Rheology of Complex Materials

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Lecture – 39
Survey of Material Functions Polymeric Solutions, Melts and Gels

In the lectures on rheology so far, we have taken a look at several material functions and we have seen that there are several types of flows in which we can define the controlled conditions and under these control conditions, we define the material functions. And the material functions are very useful for quantifying the response of the complex materials.

In this set of lectures, our objective will be to look at some of the real data that is available on different material systems and we will try to get a feel and understanding of how rheology is different for different class of material systems? And what can we learn at a generic level in terms of this material functions? And how they actually characterize the material response? As well as how the material response gives us clues regarding the microstructure of materials?

So, in the first segment we will look at the response of a polymer solutions melts and gels. So, as we have seen earlier the overall set of material functions that we will.

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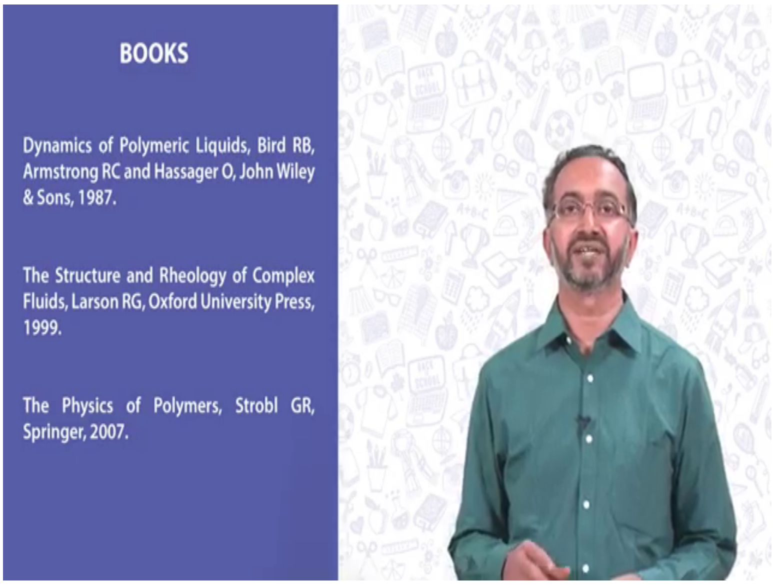

BOOKS

Dynamics of Polymeric Liquids, Bird RB, Armstrong RC and Hassager O, John Wiley & Sons, 1987.

The Structure and Rheology of Complex Fluids, Larson RG, Oxford University Press, 1999.

The Physics of Polymers, Strobl GR, Springer, 2007.

Look at in the set of lectures, will are predominantly based on classical data available from literature. I have a taken fare number of discussions from these 3 books. These are very exhaustive books couple of them on rheology and the other one on polymers and they discuss several aspects of a polymer viscoelasticity both linear and non-linear. And so, the data and discussion for those who are interested in more different descriptions of these the material functions can actually consult these books at the same time.

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CLASS OF MATERIAL SYSTEMS

- POLYMER SOLUTIONS
- POLYMER MELTS
- PARTICULATE DISPERSIONS AND EMULSIONS
- GELS
  - CROSSEDLINKED POLYMERIC GELS
    PHYSICAL CROSSLINKING
    CHEMICAL CROSSLINKING
  - PARTICULATE
- GLASSES
  POLYMER
  PARTICULATE

MACROMOLECULAR SYSTEM

MULTIPHASE SYSTEM

MACROMOLECULAR
MULTIPHASE
SYSTEM

I have also taken some of the data from more recent sources so, it is a compilation of a material functions data for a different class of materials.

We have seen that in general is helpful to classify the material systems. In terms of several classes, we saw that we can think of them a solutions and melts, we can think of them as dispersions we can think of them as gel and glass. And many of these systems are macromolecular in nature and some of these systems are belonging to multiphase and quite often colloidal or a emulsions or a disperse phase systems.

And so, during this survey also, we will take a look at materials and their response in the same classification. So, we have both macromolecular and multiphase system as part of this survey and at the end of the survey towards the end of the survey, we will also take a look at the combinations of these. Where, we will have multiphase and macromolecular systems together and by looking at systematically these data, we hope to gain understanding of how material functions vary for some of the real systems? And also, how by looking at the variation of these material functions we can get ideas about the microstructure of materials.

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Type of Rheological Experiment

STEADY SHEAR

STEADY EXTENSION

STRESS RELAXATION

CREEP

OSCILLATORY SHEAR

Material Functions

VISCOSITY

ELONGATIONAL VISCOSITY

RELAXATION MODULUS

CREEP COMPLIANCE

STORAGE LOSS MODULUS

DYNAMIC VISCOSITY

So, if these are the rheological properties we that we have already seen we have seen a steady shear, steady extension, stress relaxation, creep and oscillatory shear. We looked at each of these modes of rheological analysis and using this modes, we define the material functions viscosity, the elongation, viscosity, relaxation modulus, creep compliance, the modulai a storage and loss. We also defined the compliances the in phase and out of phase compliances and similarly, we also define viscosities the dynamic viscosity and which again has 2 components.

So, therefore, we will through this survey, we will look at some of the variations which involve characterization of these properties for the materials.

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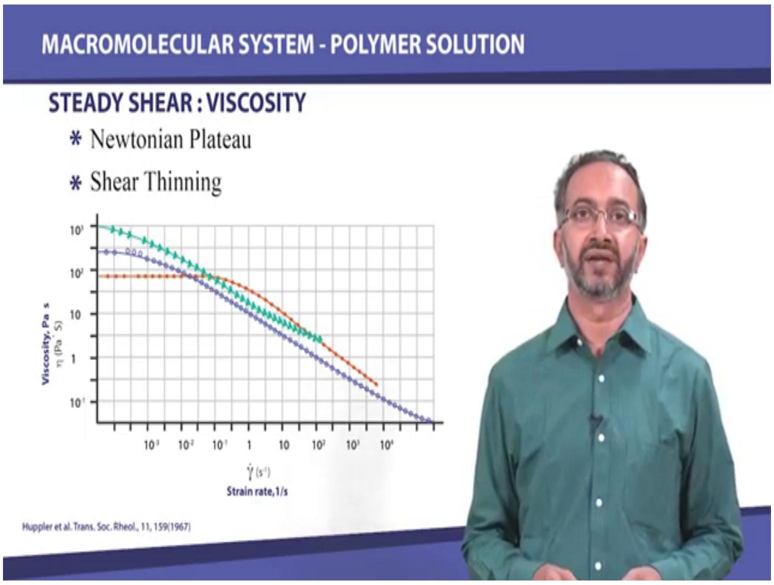

MACROMOLECULAR SYSTEM - POLYMER SOLUTION

STEADY SHEAR : VISCOSITY

- Newtonian Plateau
- Shear Thinning

Huppler et al. Trans. Soc. Rheol., 11, 159(1967)

So, let us begin with the macromolecular system which are polymer solutions and the first example that we will look at is related to viscosity. And as we have seen it is a measurement in steady shear, just to remind us that steady shear implies that we apply a constant strain rate on the material. And since, we are calling it steady shear the application is in simple shear mode and we wait for the stress to reach a constant stead value also. And then measure the stress and the ratio of stress to strain rate is the viscosity.

So, if you look at the data given here for 3 different solutions we can see if qualitative there are some observations that can be made.

For one of the solutions, we can see that viscosity is constant at low strain rates. And as strain rate increases for all the 3 solutions we can see there is a pronounced decrease in viscosity. Another thing to notice about such data is the fact that we are usually plotting these properties on a log scale. Because, the variation in these property is orders of magnitude it is necessary for us to look at log, log scale. So, both y axis and x axis on log, log scale and we can see that actually viscosity varies about 4 orders of magnitude and the strain rate at which we are examining the material is also about 7 orders of magnitude different. And these different orders of magnitudes of strain rates are also important because from a practical point of you from an engineering application point of view different conditions require different strain rate..

For example, if we are looking at pumping and transport the strain rate may belong to one category while if we are looking at let say injection moulding as a process we may have another strain rate. So, in general in these processes we will have different strain rates involved and therefore, from a complete characterization point of view for these materials we examine them in as wide strain rate range as possible.

So, the 2 main features that we can see for 2 of the solutions that there is a Newtonian plateau at the low strain rate and there are there is shear thinning at high strain rates. The third solution it appears can possibly have a Newtonian plateau. If we continue the measurements at still lower strain rates and later on in the course, we will also see some examples where the Newtonian plateau would completely be absent and that is an indicator of yield type of fluids. And in that case, the viscosity will actually increase rapidly at low strain rates and may actually diverge at when strain rate tends to 0.

So, therefore, the observations to be made here are in terms of also looking at what is the nature of decrease? And how significant is the decrease? One other thing we can see is in the decreasing range, wherever there is shear thinning. On a log log plot here, it is apparent that the viscosity verses strain rate data appear to fall in a straight line. And therefore, for many applications if the strain rate range is in the straight-line region we could actually use a power law. Because power law dependence on a log, log scale will end up being a straight line. So, therefore, power law is simplistic model which is used very often in describing the shear thinning behaviour of polymeric systems.

The other key observation that can be made from this data is the fact that the Newtonian plateau is observed for different strain rates or the departure from Newtonian plateau is observed at different strain rates. So, for example, in one solution we can see that all the way up to one strain rate strain rate of one the viscosity remains constant. So, in each of the solutions case, we can examine a critical strain rate. And this critical strain rate indicates that if the material is sheared or the material is deformed at a lower strain rate then this critical strain rate the behaviour is Newtonian.

In other words, the viscosity is constant for a certain strain rate range provided the strain rate gives the material sufficient time. And so, therefore, the critical strain rate at which we start observing the shear thinning behaviour is an indicator of the largest relaxation time which is present in the material. If we recall our discussion, which is related to relaxation processes the all the relaxation processes in a material have a characteristic relaxation time.

And we also saw that there is a spread there is a spectrum of relaxation times in whether it is a polymeric system or a colloidal system. And therefore, given that there is a spread of relaxation times, if we shear the material as slow as possible, then we give even the longest relaxation time for that process to relax. And therefore, give the dissipative response and therefore, it is not surprising that when we shear the materials at extremely low strain rates. All the relaxation modes lead to relaxation dissipated behaviour and therefore, we observe and viscous response and that viscous response is also signified based on the constant viscosity or a Newtonian plateau.

So, this steady shear test gives us an idea about the fact that the material shows viscous response below certain strain rates. So, we can try to characterize the largest relaxation time which is present in the material. We also have the choice to ignore the relaxation processes in the material in terms of their viscoelastic contribution.

But, just say that we are only interested in viscosity alone and therefore, we could use power law model or a carreau yasudamodel or any mediates of models which are available to describe viscosity as a function of strain rate. So, when we use viscosity as a function of strain rate alone, and do not talk about the relaxation processes and the viscoelastic mechanisms which are available in the material we choose to look at this polymer solution as a pure viscous material and describe the flow behaviour based on that viscous behaviour.

But looking at viscosity itself and especially looking at viscosity at very large deformations. Whenever, we are applying large strain rates necessarily we are also applying large deformations. So, therefore, this kind of data gives us indications of significant viscoelastic contributions which are present in the material. And because, we are talking about large deformations we are also talking about non-linear viscoelastic mechanisms, mechanisms which are valid for large deformation.

Only at small strain rates, when viscosity is constant, we can use the understanding related to linear viscoelasticity to talk about the 0-shear viscosity or the Newtonian plateau viscosity.

So, you can see that from a given set of data, there are number of observations that can be made. The specific solutions that are there of course, quantitatively behave differently. In the sense that, the magnitude of viscosity itself is different for each and every system and in rheology, our attempt is also to arrive at a generic understanding of polymer solutions and also to look at the quantitative variations. So, in cases when we are looking at a new material system sometimes we will change composition or temperature or any of the variable such as Ph. Whatever maybe affecting the rheology and we characterize viscosity as a function of these parameters and then try to understand whether the qualitative nature of viscosity itself changes as the function of strain rate.

And for let us say, different values of Ph we get similar responses. Then we know that the mechanisms underlying mechanisms remain the same; however, the extent of their contributions made change it maybe also that the qualitative variation would be entirely different. Then we know that we have to look for mechanisms changing when the Ph changes.

So, in the given 3 solutions case one observation we can clearly make is the fact that the qualitative variations is the same. So, regardless of the chemical makeup of the solvents and the polymer involved, we could use a generic explanation to describe the Newtonian plateau, the critical strain rate as well as shear thinning in these materials.

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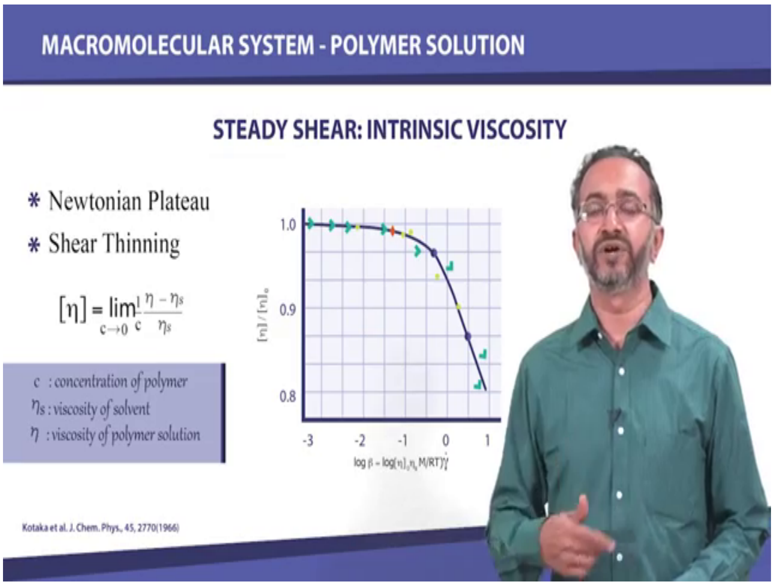

MACROMOLECULAR SYSTEM - POLYMER SOLUTION

STEADY SHEAR: INTRINSIC VISCOSITY

* Newtonian Plateau
* Shear Thinning

$$[\eta] = \lim_{c \to 0} \frac{1}{c} \frac{\eta - \eta_s}{\eta_s}$$

c : concentration of polymer
η_s : viscosity of solvent
η : viscosity of polymer solution

Kotaka et al. J. Chem. Phys., 45, 2770(1966)

Now, moving on to the next aspect of the polymer solution viscosity, if we look at extremely dilute polymer solutions, where interaction between polymer molecule and another polymer molecule is absent. So, that polymer molecules are basically isolated. So, they only interact with the surrounding solvent and of course, since polymer itself is fairly large, the different segments of polymers would also interact with each other.

So, given that we are only looking at polymer solvent interactions in a dominant mode. It helps to try to ask the question as to what is the modification to the viscosity of the solution that is brought about by the presence of the polymer.

So, therefore, we can define a relative viscosity which is viscosity of the solution and related to the viscosity of the solvent. So, therefore, you can say let us say that, eta which is the viscosity of the solution minus eta s will be the overall increase in viscosity which is due to adding of the polymer. Now, if you divide that by the solvent viscosity then this is the relative change in viscosity which is brought about because of addition of solvent. Now, students of chemistry and chemical engineer would also know of a infinite dilution activity coefficient and this is very useful in terms of a looking at the non-ideal behaviour in thermodynamics.

So, if we have a and b as 2 components and if a interactions and b b interactions are same as a and b interactions. Then we know it will form in ideal solution, but if a b interactions are different compared to a a and b b interactions then a mixture of a and b will have a non-ideal response. And to characterize this the question that we ask is if I have largely b and if I add just a small amount of a or the other extreme where I have largely a and add a small amount of b how do the nature of interactions play out. And so, infinite dilution activity coefficient is a good measure of what the non-ideal interactions are between a binary system a and b.

So, similarly in this case also, we have a dilute solution we add a polymer to a solvent and in earlier the only it was solvent solvent molecules which were interacting. Now, we have polymer solvent interactions come in strongly. So, therefore, adding a very small amount of polymer, how does it change the viscosity of the solution? So, the best way to take the contribution of polymer to the solution viscosity, is to say that what is the polymer modification at infinite dilution. And so, that is why we define an intrinsic viscosity which takes this relative viscosity we have define which is eta minus eta s divided by eta s. We divide this quantity by concentration and define intrinsic viscosity when concentration tends to 0.

Experimentally, how we do this? Is to measure prepare different concentrations of polymer solutions measured this quantity and then by extrapolating we measure the intrinsic viscosity of a polymer solvent binary system.

So, this intrinsic viscosity is an inherent indicator of the interactions between polymer and solvent. And therefore, it is very helpful to look at intrinsic viscosity of a polymer solutions to get this idea about interactions. And so, this particular data here, shows how intrinsic viscosity varies as a function of strain rate for different polymer solutions.

Now, remember in the previous slide we had discussed the fact that, the overall viscosity is a function of strain rate. Because, of viscoelastic contributions therefore, when we measure the intrinsic viscosity the experimental measurement of intrinsic viscosity could be done at different strain rate. Because, eta itself could be measured at different strain rates and since eta is a function of strain rate the intrinsic viscosity is also a function of strain rate.

Now, what is remarkable about the data shown here is the fact that even though we have a different set of materials they all seem to fall on the same curve. And of course, this data has been normalised with respect to certain variables involved in the problem. For example, the intrinsic viscosity is normalized to one with respect to the intrinsic viscosity of that particular polymer solvent system when strain rate is extremely small.

But the qualitative features. Which are remarkably similar for all the material systems including the extent of shear thinning also because, all the data lie on the same graph is. So, therefore, the fact that the Newtonian viscosity is observed or the viscous intrinsic viscosity is constant for a significant amount of strain rate. And then beyond a critical strain rate we can see a decrease in the intrinsic viscosity.

So, the polymer solvent interactions the way they play out their contributions is similar over a amount of strain rate. So, that the relaxation processes are all relax away or lead to only dissipation and therefore, you get the overall viscous response and only at higher and higher strain rates, other mechanisms play important role. And the fact that different polymer solvent systems have a different set of interactions is hidden in this data because we are normalising intrinsic viscosity.

Similarly, the dependence of strain rate quantitative dependence at the strain rate at which the thinning is observed in intrinsic viscosity may also be different, but in the scaled plot we see that all of them are similar so such convergence of data from different material systems when it leads for us to think in direction that there is a generic explanation possible for such material systems.

And we need not worry about the overall chemical specific details to search for this generic explanations.

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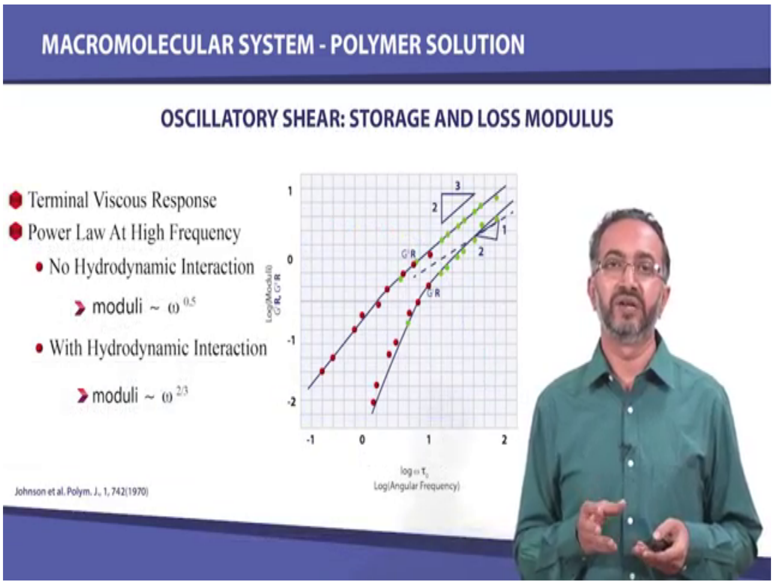

MACROMOLECULAR SYSTEM - POLYMER SOLUTION

OSCILLATORY SHEAR: STORAGE AND LOSS MODULUS

- Terminal Viscous Response
- Power Law At High Frequency
  - No Hydrodynamic Interaction
    - moduli ~ $\omega^{0.5}$
  - With Hydrodynamic Interaction
    - moduli ~ $\omega^{2/3}$

Johnson et al. Polym. J., 1, 742(1970)

Now, when we look at the oscillatory shear response, in terms of moduli of these polymer solutions, we see again broadly 2 qualitative features at very low frequencies. We see the terminal viscous response which is as we saw for all viscous materials at very low frequencies, the g prime is proportional to omega square and g double prime is proportional to omega. And so, the elastic modulus increases far more rapidly at low frequencies when compared to g double prime.

And. So, that behaviour is clearly observed in the polymer solutions that data that is being shown here. Now, what is interesting about the data is that when we reach the higher frequency, we see that we do not observe the glassy response as was let us say predicted by Maxwell model. And we have seen also that Maxwell model shows the behaviour going from viscous to glassy response in just 2 decades itself. While we also have noticed and remarked earlier that. In fact, most real materials the transition may happen over several orders of magnitude.

So, clearly for this polymer solutions, by going to high frequency the glassy modes are not observed the glassy response is not observed, but what is very interesting is the fact that we observe the behaviour to be a specific dependence of moduli on frequency. And so, this aspect we will continue the discussion in the next segment of the lecture.