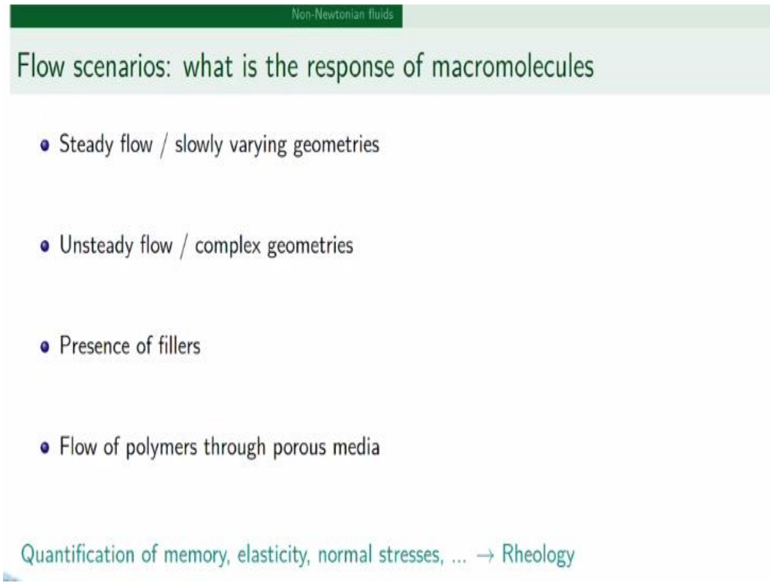

So generally, rheology is useful because all the aspects that I talked about in the lecture in terms of memory, elasticity, normal stresses all of these can be quantified using rheology. So, rheology is basically useful in terms of quantification of fluid flow behavior and with that we will stop now.

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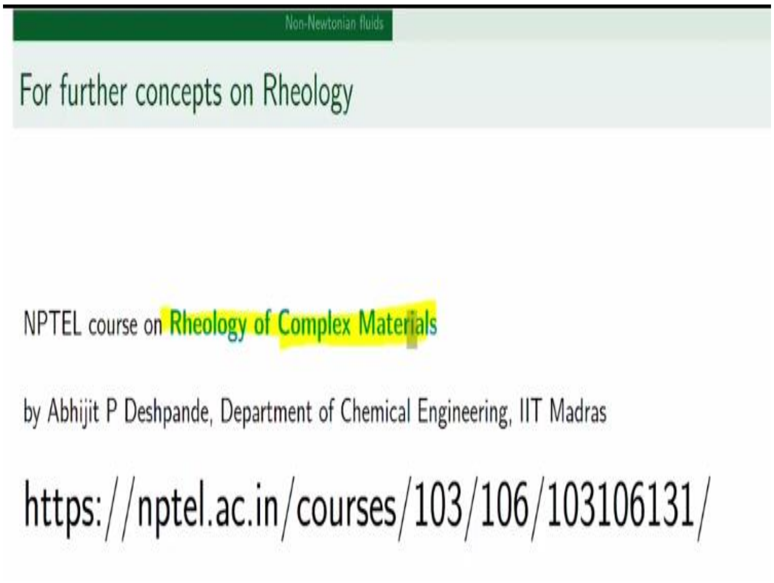

If you are interested in knowing much more details about rheology, there is a course that I have related to Rheology of Complex Materials, so which discusses, it is a full-length course on rheology and you could look at not just macromolecular systems but colloidal systems and all the complex materials which are important in terms of understanding their flow behavior. So, with this, we will close the lecture. Thank you.