Rheology of Complex Materials
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Survey of Material Functions: Multiphase systems And Macromolecular/ Multiphase Systems
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Survey of material functions for polymers 4

So, in this segment of polymer survey of polymer material functions. We are going to look at polymeric solutions melts and gels; what we are doing is looking at some of the classical data that has been recorded over a few decades, which gives us an idea about the viscoelastic response of these polymeric systems. And in general when we work with a new material it is very useful to first compare the set of data that we obtain with some of this classical data for us to get an idea and understanding about what the new materials that we are investigating.

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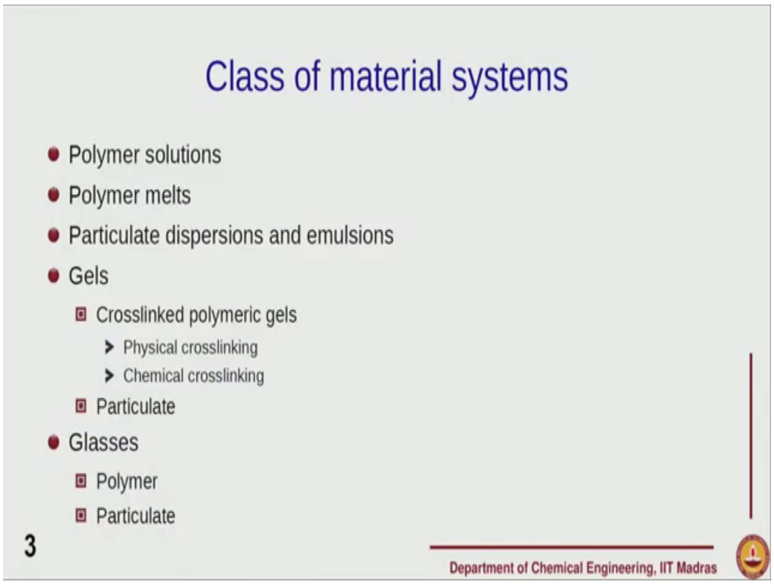

Class of material systems

- Polymer solutions
- Polymer melts
- Particulate dispersions and emulsions
- Gels
  - Crosslinked polymeric gels
    - Physical crosslinking
    - Chemical crosslinking
  - Particulate
- Glasses
  - Polymer
  - Particulate

And so, we are following the same class of material systems that we had discussed during our introductory section where we said that we can look at solution melts we can look at dispersions emulsions, we can look at gels and glasses and specifically now we are looking at polymeric systems and so. In the previous three lectures we looked at the solutions and melts and the gels and so.

Today, we will finish up with some discussion, which is related to the glassy state of polymer and from a rheological point of view, what more important is this transition from the glassy state to the rubbery state.

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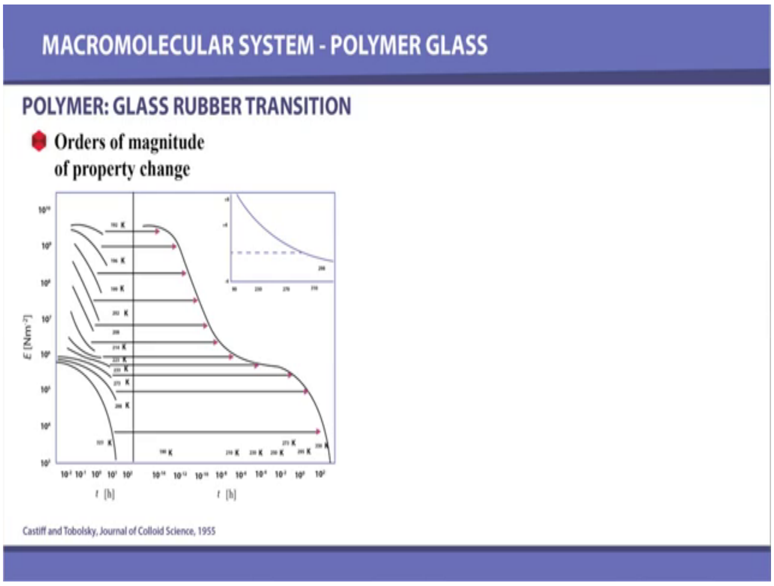

MACROMOLECULAR SYSTEM - POLYMER GLASS

POLYMER: GLASS RUBBER TRANSITION

- Orders of magnitude of property change

Castiff and Tobolsky, Journal of Colloid Science, 1955

And, so, what we will do is? Look at experimental measurements that have been done on a polymer. In this case this is a poly isobutylene polymer and what we can see is? The fact that the experiment is done for about 10 hours and the measurements are done at various different temperatures and the temperatures ranging from 192 all the way up to slightly higher than room temperature around 50 degrees Celsius.

So, the idea is to do the experiment for a limited amount of time over a broad range of temperature and then use time temperature superposition to use this data to actually correspond to data at a given reference temperature. So, in this case for example, the temperature reference temperature which has been chosen is 298.

So, therefore, keeping the 298 data at it is place we will need to shift the data below above to the left or to the right. So, one thing that you might want to think about is in terms of which data will get shifted to the left and which data will get shifted to the right the other way to ask this question is the property which is measured at 323 Kelvin at what times will it be similar to the property at 298 or conversely properties which are let us say measured at 202; and what times will they be similar to the properties at 298.

So, we always have to remember in this that we when we discuss time temperature superposition; we discussed that longer times is analogous to higher temperature and therefore, whenever we have either provide longer times to materials or we take materials to higher temperature we get more viscous response correspondingly if we go to lower times or if we go to lower temperatures, then we get more elastic response and so. In this case also we can see that given that the test is being done at lower and lower temperature which means the relaxation times of materials at lower temperature would be higher and higher. So, more and more elastic response is expected.

So, therefore, at 298, if we were to observe the same kind of response we would have to go to much lower times. So, at 298 if we go to lower times we will see more and elastic response similarly at 298; if we go more and more we will see more viscous response and. So, 323 will have to be shifted to the right. So, that since this is a higher temperature we naturally expect more viscous response or relaxation times to be lower. So, that will indicate response at very larger times.

So, the 323 will have to be shifted to the right and therefore, you can see now that the data which was obtained for about 10 hours. Now because of shifting to the right has increased to more than 100 hours; similarly all the data which was req acquired at the temperatures far below 298 Kelvin all of them will be shifted to the left and. So, we obtain data which is at much lower and lower time and so. In fact, 192 Kelvin as the plot suggests is actually data which is now corresponding to ten to the power minus 14 hours.

So, by doing this time temperature superposition in effect what we have done is obtained the material performance from an extremely short time of 10 to the power minus 14 hours to 10 to the power 2 or 10 to the power 3 hours. So, even though the experiments were done for a limited amount of time using time temperature superposition a broad range has been obtained and, what we can see; now in this time domain graph is a systematic transition.

So, if we subject the material to extremely low times of stress relaxation experiment or what we would see is basically the material model being constant and it being very high. So, we are talking about giga Pascal range. So, material in this state is a glassy material and as the more and more time is allowed to the material we get. In fact, a more softening of the material and we can see that there is an orders of magnitude change over

3 or 4 orders of magnitude and then the modulus becomes again constant which is the rubbery region and. So, beyond again if you allow further time then we again have material. In fact, undergoing even more softening and.

So, what we see effectively in this case is a glass to rubber transition same thing could be done if we had the luxury of actually measuring these things at 298 k and such times which are 10 to the power minus 14 and minus 12. Since that is not possible the only way we can observe this glass to rubber transition is we let us say start from a very low temperature and then measure the modulus of the material and; that is what could have been also done that we take a fixed time and we measure the modulus at different temperatures and. So, that also you can see initially is very high then it goes down and then it. So, therefore, different times we can see that the temp in general modulus decreases as a function of increasing temperature.

So, in this case modulus also decreases at constant temperature as a function of increasing time. So, we can again see time temperature equivalence and this variation is due to the mobility of polymeric chains the fact that if we perturb them at very short amount of time. The time is not enough for the segments to respond for even single bonds to rotate the only possibilities of ah some of the vibrations of bonds and such motions may be allowed; however, bond rotations and segmental motions are not possible at such short times, because generally the time scales involved in these phenomena are much higher.

So, but when we now perturb the material to over a longer duration of time, then we can see that segmental mobility plays to plays a role and therefore, materials eh appears to be far more flexible compared to when it was in the glassy state. So, between glassy state and rubbery state the key differences in terms of segmental mobility and when we go further higher in temperature then. In fact, the segmental mobility becomes easier and easier with more thermal energy available or when we go to higher and higher times given that we are allowing more time for the material, then it is possible for entanglement chain slippage and several other such contributions to play an important role.

And therefore, the material appears to be even more flexible another key thing to note in such time temperature superposition is how much was the shift which was used as a function of temperature and. So, one can see that at 298 of course, the shift factor would be one and therefore, log of 80 is 0, but one set of shift factors are used which are to the left take the material to the to the properties to the left and one set of shift factors which are to the right and of course, if this corresponds to our knowledge in terms of wlf or Arrhenius; then we know that the shift is not arbitrary and therefore, the overall shifting is indicated and.

So, this is an example of how material response would be if we appear closer and closer to glassy state and we will have to perturb the material at lower and lower times or we will have to perturb the material at lower temperatures similar data is also shown here in terms of oscillatory shear. Now, most often in the course we have discussed the oscillatory shear response in terms of G prime and G double prime which are the shear moduli or at times in terms of eta prime and eta double prime which are the viscosities in phase viscosity and out of phase viscosity. Similarly, we could also talk in terms of a compliance remember that compliance is strain divided by stress. So, if we generally use the complex notation and complex variable as we have seen in earlier classes that we could write complex modulus as a function of complex viscosity.

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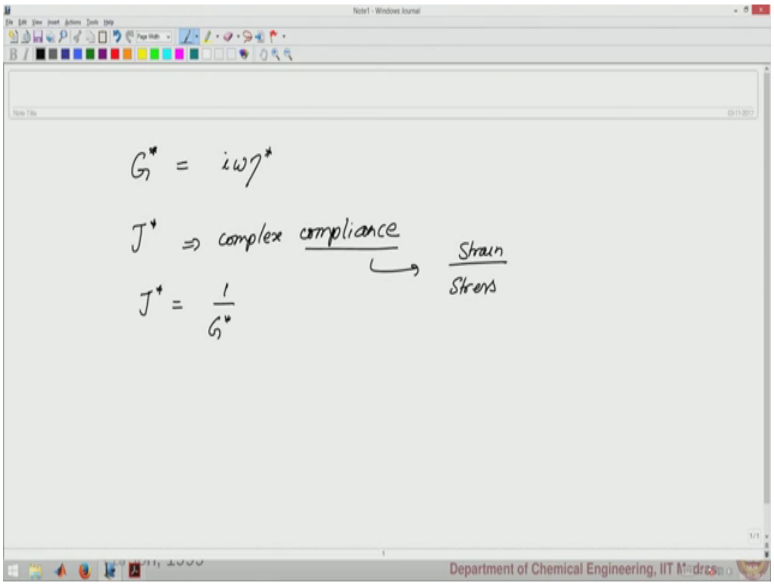

$G^* = i\omega\eta^*$

$J^* \Rightarrow$ complex compliance $\hookrightarrow \frac{\text{Strain}}{\text{Stress}}$

$J^* = \frac{1}{G^*}$

Similarly, we can also define a complex compliance and this is equal to 1 over G star. So, since compliance is actually strain over stress. So, therefore, it is natural that the; it is inverse of modulus.

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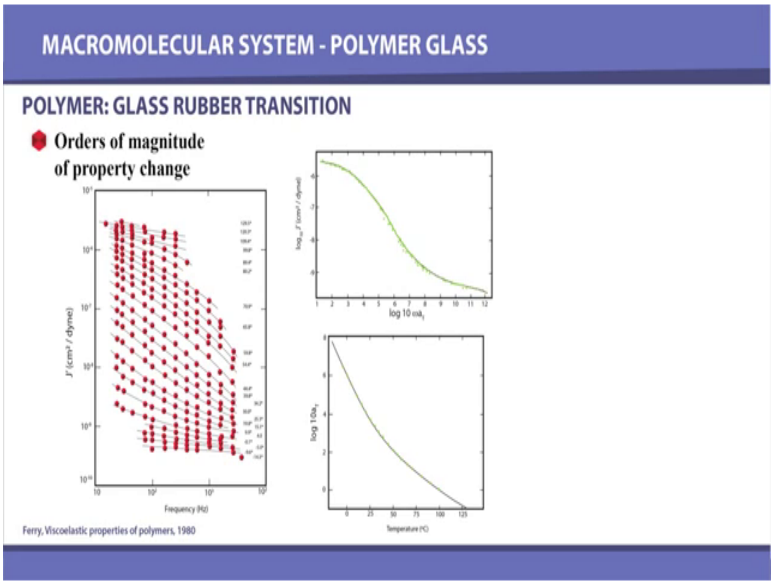

MACROMOLECULAR SYSTEM - POLYMER GLASS

POLYMER: GLASS RUBBER TRANSITION

- Orders of magnitude of property change

Ferry, Viscoelastic properties of polymers, 1980

So, in this plot the data that is shown again a classical data where we look at the compliance for a methacrylate polymer and again this measurement is being again done at different temperature. Now, since we are talking about oscillatory shear, now the frequency is varied and generally for most rheo meters the frequency range of interest is usually from about 0.1 to 100 radians per second and therefore, the measurements here are also done and similar range and now what we are looking at is at different temperatures.

So, we have 129.5 all the way till minus 14.3 and since we are looking at the elastic part of the compliance we are looking at the storage compliance. So, this is a analogous to the storage modulus and what we would see is just like we expect that at lower temperature the modulus should be higher we would expect that at lower temperature compliance should be lower.

So, as the temperature is increased the compliance becomes higher and higher. So, here we have low temperature and compliance is very low or in other word modulus is very high and as we increase the temperature the compliance starts becoming more and more or the material has less and less modulus and you can see that there is a systematic variation and again there is a 3 or 4 orders of magnitude of change in the compliance when one goes from minus 14 to 129.5.

And, again because we are seeing that this is a polymeric system in which change in temperature leads to about three four orders of magnitude in the compliance. We would know that therefore, somewhere in between is the glass transition temperature. So, when we are at very low temperatures the material is in the glassy state therefore, the compliance is very low again, because there is no segmental mobility and all relaxation modes are frozen the material has predominantly elastic contributions and also there are no dissipative mechanisms which are very active and as the temperature is increased at the same frequencies. Now some of the dissipative mechanisms and relaxation processes can happen.

And so, the compliance naturally goes up and at higher temperature when let us say the material has reached the rubbery state then it is possible for segments to move about, because of segmental flexibility significantly more dissipation can happen and at the same time there is a significant degree of flexibility in the material system. And so, when we again can do a time temperature super position in this case the temperature frequency superposition and again it will help for us to think about; what will be the analogous shifting? In this case if we choose a reference temperature.

So, in this particular case for example, 373 is chosen as the reference temperature and therefore, that is this temperature here which is 99 degrees. So, if this temperature is chosen as the reference point, then the question to ask is 129 degrees Celsius at what frequencies will the data of 129 correspond to the data at 100 degrees 90.3 degrees 99.8 degree Celsius. Similarly the converse question is at what frequencies; will the data which was measured at 60 a 6 be analogous to data at 99. And again we recall that higher temperature means lower relaxation times and more dissipative or viscous response lower times means lower temperature means less dissipative response and higher relaxation times.

So, we can now change this in terms of frequency lower frequency implies more dissipative response higher frequency implies more elastic response. So, therefore, made measurements which were done at lower temperature will correspond to higher and higher frequencies, because lower temperature is analogous to lower relaxation times and we would have to do experiments at lower timescales or higher frequencies to get the analogous data at 99.8 degrees.

So, all the curves which are above 99.8 will have to be shifted to the left in the sense that higher temperature data gives us more viscous response and more dissipative response which is analogous to low frequency data therefore, they will all shift to the left and all the data which is at lower and lower temperature will all shift to the right. So, for example, when a master curve is constructed as shown here; now we can go in terms of frequency from a very small frequency of 1 to about 10 to the power 12. So, you can see the power of time temperature superposition or in this case frequency temperature superposition that we can get material response over 10 or 14 orders 12 orders of magnitude.

So, by doing experiments over a limited temperature range the overall set of data that we obtain is over a much wider range and the hope when we do such characterization is that we have covered a significant set of relaxation processes which are present in the material the tests of course, when we are doing at different temperature we are similarly exploring different set of relaxation processes or relaxation processes which are more active or less active depending on the temperature involved.

Similarly, when we have testing being done at remarkably large wave window of frequency we are probing different set of relaxation processes at different frequencies and. So, clearly at very low frequency most of the relaxation processes are possible and therefore, compliance of the material appears to be extremely high at the same time if we go to very high frequency then pretty much all the relaxation processes are frozen and therefore, the compliance of the material is very low we could also say this in terms of segmental mobility by saying that since we are probing the material at low frequencies segmental mobility is possible. When we probe the material at higher and higher frequency the segments appear to be completely frozen and therefore, the material compliance is lower again.

In this case if we look at, what is the amount of shift that was used? And again we will see that this one corresponds to the 100 temperature or 99.8 temperature which was used as reference and data points which are corresponding to temperatures which are higher will have to be shifted to the left while the data which corresponds to lower temperature will have to be shifted to the right and what you can see is remarkably the good quality of the master curve given that these are separate experiments done at different temperatures by shifting them using a theoretically possible expression we can I obtain a master curve which seems to be truly super imposing on each other.

So, therefore, with these couple of examples what we have seen is the fact that how in glassy state the polymer properties are extremely stiff like materials. So, for example, modulus is very high or compliance is very low and the fact that if to access the glass to rubber transition which happens over a significant temperature range or which also happens over significant time or frequency range.

We can generally use time temperature superposition to capture the data over a very wide range of time or frequencies and if the overall master curve preparation and the shift factors which are being used correspond to the theoretically expected shift factors based on either Arrhenius or wlf, then we know that the overall time temperature superposition is working quite well and we can then rely on the data that we get in terms of master curve.

As far as the shift factors theory for glass to rubber transition is concerned we should always remember that it is wlf which is used originally wlf was based on the free volume in the material and it is useful near the glass transition temperature of polymers the Arrhenius shift factors are used generally in the melt of the polymer or in the solution state where there is sufficient thermal flexibility thermal energy available for activated processes to be operational and.

So, given that in the glassy state we are looking at more cooperative phenomena we are looking at processes where independent modes of relaxation may not be present in the sense relaxation modes coupled with each other then in that case wlf equation has been found to be working near for the time temperature superposition. So, in both the cases that we have seen in this which is glass to rubber transition the shift factors. In fact, were could be described based on wlf expression.

So, with this we have come to close the overall discussion related to survey of material functions for polymeric systems we saw polymeric solutions we saw melts we have also seen gels and glasses we have also predominantly looked at steady shear and oscillatory shear data. In the next segments of the course what we will see is again a survey of material functions for a multi phase colloidal systems and also systems where both macromolecules or polymers are together with colloidal systems and we will also try to explore various alternate material functions that we have defined in the course so far.