Rheology of Complex Materials
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Lecture – 40
Survey of Material Functions Polymeric Solutions, Melts and Gels

So, in these set of lectures we are doing a survey of a material functions and we have started out by looking at the polymer solution response.

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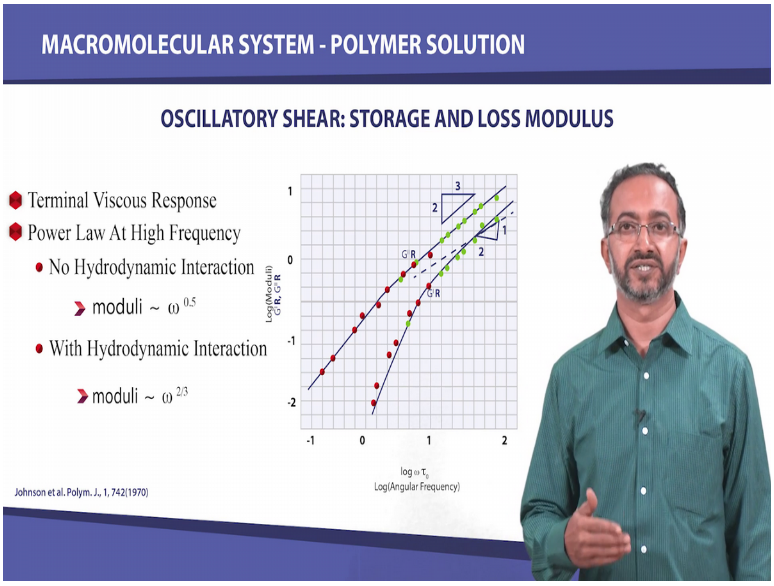

MACROMOLECULAR SYSTEM - POLYMER SOLUTION

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)

And where we stopped in the last segment was we were looking at the oscillatory shear response of a polymer solution and interestingly at low frequency we observed what was expected in terms of the terminal viscous response and what was again interesting was the fact that at higher frequencies the glassy response was not observed again which is expected given that we have a polymer solution and at the frequencies which are 100 or 1000 at such frequency ranges the overall the macromolecular sub segmental motions or even the solvent relaxation modes are not going to appear frozen one will have to go to much higher frequencies for the material to show glassy response.

And therefore, even at high frequencies we observe that the storage modulus for example, is an increasing function of frequency, we know that in the glassy state generally we would observe the loss modulus to be decreasing function of frequency in this case again in a polymer solution we see that even at high frequencies the loss modulus also continues to increase and since the loss modulus is all increasing and the storage modulus is also increasing it is of interest to try to understand what is behaviour or what is the variation of storage and loss moduli as a function of frequency.

And what is observed for a many of this polymer solutions is the fact that there is a power law dependence which again indicates straight line behaviour in a log plot as we are looking at 4 orders of magnitude variation and frequency as well as in modulus.

So, given that both storage and loss moduli are same or similar functions of frequency we can say that the power law dependence is governed by the same exponent and if you look at the polymer solution theories the initial theory by Rawls was developed in which case the overall polymer segment and all the relaxation modes associated with polymers were incorporated and the prediction of Rawls theory was that both storage and loss moduli will be functions of frequency to the power half.

So, clearly since the experiments such as shown in the data here show an exponent which is not half we know that other sets of mechanisms are needed to explain this behaviour and of course, the theory of Jim which accounted for the hydrodynamic interactions. So, the hydrodynamic interactions as we will see later on also are the set of interactions between polymer segments, but they are mediated by the solvent we have seen the example for example, in fluid mechanics we look at particle settling and it is terminal velocity.

Now, the question that can be asked is what happens to the terminal settling velocity of a particle if there are other particles also settling and this is a question where the 2 particles or multiple particles interact with each other through the motion of the surrounding fluid. So, that is why it is called hydrodynamic interaction.

So, similarly in this case when a polymer segment moves it disturbs the solvent around it that disturbed solvent flow field is seen by the other polymer part of the other segment and in turn it will affect how the solvent and polymer move which is again seen by other segments. So, there is interaction between polymer segments which is through the motion of the solvent and therefore, this is called the hydrodynamic interaction and it is also a long range interaction while discussing the behaviour of a theta solvents and good solvents we talked about intermolecular interactions and those are short range interactions while hydrodynamic interactions are long range interactions.

So, the Jim theory which accounts for the hydrodynamic interactions correctly predicts that both storage and loss moduli will vary with power law dependence of a slope of a 0.66. So, therefore, we know that if we have to describe the polymer solution response at high frequencies hydrodynamic interactions must be included when we have extremely low frequencies then in that case the inclusion of hydrodynamic interaction does not play any role because the material and the segments are being sheared at such low rates that the overall response is anyway viscous and therefore, it is independent of the inclusion of hydrodynamic interactions or not.

So, we can see that depending on the time scales of interest the inclusion of mechanisms may also be different and in such cases therefore, it is always important to examine the material response as at adds white a frequency range as possible. So, that different mechanism maybe at play when we have different frequency ranges.

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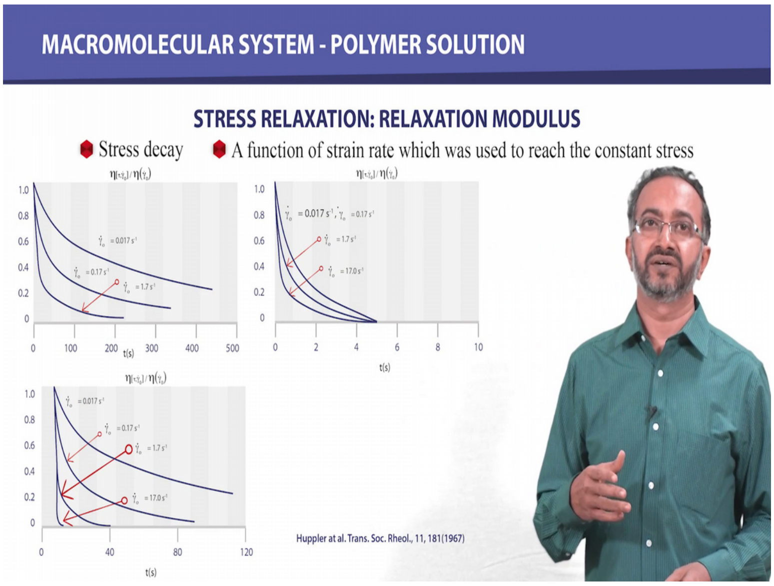

MACROMOLECULAR SYSTEM - POLYMER SOLUTION

STRESS RELAXATION: RELAXATION MODULUS

- Stress decay
- A function of strain rate which was used to reach the constant stress

Huppler at al. Trans. Soc. Rheol., 11, 181(1967)

So, now moving on one can also look at the stress relaxation response of the relaxation modulus and in terms of relaxation modulus of polymer solutions and we know that the polymer solutions will have some elastic contributions and therefore, the relaxation will not be instantaneous and that rate of decay can be examined and the data here shows for a different set of polymer solutions at difference when the overall strain that was applied is arrived at a different strain rate.

We always should remind ourselves of the instrumental limitations or when we actually perform an experiment how it is done. So, we have discussed in course already that stress relaxation implies an application of a step strain. So, at time T is equal to 0 a constant strain is applied on the material now when we perform such an experiment what we in instruct the instrument is to apply the strain; however, no instrument can apply the strain instantaneously there is always a finite time required for the motor to get current and for the motor to rotate and therefore, apply the strain in case of let us say rotational rheometer.

So, therefore, there is always finite times involved in such application now an important aspect therefore, is the fact that in theory while defining we have said a step strain, but in experiments when we are doing the measurement we are always taking a finite time. So, is the material response dependent on whatever is the finite time taken for the application of strain.

So, this is an important consideration and one always should go back and forth in terms of looking at whether the assumptions that we are applying while developing defining material functions developing governing equations are they being actually met when we are trying to do experiments when we are trying to do characterization of materials in a laboratory.

So, therefore, in this case one way to examine this question is to tell the instrument that why do not the strain be increased at a given rate and this rate can be controlled and if let us say for a significant range of strain rate we see a similar response then we could go back and say that the application of strain is important and the rate at which the stain is reached is not really important..

So, in this particular data you can see that the different strain rates when they are applied in order to reach the constant strain value that does significantly influence the stress relaxation behaviour later on and again this is understood from the point of view of the elastic contributions which are there in the material given that at very high strain rates the overall elastic contributions basically respond and so, the material the way it relaxes is different compared to when the strain is been reached at a very slow strain rate.

And so, one can do experiments in terms of providing the instruction to an instrument saying apply a strain and then just look at the overall response and try to gather what can come from it, but it is important also at times to then say that let me see if there is a dependence of how much finite time the instrument takes and therefore, we sit we design a set of experiments to actually examine that question.

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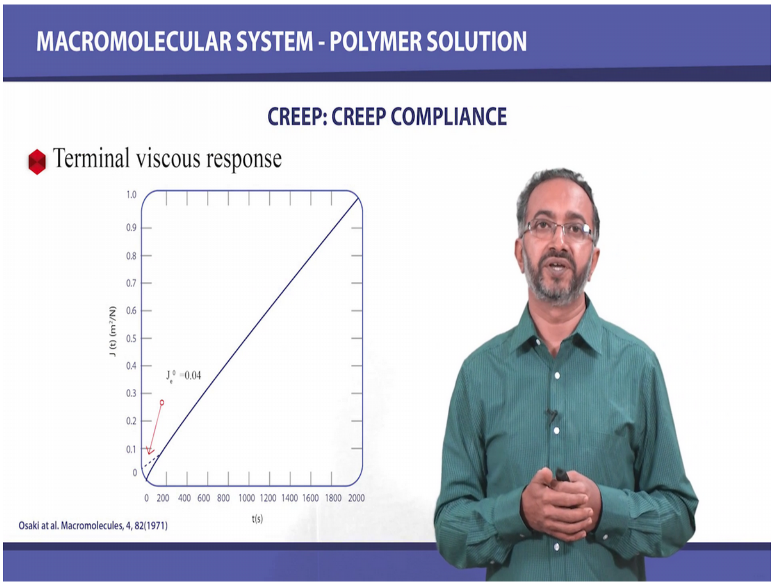

MACROMOLECULAR SYSTEM - POLYMER SOLUTION

CREEP: CREEP COMPLIANCE

- Terminal viscous response

Osaki at al. Macromolecules, 4, 82(1971)

The other property which we have defined and at under some conditions may be useful for polymeric solutions is creep. In fact, you can use creep also to measure the viscosity of a polymer solution or any other predominate let us say more viscous dominating material, when we look at steady shear we apply a constant strain rate weight for a constant stress value to reach and the ratio of stress and strain right is viscosity.

Now, similarly in a creep experiment when we apply a constant stress the material deforms and as the time goes on the strain keeps on increasing and so for a fluid like material which many of the polymer solutions will be what happens is beyond a certain time rate you can see that the strain basically increases at a constant rate which means a constant strain rate has been reached. So, creep is performed when a constant stress is applied and in the experimental response of the material a constant strain rate is reached. So, therefore, a constant stress which is applied and a constant strain rate which is reached the ratio of these 2 could give us the viscosity.

So, therefore, creep can be used for measuring the viscosity of the material system also and. So, in this case what we can see is there is a terminal viscous response and we talked about terminal viscous response in earlier cases whenever we applied very low strain rates or when we applied low frequencies in creep or stress relaxation the terminal viscous response is observed basically at very large times which is analogous to very low strain rates or low frequency.

So, at large times we can see that the strain rate becomes constant and therefore, which is a viscous response and more fluid like response and one can see that at very small short times the overall responses not a linear increase in deformation and therefore, creep compliance has a more complicated time dependence and that is where all the elastic contributions are and so by looking closely at how the overall compliance changes at short times we can get an idea about the relaxation processes in the material or in other words we can get an idea about elasticity of the polymer solutions by looking and focusing on the short time scales.

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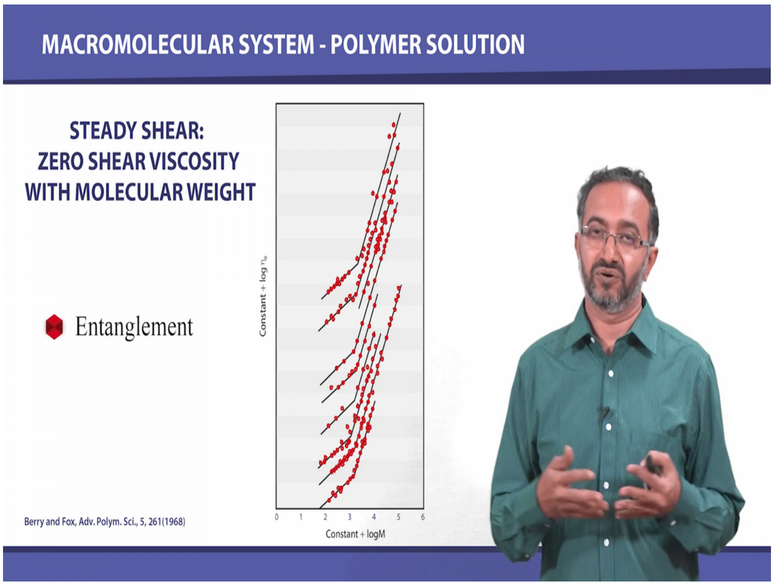

MACROMOLECULAR SYSTEM - POLYMER SOLUTION

STEADY SHEAR:
ZERO SHEAR VISCOSITY
WITH MOLECULAR WEIGHT

- Entanglement

Berry and Fox, Adv. Polym. Sci., 5, 261(1968)

Now, looking now we will change gear and now look at polymer melt systems. So, in we have seen so far that in the polymer solutions we had interactions between polymer and solvent play an important role also interactions between polymer and polymer which is mediated by solvent also played an important role and the interaction between polymer polymer in terms of excluded volume played also an important role. So, these were the basic mechanisms which are important in addition to of course, the segmental motion of polymers.

So, in case of melt the most important feature is entanglement and that is very beautifully described in this set of data where the experiments are done on different sets of polymers and each and every polymer different molecular weights are chosen. So, the data shows here viscosity and as a function of molecular weight. So, as the molecular weight increases we expect the viscosity to increase, but what is very interesting from this data is all of them have a very discontinuous very strong change in viscosity at a given molecular weight.

In other words viscosity depends on molecular weight as sum function and beyond a critical point the viscosity dependence on molecular weight is extremely high. In fact, in the low molecular weight viscosity is directly proportional to molecular weight. So, as molecular weight increases viscosity also increases proportionally, but beyond certain point the molecular weight increase leads to a much stronger increase in viscosity and. In fact so, the points where we observe this change the discrete change in slope or a pronounced increase in viscosity is because of the entanglement.

If we have low molecular weight material if we have low molecular weight polymers then entanglement is less likely and this is quite evident when we eat in a bowl of noodles if the noodles are very long then it is very difficult to extricate one noodle out and therefore, entanglements are very strong, but if we chop the noodles and have them very short then of course, question of entanglement does not arise and. So, as we systematically change the noodle length we will see that entanglement will start playing a role beyond a certain noodle length and that is what is being seen here in this data whereas the molecular weight is increased we can see a clear indication of the entanglement point or molecular weight beyond which entanglements play a very significant role.

We will also see in the survey of material functions the fact that entanglements play a very significant role in describing a whole lot of polymer melt behaviour. We will see that there are timescales beyond which entanglements will stop playing a role and therefore, in that case we will see a viscous response and otherwise entanglements and it is response of polymer motion due to this entanglement is how polymer viscoelasticity is understood.

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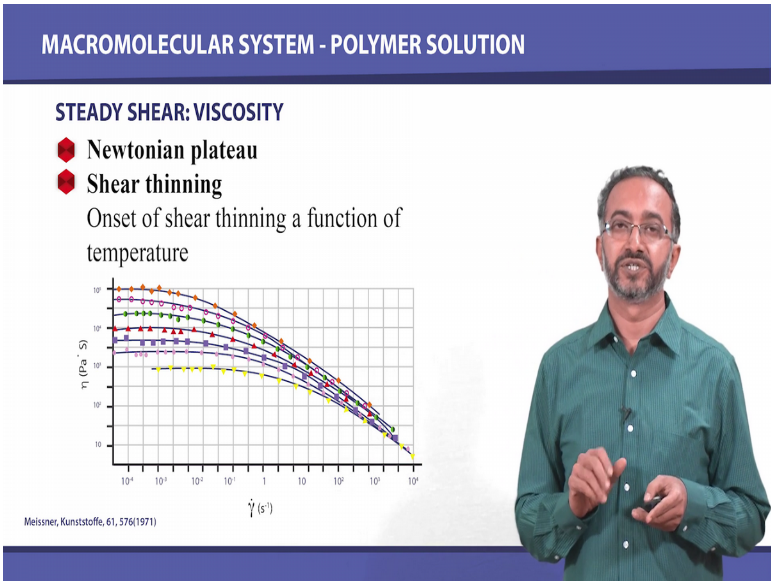

MACROMOLECULAR SYSTEM - POLYMER SOLUTION

STEADY SHEAR: VISCOSITY

- **Newtonian plateau**
- **Shear thinning**

  Onset of shear thinning a function of temperature

Meissner, Kunststoffe, 61, 576(1971)

So, let us start with the looking at viscosity which is a measured in steady shear for a polymer melt the data which are shown here are for a commercial polyethylene melt and when we say it is a commercial polyethylene melt basically what that implies is the molecular weight of a molecules which are there in this melt will be different. So, what is called a polydisperse polymer melt later on we will also examine the experimental data for a monodisperse polymer in which case all the polymer molecules in the melt will have essentially the same molecular weight.

And we will see that how the distribution of molecular weight plays an important role in describing the overall melt behaviour in case of polymers and this is quite natural because as we saw in the previous slide entanglements and the extent of entanglements depend on the molecular weight and. So, clearly if we have a distribution of molecular weights the way entanglements will play a role in terms of determining the viscoelastic response of polymer system will be different and. So, in this particular case we have a polymer which is wide molecular weight distribution and the viscosity is being measured at different temperatures and different strain rates.

So, what you can see again is basic features which we also already have seen in terms of polymer solutions the fact that we observe a constant viscosity region the so, called Newtonian plateau and then we also observed a pronounced shear thinning, again we should see that the strain rate is being measured over at least 7 or 8 orders of magnitude and the overall viscosity variation is also again 4 to 5 orders of magnitude. So, the change in viscosity is quite significant over a wide range of strain rates and what you can see the observations, which are important, is the fact that the viscosity is a function of temperature, again which is expected we generally expect that at higher temperature the viscosity would be lower and that is what is also seen.

The other observation though one can make is the qualitative nature of variations seems to be similar. So, regardless of the temperature we see constant region and then we see a shear thinning, what we can also see is all the curve seem to be approaching similar behaviour. So, at low strain rates the effect of temperature seems to be much stronger at higher strain rate the effect of temperature is much less.

So, clearly this should give us an idea that there is an interplay between the temperature effect or the influence of temperature on the overall viscoelastic response as suppose to the strain rate and how the material the time scales which are given the to the material to respond, how they are influencing the overall material behaviour and the other observation that we can make is the onset of shear thinning that is observed seems to be different at different temperatures.

In fact, what you can see is for lower temperature the viscosity is higher and the critical strain at which shear thinning is observed or onset of shear thinning is also at a lower strain rate which implies that the overall material response seems to have a relaxation time which is much larger. So, that you have to go to lower and lower strain rate to observe the overall viscous response in which case all relaxation processes have to lead to only dissipation or the relaxation processes have to be complete or the relaxation processes are contributing only overall viscous contributions and there are no elastic contributions.

On the other hand for a higher temperature we see that one can go to higher strain rates and still observe Newtonian fluid, Newtonian fluid like response or the Newtonian plateau is observed for a larger strain rate which means the largest relaxation time would have decreased at a higher temperature. We have seen this when we were discussing the relaxation time spectrum and the time temperature position that our expectation is the fact that at higher and higher temperature the relaxation times would decrease and. So, given this basic expectation we know that therefore, the largest relaxation time would also decrease at higher and higher temperature.

So, that systematic variation is very evident in this data whereas the temperature is increased the critical relaxation time or the largest relaxation time in the material also decreases now. So, we can then also try to do further analysis with such data and try to get weather what sort of mechanism should be built in to explain the overall shear thinning nature and such polymeric melts by non dimensionalising this data like what we did for polymer solutions and many of these things were done historically to try to arrive at a more holistic understanding of the polymer melt viscoelastic behaviour.

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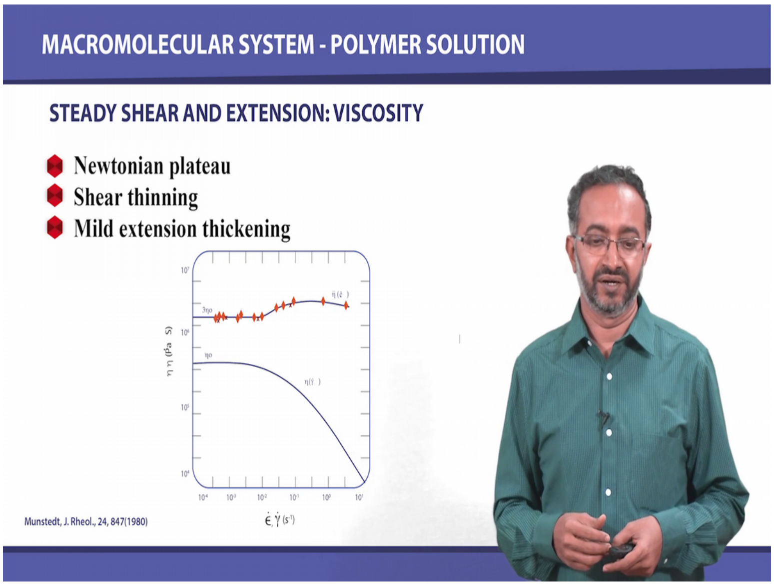

MACROMOLECULAR SYSTEM - POLYMER SOLUTION

STEADY SHEAR AND EXTENSION: VISCOSITY

- Newtonian plateau
- Shear thinning
- Mild extension thickening

Munstedt, J. Rheol., 24, 847(1980)

Now, when we look at the extensional viscosity the picture is quite different and in fact, it is quite commonly said that to polymer melts which may have exactly same or very similar shear viscosity all across the strain rate may show very different extensional behaviour. And this data here actually shows that there is no correspondence between the viscosity observed for steady shear and the viscosity observed in steady extension.

In this case we again see that the shear thinning is observed and then there is a Newtonian plateau. So, at low strain rates we see viscosity becoming constant and again this is an indicator of purely viscous response of the material, when the response is purely viscous we know that the viscosity in shear and extension are related to each other. In fact, the extension viscosity is 3 times the shear viscosity and so that is again evident from the data. Now, as the strain rate is increased in case of shear thinning, we see in case of rates shear we see a thinning behaviour which means at higher and higher strain rates the viscosity goes down.

However for extensional viscosity we see the opposite trend were in fact, the viscosity goes up slightly and so, clearly now by characterizing the shear response one cannot really extrapolate and then say what might be the extensional response. This is only possible for purely viscous fluids and in that case we have the somewhat trivial response in terms of saying that extensional viscosity is 3 times the shear viscosity.

What is also interesting for a many of these materials is that in extensional mode the viscosity steady mode steady value of a stress is not observed. So, when we apply a constant strain rate the stress continuous to increase and. In fact, it diverges so, in such cases there is no steady state that is observed and therefore, in such cases we only look at the stress growth viscosity. So, during defining non-linear viscoelastic response we have already looked at the stress growth in materials. So, in extensional case also we only look at stress growth and then we can compare and contrast the response in shear and extension and then try to understand, what are the mechanisms under play?

Now, for a polymer melt in case of a higher and higher strain rates in shears it appears as if the entanglements appear to play less roll or in other words because of the orientation of macromolecules the entanglements it is easier for entanglements to be slipped past the molecule is able to move despite the entanglements being there and therefore, the viscosity appears to be less and less.

On the other hand in case of extensional response it appears that the entanglement. In fact, plays a role like a cross link. So, given the time scale at which the material is being deformed at very low strain rates it does not matter whether you are in shear or extension the entanglements do not play a role because sufficient time is given to the material, but at higher strain rates the molecular orientation and the slipping of entanglements leads to shear thinning, but in an extensional mode the entanglements appear to play a role almost that of a cross link and therefore, the polymer segments between the 2 entanglements points actually stretch and the more they stretch the higher force is required for their stretching because the polymer segments behave like non-linear elastic springs.

And so, clearly this mechanism of the non-linear elasticity of the polymer molecules will be important to explain the extensional behaviour while in case of shear thinning we may need that to a lesser degree only when we are trying to explain the quantitative response we may need the specific feature otherwise it appears as if the shear thinning can be explained based on the fact that molecular orientation and less importance of entanglements as the strain rates is higher, while in case of extension it is the fact that entanglements play all most like rigid cross links that needs to be brought in along with the non-linear elasticity of springs.

So, therefore, examining of data such as this tells us little bit more about what might be the basic mechanisms which are involved in these material systems.

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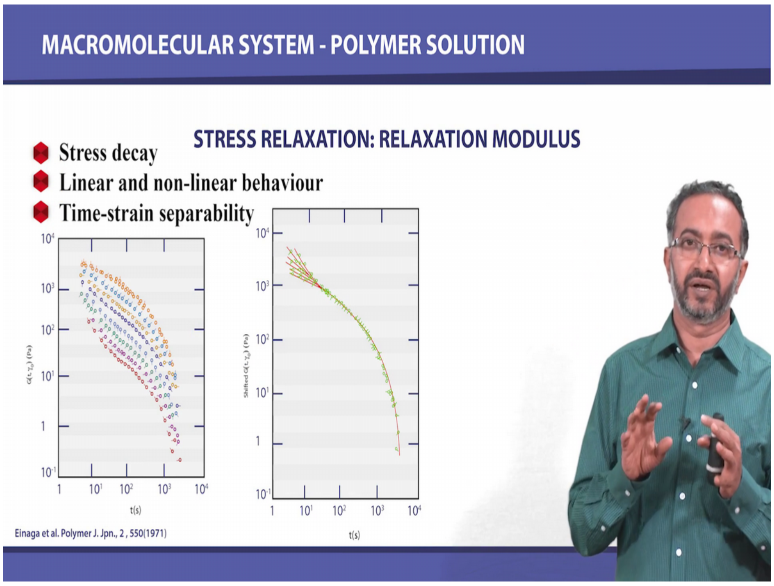

MACROMOLECULAR SYSTEM - POLYMER SOLUTION

STRESS RELAXATION: RELAXATION MODULUS

- Stress decay
- Linear and non-linear behaviour
- Time-strain separability

Einaga et al. Polymer J. Jpn., 2 , 550(1971)

Now, looking at another example of a material function for polymer melts in this case we are looking at a stress relaxation where again a constant strain is applied on the material and relaxation modulus as a function of time is observed. And generally we see the response that stress decay is over the time and if stress decay is to very small values we know that it is overall fluid like response if stress decays to a constant, but non 0 value then we know that it is a more solid like response.

So, clearly because this is a polymer melt we see that exceedingly low values of stress relaxation modulus are observed at high times. So, overall fluid like response is observed in this set of data what is interesting to note is the fact that when strain which is being applied changes the overall response of the material is also different. So, when we apply small strains we see that the relaxation modulus is independent of strain and that is basically the set of data which are on the top of the set where the 2 3 strains which are different strains being applied, but the overall relaxation modulus only depends on time and while defining the material function we had also remarked that for stress relaxation experiment the relaxation modulus is only a function of time in the linear regime.

So, therefore, we can demark it the linear regime in this case by knowing that we systematically increase the strain value and whenever the relaxation modulus starts becoming a function of strain we know that we have reached the non-linear behaviour of material. Now, what is very interesting in his data is if I scale out the strain dependence do I observe similar time response in other words if I shift the curves vertically which means I am taking the strain dependence out do I get the overall same response and that is what is being shown on the right hand side graph where if you just shift the data on one on top of the other. In fact, you see that all of them correspond to the same time dependence.

So, this gives us the overall idea of time strain separability which is quite crucial in trying to understand the non-linear viscoelastic response of various materials and it is also very useful in developing models. So, what we say here is that in the non-linear regime the overall relaxation modulus which is a function of time as well as that of strain happens to be a function which is product of 2 functions.

So, this stress the relaxation modulus is a function of time like in the linear regime which is g of t, but then too that another function which is a function of strain only gets multiplied. Naturally we can see that when strains are very small or we are in the linear regime the h of gamma will actually be just unity. So, in that case the overall non-linear relaxation modulus is same as linear relaxation modulus and the same time dependence is observed.

This is a very important indicator of the basic mechanisms and how they respond what we are saying is when a large deformations are applied the overall response of the material as a function of time is still similar it is just that the extent of which the response is which is strain dependent and. So, the quantitative nature of the response varies, but the overall qualitative response with respect to time still remains the same and so, with this we have finished our partial survey of the polymeric material systems in the next segment we will continue by looking at more set of material functions for the polymeric systems.