Rheology of Complex Materials

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Survey of Material Functions Polymeric Solutions, Melts and Gels
Lecture-41
Survey of Material Functions for Polymers- 3

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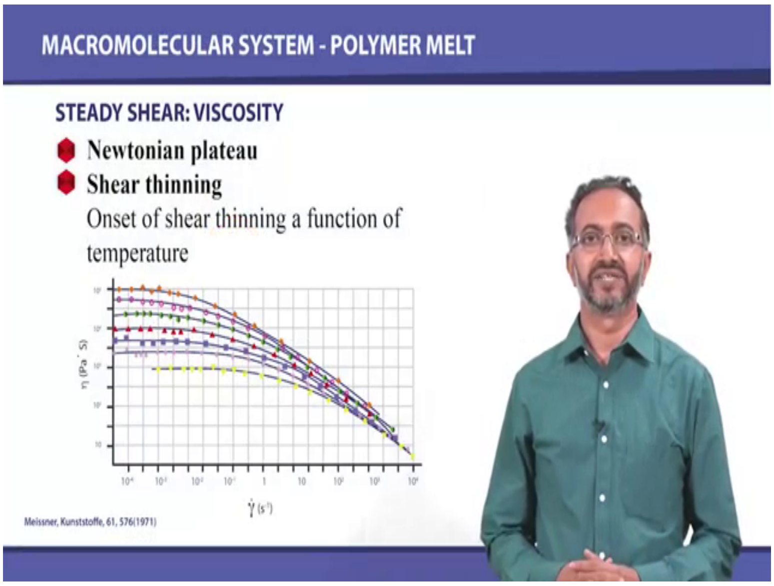

MACROMOLECULAR SYSTEM - POLYMER MELT

STEADY SHEAR: VISCOSITY

- Newtonian plateau
- Shear thinning

  Onset of shear thinning a function of temperature

Meissner, Kunststoffe, 61, 576(1971)

So, we will continue the survey of material functions in this set of lectures.

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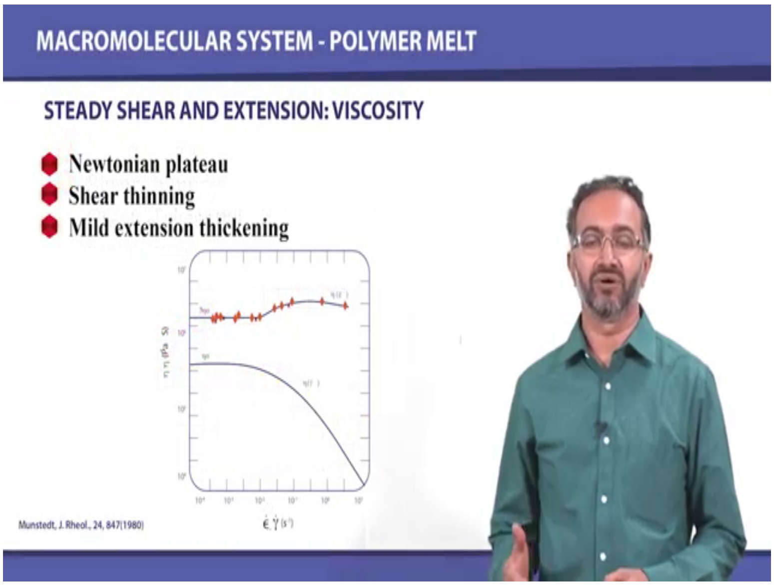

MACROMOLECULAR SYSTEM - POLYMER MELT

STEADY SHEAR AND EXTENSION: VISCOSITY

- Newtonian plateau
- Shear thinning
- Mild extension thickening

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

We are looking at the response of polymer solutions melts, and we will also look at the response of gels. We were examining the response of the melts systems where we looked at the overall shear thinning nature of the viscosity, and how viscosity decreases as a function of strain rate and the dependence on temperature.

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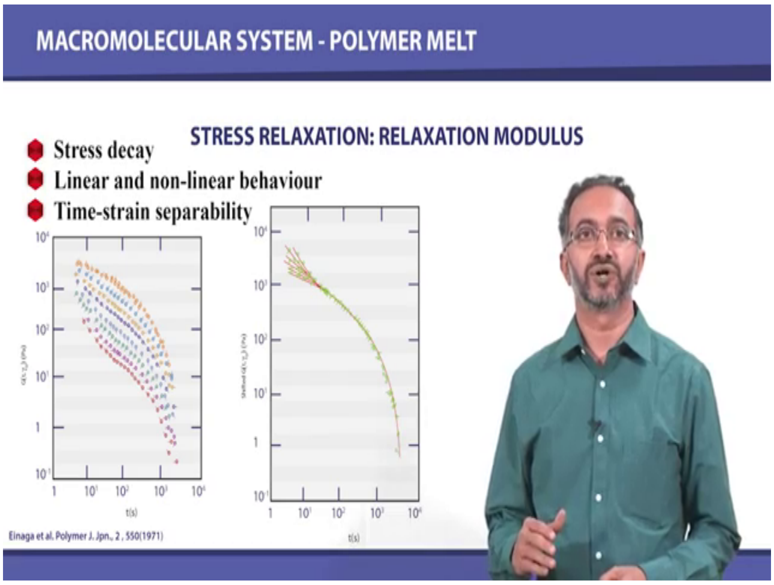

MACROMOLECULAR SYSTEM - POLYMER MELT

STRESS RELAXATION: RELAXATION MODULUS

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

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

We also saw the different responses that are seen in shear and extension and the fact that only at very low strain rates the shear and extensional viscosity as related to each other which is based on the viscous response. We also saw the relaxation modulus and the fact that one can recognize the onset of non-linear response based on testing at different strains; and very importantly the concept of time strain separability the fact that the overall stress relaxation modulus is a composite function in the sense that it is a function of time multiplied with a function of strain alone.

So, the overall stress relaxation which is a function of time and strain can be separated into two functions. And at very low strains, basically the damping function h goes to unity or goes to one and therefore, we have the linear response which is signified by G of t .

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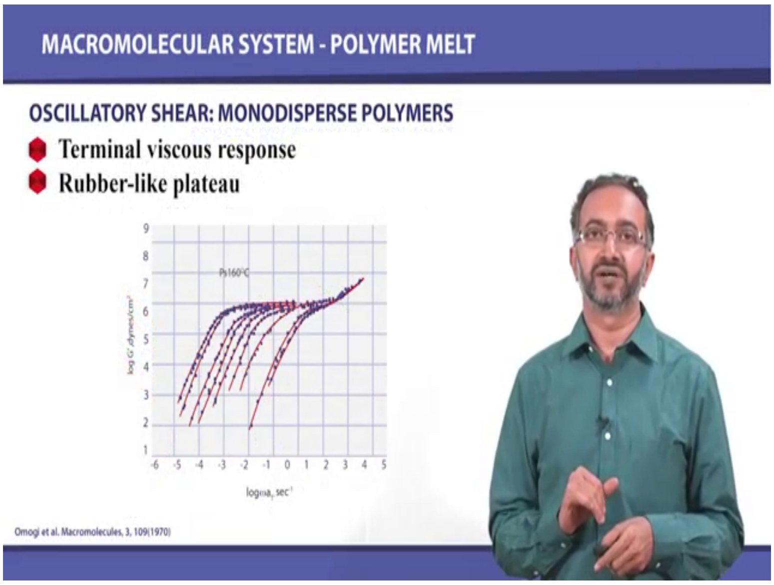

MACROMOLECULAR SYSTEM - POLYMER MELT

OSCILLATORY SHEAR: MONODISPERSE POLYMERS

- Terminal viscous response
- Rubber-like plateau

Omogi et al. Macromolecules, 3, 109(1970)

And now let us come to another interesting oscillatory response in this case we are looking at the storage modulus or the elastic modulus of a polymeric melt system. The polymeric melt is of different molecular weights. And so there are several observations again one can make from this set of data. We can see that at very low frequencies all of them show the overall increase in storage modulus as a function of frequency, you can see that all the slopes are essentially going to be two.

So, you have G prime increasing with as omega squared for low frequencies; and it does not matter what is the molecular weight all of them at low in a frequency show this response. At any given frequency you can see that the modulus is dependent on the molecular weight. The what is common for all is the fact that G prime scales as omega squared for all of them and this we have seen also earlier the fact that when we were looking at viscosity as a function of molecular weight viscosity increases as a function of molecular weight.

So, similarly here also at a given frequency for a given molecular weight, there is one value of G prime; at that same frequency when we observe another molecular weight clearly the G prime will be different, but what is important is the overall viscous terminal response being observed for all materials. And since this is a polymer melt, we can see that the there is beyond a frequency or less than a critical frequency, we will observe the overall terminal viscous response.

Now, what we can also see is the fact that beyond a certain frequency at high in a frequency all the curves in fact merge, and there is only one set of curves which can describe the overall behavior. And so that again indicates that molecular weight of the polymer is important when we are examining the material at low frequency, but the molecular weight appears to be irrelevant as far as the high frequency behavior of these polymer melts are concerned. So, clearly the overall polymer and its length is not important, but what is important in this case is the length between entanglement points and so the overall response that is pictured in these data is due to the entanglement behavior of polymeric melts.

So, at very low polymer molecular weight, what we see is the fact that there is a terminal viscous response, the modulus increases and then we have a very small region in which entanglements play a critical role. And then we again observe a response which is independent of the molecular weight which means segments which are much smaller than the overall entanglement length play an important role in that segment. And since segments sub segmental behavior is independent of what is the overall molecular weight we see that all of them show same response.

But if you look at the other extreme of molecular weight where molecular weight is extremely high, what we see is a behavior where there is an initial increase. So, we see that the modulus increases initially then it becomes constant. And there is a significant frequency range two-three orders of magnitude depending on what molecular weight you have, where the overall modulus appears to be reasonably constant. And then again beyond a certain frequency it increases.

So, what we can see is the fact that initially terminal viscous response is observed which means the material is being sheared at such low frequencies that the entanglements can relax, the entanglement can slip out the overall repetition of motion of molecule is possible completely easily because entanglements are also relaxing away. So, we observe the terminal viscous response. Now, at these middle frequency ranges, it appears as if the entanglements are causing the repetition only to take place. So, polymer molecule can move only like a true repetition.

And, so, in this case the entanglement point appear to be playing a role of cross links. And therefore, the polymer molecule which is only between segments can deform. The reputation is fluff far slower, so therefore, it does not really contribute as significantly. However, the segmental motion between two cross linked points start contributing significantly. And this is a response which is very analogous to a cross linked rubber. If you have polymer chains which are thermal energy is enough for them to be dangling about and moving, but at the same time the polymer chains are cross linked at the end, then we get the overall rubber like response which is predominantly elastic. And therefore, in this case also the entanglement points given the middle frequency range appear to act like cross links and between the cross links the segmental motion gives an overall rubber like plateau.

So, for these set of mono dispersed polymers where each and every sample has a definite molecular weight in a very narrow range. What we can see is the fact that the at low frequencies, there is a terminal viscous response, then there is an entanglement plateau or the rubber like plateau. And then beyond at higher frequencies, we probe smaller and smaller lengths of polymer molecule or we probes shorter and shorter relaxation as shorter and shorter time relaxation processes, we see that the overall sub segmental modes of relaxation being examined. And so there of course, there is no molecular weight dependence at all.

Now, the length of the rubber like plateau region is a strong function of the molecular weight of the polymer. So, if the polymers are long then the rubber like plateau is more significant. This is again understandable because the extent of entanglements will be much larger with the longer length; and therefore, over a wider range of timescales we see the rubber like plateau. Af we have very low molecular weight then entanglement points are fewer and therefore, the overall rubber like plateau is observed only over short timescales and that is what we see that each and every polymer molecular weight it initially increases, then it joins the curves at rubber like plateau. And beyond rubber like plateau there is a systematic increase which is independent of molecular weight.

So, this set of data actually very nicely shows how molecular weight and entanglement play an important role in determining the linear viscoelastic response of polymer melt. One can think of what would happen if one mixes all these polymer melts and then looks at the oscillatory response. So, in what is called the commercial polymer sample this is likely to be the scenario. So, it is a good thing to think about what would happen if these samples which were different and they all had the mono dispersed sample or each and every sample had only one molecular weight with very very narrow distribution. Now, if these are mixed together and a sample is prepared which has a very broad molecular weight distribution, how would it response be in the as a function of frequency and that is what is can be seen later on when we look at the overall the polymer melt response for a commercial polymer melt.

What we will see is given that all these different molecular weight samples are together, we will be unable to see a very pronounced rubber like plateau in fact, what we will see is the G prime at the low frequency range, we will have again the terminal viscous response, but beyond that there will be a gradual increase. And, so, the viscosity keeps on in the G prime and G double prime keep on increasing monotonically without a plateau behaviour in case of a poly disperse sample. So, careful experimentation with very controlled samples gives give us a better idea of what the inherent mechanisms are. And, so, in this case doing experiments with mon mono dispersed polymer gives a much better idea about the role of entanglement, reputation and the presence of rubber like plateau in case of polymer melts.

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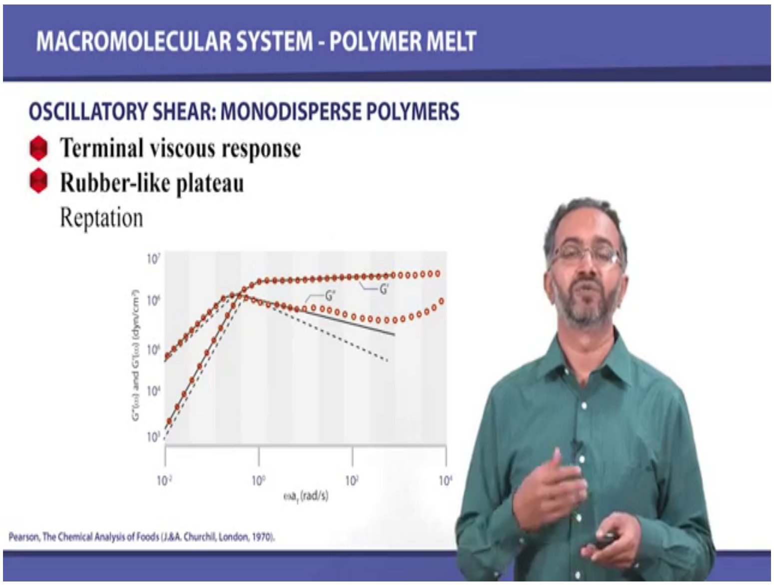

MACROMOLECULAR SYSTEM - POLYMER MELT

OSCILLATORY SHEAR: MONODISPERSE POLYMERS

- Terminal viscous response
- Rubber-like plateau

Reptation

Pearson, The Chemical Analysis of Foods (J.&A. Churchill, London, 1970).

Similarly, the polymer melts with mono dispersed polymers were also very useful in quantifying the overall dependence of G prime and G double prime on molecular weight and on frequency. And for example, this set of data here for which shows terminal response and then overall G prime, G double prime variation in case of the rubber like plateau. What we can see is that the predictions based on reputation theory are in fairly good agreement. Of course, we can see that there is a limited agreement, so therefore, the basic reputation theory has been improved upon over the last couple of decades to incorporate more and more realistic feature which can capture even a wider range of frequency response, so that we can explain more quantitatively the overall response of polymer melts.

And in case of when we have poly dispersed polymers clearly to develop a theory using reputation or any other such fundamental theory will be more challenging. And, so quite often therefore, we still use models which are semi empirical in nature which try to capture the overall response in an effective way though we may not have complete idea about how do the parameters vary or how do what is the systematic variation of parameters for molecular weight or any other such compositional dependence that we may have on the parameters.

So, therefore, we always have these two sets of investigations; on one side we try to do very controlled experiment with very controlled samples, mono disperse may be uniform size of particles in case of colloidal systems. So, all of these to understand and try to see what is the mechanisms at play. And then on the other side, in an engineering application we usually have poly dispersed polymer or a set of particles which need not be sphere, but mixture of sphere and near spherical particles. And and therefore, we use some of the mechanisms that we have understood to try to develop better and better semi empirical models for a engineering system. And therefore, it is important for us to look at the experimental observation for both of these systems. And in the research domain more often than not we are looking at more controlled types of material systems.

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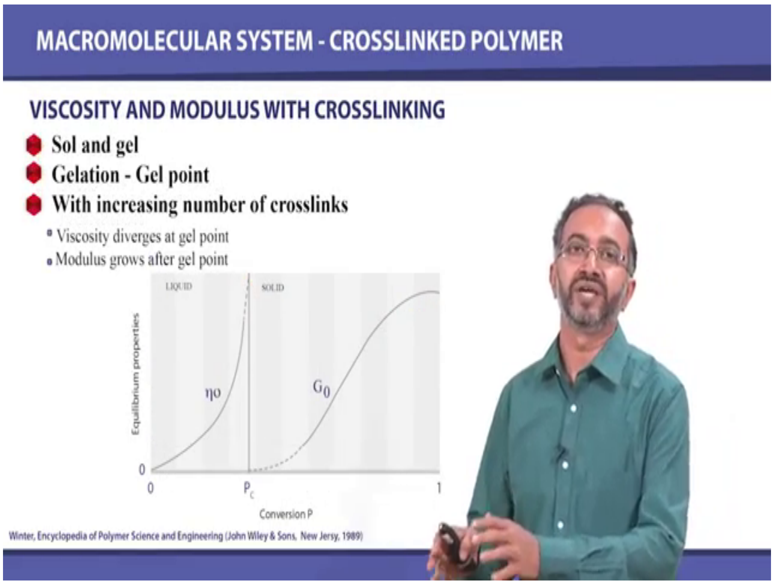

MACROMOLECULAR SYSTEM - CROSSLINKED POLYMER

VISCOSITY AND MODULUS WITH CROSSLINKING

- Sol and gel
- Gelation - Gel point
- With increasing number of crosslinks
  - Viscosity diverges at gel point
  - Modulus grows after gel point

Winter, Encyclopedia of Polymer Science and Engineering (John Wiley & Sons, New Jersy, 1989)

So, now we will look at the other set of polymeric systems, we have finished looking at solutions and melts. So, in the remaining segment of this lecture, we will look at the cross-linked polymer; cross-linked polymer in the form of rubber is known and that is a more solid like material with it its response is also important. We will also see if the polymer is cross-linked, and it has significant amount of solvent in it. So, so generally we will tend to describe these two material systems differently.

When we say rubber we are talking about a polymer molecules cross-linked and with no presence of a solvent and generally this material is flexible and it deforms to a great extent at under room temperature conditions. On the other hand, we have cross linked polymers. In addition to the cross linked polymer it has absorbed lots of solvents a large amount of solvent, and therefore, it is in a gel state. And generally these gels may not deform as significantly as rubber. And they have a far more gel like or soft material like texture as opposed to rubber which has a far more solid like texture. And, so generally when we have gelation reactions or cross linking reactions which lead to gel what we do is we start with sol or which is a very low molecular weight material.

So, it could be solvent and monomer mixed together and then as reaction goes on the monomer start reacting and polymer starts getting formed. And beyond a certain the extent of reaction what we have is an infinite molecular weight formed in the system. And in that case what happens is the viscosity therefore diverges viscosity becomes infinite and then the modulus that point onwards starts increasing. And, so we have what is called a gel point the extent of gelation is characterized using this gel point. This is fairly important from the point of view of processing of materials, because once the gel point is observed given the three-dimensional network structure that is seen in the material, the shaping of the materials is not possible beyond gel point. So, all the shaping of the materials has to finish before the gel point is observed.

So, generally gel point measurements are very common for cross-linked materials whether gel type or rubber type. And, so, here qualitatively the data is shown that when we have the reaction going on with monomer reacting to form the polymer what we have is the increase in viscosity. Since, molecular weight increases we know and we have seen data in the survey itself that the viscosity would increase with higher molecular weight. And as we approach the gelation point the viscosity becomes infinite because at gel point we have a three-dimensional network basically there is one molecule which I which has infinite molecular weight and it spans the overall sample itself.

So, if you are doing this in a beaker, there is at the gel point, the overall beaker contains a polymer molecule which you can start from one end of the beaker and reach the other end of the beaker. At the gel point though there are several other fragments at different molecular weights, there also would be monomer and so therefore, reaction can still proceed further and the and that is what is depicted in the graph here. That when reaction proceeds further, this material which has become solid like because of the presence of an infinite molecular weight material starts exhibiting higher and higher modulus.

And, so, modulus starts becoming more and more significant and it increases. So, therefore, we can see that viscosity diverges at gel point and the equilibrium shear modulus becomes significant beyond the gel point. So, these two could be used as a measure of gelation in materials which undergo this cross linking and achieving a three-dimensional network.

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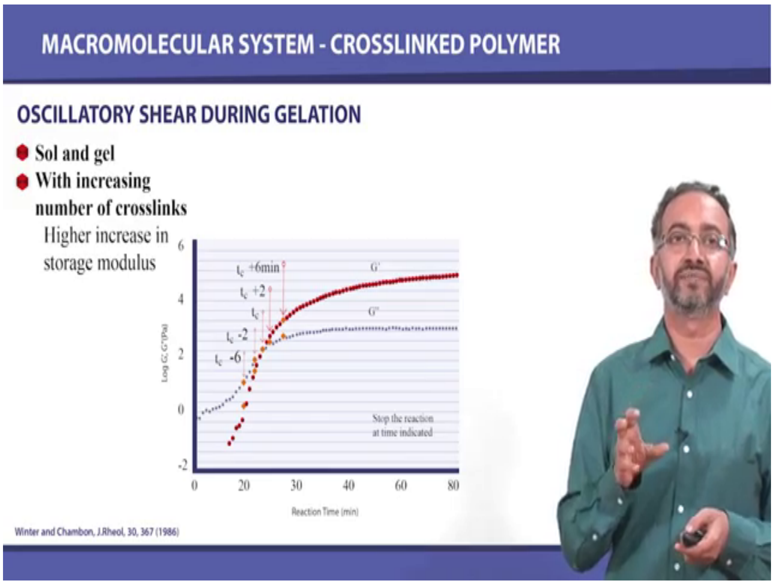

MACROMOLECULAR SYSTEM - CROSSLINKED POLYMER

OSCILLATORY SHEAR DURING GELATION

- Sol and gel
- With increasing number of crosslinks

  Higher increase in storage modulus

Winter and Chambon, J.Rheol, 30, 367 (1986)

And, so, this can be done using an oscillatory shear experiment also. In the previous slide, what we saw is measurement of viscosity and also the measurement of shear modulus which is equilibrium shear modulus which means a very low frequency measurement, but we could actually measure the oscillatory shear at different frequencies. And one such frequency data is shown in this graph here. So, again what we see is at very short times of reaction the material is predominantly sol or low molecular weight material. And as the reaction goes on the molecular weight starts increasing because monomer starts attaching onto each other and we get longer and longer chains; of course, these chains are also cross linked because we are looking at a cross linked system. So, there is a cross linker also which is put which is a part of the reaction ingredients which leads to cross linking between these polymer segments which are growing.

And, so, with increasing number of cross links what we see is the G prime starts increasing more rapidly. The elastic contributions play a more significant role as molecular weight is higher because of the between the two cross linked points the segmental mobility and due to the entropy of these segments, basically we will start seeing more and more entropic elasticity developing in the material. And of course, at the gel point, we have a three-dimensional structure and because of this three-dimensional structure we have basically the incipient network elasticity which starts playing an important role.

So, one can say that the gel point is observed where G prime crosses G double prime. So, we have two regimes, regime where G double prime or the viscous response of the material is significant because sol behaviour dominates. And then beyond a certain time the gel behaviour dominates and the three-dimensional network elasticity of the material plays a more significant role. And therefore, the gel point d markets these two regions.

So, in this graph for example, it is also shown that how if you were to freeze the reaction at different times let us say two or four or two or four any both sides of the gel point, then you would see that you have frozen the material in the solid state or you have frozen the material in gel state, but beyond gel point. And, so, at different times you would observe that the overall fraction of sol and gel would keep on varying in this material as time goes on. What you can see is at the large times when we have extremely large times the reaction is pretty much complete; and in that case both G prime and G double prime become constant. And they become independent of time, and therefore, now the overall cross linked polymer has been obtained and the reaction has been completed.

And in that stage again we observe a typical gel like or rubber like response depending on whether we have solvent in the cross-linked polymer or not; and in both cases G prime is significantly higher at least an order of magnitude or even higher than G double prime. And if we were to do frequency response of the completely cured system or completely reacted system, we would also generally see that G prime and G double prime are independent of frequency. We will see this in the couple of slides later. So, therefore, we can monitor the overall gelation process or the overall cross linking process in the material by examining the oscillatory shear response of the material. And the one issue with such measurements is the fact that both G prime and G double prime are functions of frequency.

So, if one were to do these set of experiments at a different frequencies, we may observe that the crossover between G prime and G double prime is observed at different time and. So, the gel point measure mention measurement or the estimation of gel time would depend on what frequency has been chosen to measure the G prime and G double prime. So, this can be used as an engineering estimate to say what is the gel time, but from a theoretical point of view it would be far more satisfying.

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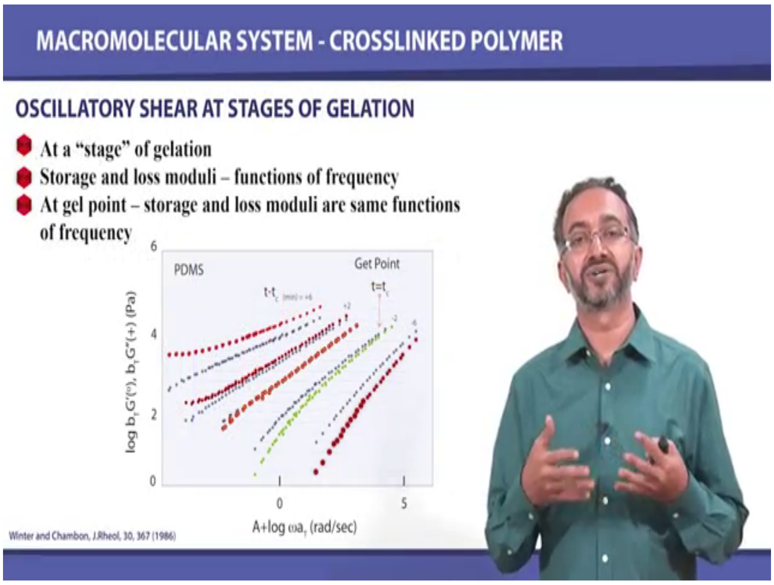

MACROMOLECULAR SYSTEM - CROSSLINKED POLYMER

OSCILLATORY SHEAR AT STAGES OF GELATION

- At a "stage" of gelation
- Storage and loss moduli – functions of frequency
- At gel point – storage and loss moduli are same functions of frequency

Winter and Chambon, J.Rheol, 30, 367 (1986)

If we were to get a measurement of gel time which is not dependent on how the gel time is being measured. Because our basic idea of what is happening during gelation is the fact that monomer reacting forming larger polymer segments, polymer segments cross linking with each other eventually forming a three-dimensional network and this three-dimensional network is responsible for the salt to gel transition. So, there is one critical point at which this three-dimensional critical network is observed and that observation of this three-dimensional critical network is not dependent on what frequency the measurement is being done.

So, if you look at let us say the data at these different times, and this is again classical data which tries to show as to what happens to the sample at when we look at the gel point and little bit away from gel point that is both when the gel was not formed as we are approaching the gel or once the gel has formed and we go beyond. So, in this set of data, we can see that when the material is predominantly in the sol state or there is predominantly low molecular weight material, the extent of reaction is small, the overall response is liquid like. And we see predominantly just power law dependence basically straight lines on a log log plot, where the dependence of G prime and G double prime is according to overall general viscous terminal response.

And as reaction proceeds we again see that the other extreme where the overall G prime of the material has become constant as a function of frequency in the lower frequency range, and then of course, there is a frequency dependence as frequency increases. So, there is somewhat reminiscent of a polymer melt like response, where at low frequency we had terminal viscous response, here we have a terminal solid like response. So, G prime is completely constant as a function of frequency and then later on you have frequency dependence. In case of polymer melt, we saw that there was initially terminal response, then a rubber like plateau and then an increase.

So, we are seeing the rubber like response here, where G prime is constant. And of course, no matter how low in frequency we go we will not be able to observe the terminal viscous response in this case because these are permanently cross-linked polymer molecules. So, there is no terminal viscous response possible. Now, it between during the as the gelation is happening, we can see that G prime and G double prime start increasing which we saw earlier. And what is important in this graph to observe is how they vary as a function of frequency. And at the gel point what this data shows remarkably is that both G prime and G double prime are same functions of frequency.

So, therefore, if we were to measure tan delta for under different frequencies what we will see is tan delta is the function of reaction time, but at the gel time since G double prime and G prime are both same functions of frequency, we will have tan delta being constant. So, therefore, this kind of a data can be re plotted in terms of tan delta as a function of reaction time to get the overall gel time. Now, once the gelation is complete and we have obtained the gel or the overall cross-linked polymer.

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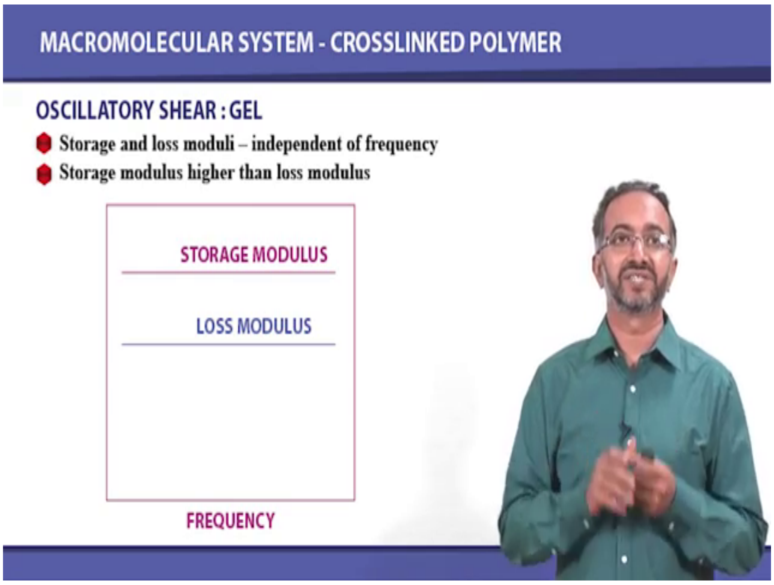

MACROMOLECULAR SYSTEM - CROSSLINKED POLYMER

OSCILLATORY SHEAR : GEL

- Storage and loss moduli – independent of frequency
- Storage modulus higher than loss modulus

Then as I have said before and pointed out that storage modulus and gel modulus become constant. And a very dominant signature of gel like response is the fact that both storage and loss moduli are independent of frequency. So, over at least three four orders of magnitude and frequency, we see that storage and loss modulus are constant. And generally storage modulus is higher because of the dominance of network elasticity significantly of course, there is a dissipative response also in the material because there is solvent and also there is sub segmental modes which can contribute to the dissipation in the material.

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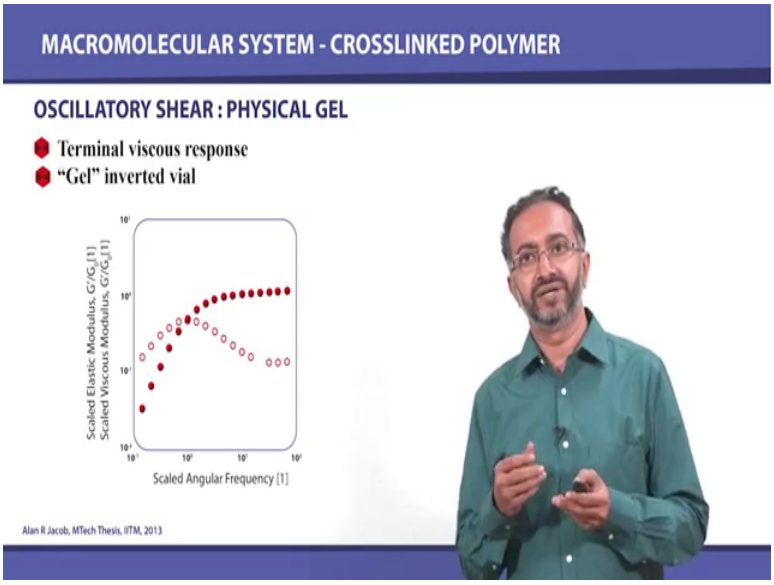

MACROMOLECULAR SYSTEM - CROSSLINKED POLYMER

OSCILLATORY SHEAR : PHYSICAL GEL

- Terminal viscous response
- "Gel" inverted vial

Alan R Jacob, MTech Thesis, IITM, 2013

Now, in common parlance, and also in the rheological literature we used the word gel sometimes to only signify the fact that if you do a short time test on the material, it seems to show a solid like response. So, for example, if we make the material in a vial, and we turn the vial upside down the material does not flow like a fluid. And sometimes this kind of materials people who are making new materials people who are examining new materials, people who are also trying to develop biomaterials would call this material a gel because it does not really flow. But if you allow enough time for example, if we turn it upside down and keep it and come next day we will see that the material is flown and it in fact has acquired the new shape whatever may be the overall lid area and the bottom of the top of the vial.

So, therefore, generally many of the gels if they are only physically cross linked will show this kind of a response. So, if they we perturb them over short timescale, so a very high frequency then they show overall solid like response. But if we allow long enough time then whatever are the physical cross linked points which are present in the material will relax, and therefore, you can have an overall viscous response in the material.

So, this data here shows an example such physical material which is formed with micellar worm like myself solutions and in this case we can see that at very low frequency, we have terminal viscous response; and at high frequency you have the overall G prime being constant. And of course, having discussed Maxwell model in class we can see that at least many features of Maxwell model are very well captured in this data. So, ah, but this is only a physical gel in the sense that it shows gel like responds only under limited frequency condition; while it has a terminal viscous response and therefore, the cross links are not permanent to show us even rubber like response that even exceedingly low frequencies.

There is also a distinguishing feature between chemical gels or gels which are cross linked through covalent bonds and physical gels which are usually cross-linked through physical bonds or Van der Waals or ionic or hydrogen bonding or such interactions. So, there is always a timescale associated with these interactions and based on the rate of perturbation we can observe these cross links to be somewhat permanent and therefore, contributing to elastic response or completely dissipative and therefore, giving us terminal viscous response.

So, therefore, we have looked at various responses of the gel material. Now, in the next segment of the class, we will look at cross linked rubber and glass rubber transition.