Rheology of Complex Materials

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Survey of Material Functions: Multiphase systems And Macromolecular/ Multiphase Systems

Lecture - 43

Survey of Material Functions for Multiphase Systems- 1

We will continue our journey in terms of looking at survey of some of the material functions and taking a look at the classical data that is available for many of the systems. In the previous set of lectures, we looked at the material functions for polymeric systems and we could find that several of those data.

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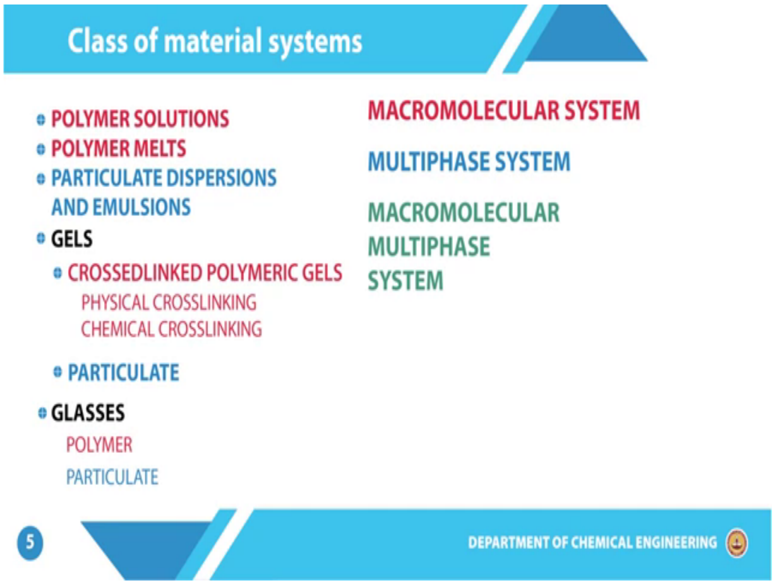

Class of material systems

- 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

For the polymeric systems came from the text books and they are very useful in terms of understanding the variation of material functions and also to compare with new materials that we would be usually working within the remaining set of lectures, we will look at the multi phase systems and again, we will adopt a similar approach in terms of looking at dispersions and emulsions and then the particulate gels in particulate glasses also in this segments, we will look at macro molecular and multi-phase systems together.

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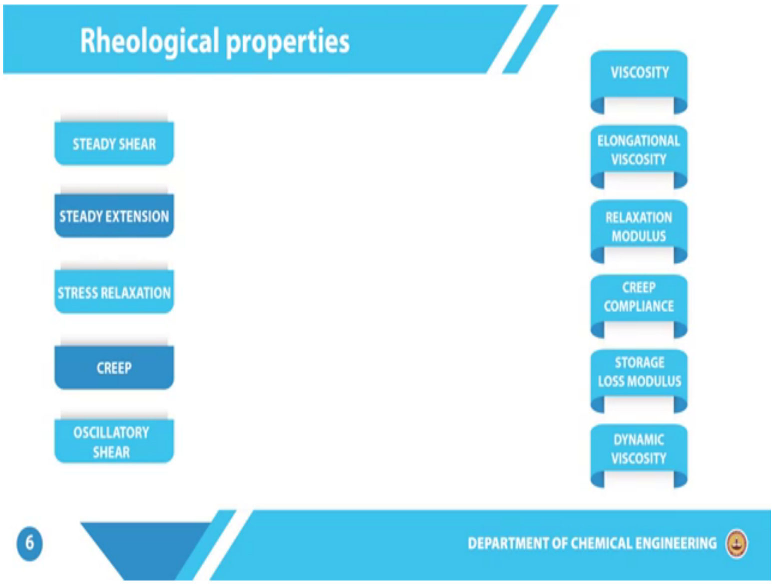

Rheological properties

STEADY SHEAR

STEADY EXTENSION

STRESS RELAXATION

CREEP

OSCILLATORY SHEAR

VISCOSITY

ELONGATIONAL VISCOSITY

RELAXATION MODULUS

CREEP COMPLIANCE

STORAGE LOSS MODULUS

DYNAMIC VISCOSITY

So, where polymers as well as particulate systems are used together in terms of material formulations and so, these are the rheological properties that we have been looking at in terms of steady shear the steady extension relaxation creep and oscillatory shear and then what we will also do; now is to look at stress growth and normal stress differences which are also the material functions that we have seen so far.

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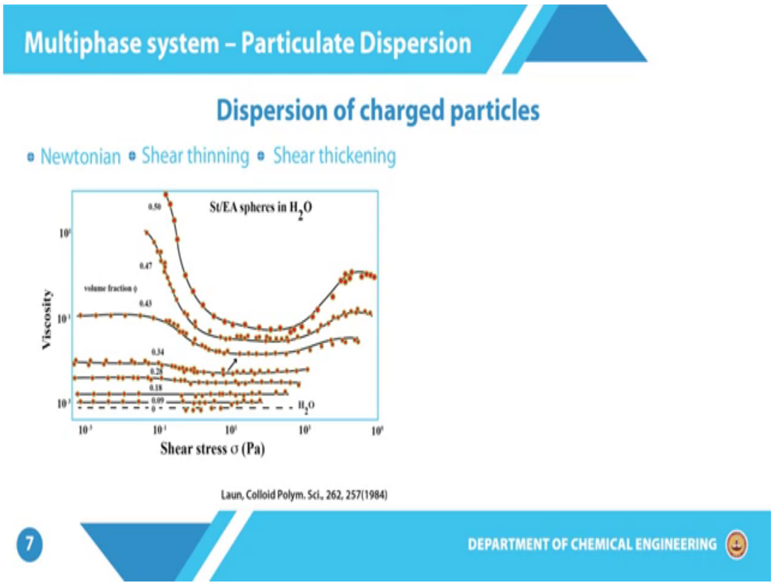

Multiphase system – Particulate Dispersion

Dispersion of charged particles

- Newtonian
- Shear thinning
- Shear thickening

Laun, Colloid Polym. Sci., 262, 257(1984)

So, the first set of data that we start out with is classical data which is related to particulate dispersions and this is viscosity as a function of the shear stress, we can represent the data also in terms of viscosity as a function of shear rate.

We will see that quite often when we are dealing with materials especially with paste like materials or materials which seem to have an yield stress, it becomes useful to plot the data in terms of stress as opposed to the shear rate because still a certain shear rate, there is no flow or till a certain stress there is no flow and therefore, we can read off the yield stress value from such data.

So, if we look at this data where the charged polystyrene ethacrylate spheres are dispersed in water and then their dispersion is measured the viscosity is measured at different concentrations of the particles themselves the particle concentration is mentioned in terms of volume fraction. So, as a volume fraction increases we would expect that viscosity would be higher.

So, at the lower the 0 of course, implies water which is one centipoise or 10 to the power minus 3 Pascal second and as the concentration increases, we expect the viscosity to be higher, but as the particle concentration increases we can see dramatic changes in terms of the qualitative behavior as a function of stress or strain rate.

So, one of the first things we notice is if the lower concentration of particles which is mixed is low then what we will see is marginal increase in viscosity more importantly the viscosity as a function of stress remains a constant value which means the overall behavior of this material seems to be Newtonian like even though particles have been added and with the added particles.

There will be additional dissipative contributions in terms of the interaction between particle and the surrounding fluid which is water in this case there may also be hydrodynamic interactions between the two particles and so, these into additional interactions lead to additional dissipation in turn leading to higher viscosity.

So, therefore, higher viscosity is observed; however, the timescales of the processes are such that they are able to give us a completely dissipative response and overall viscous response only when we start looking at higher volume fractions. So, in this case for example, 28 or 34 percent we can see that there seems to be now shear thinning in the material over a very small stress range.

So, viscosity is high at very low stresses and then viscosity decreases and then again it becomes constant. So, this is similar behavior that we had seen in case of polymeric solutions or where we had an initial Newtonian plateau then a decrease and then again a constant in that case of course, what we had was a several orders of magnitude change in viscosity.

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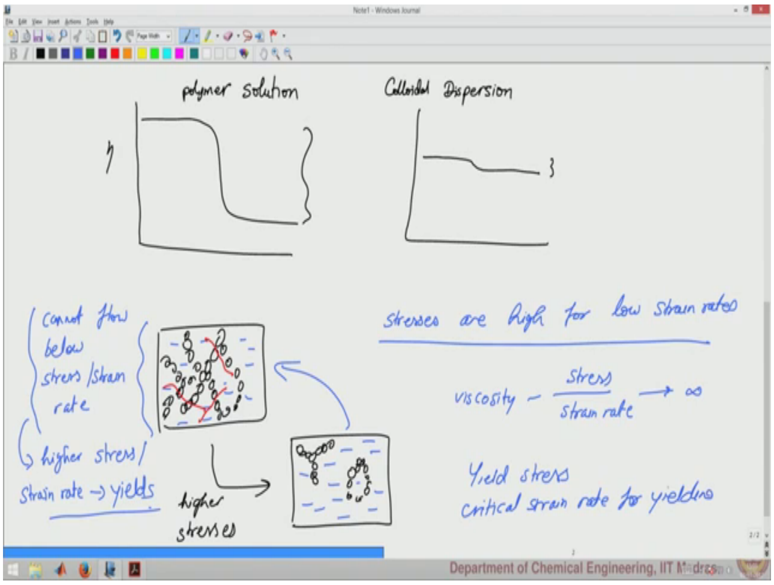

So, in such cases, it is helpful for us to think as to why is it that in one case when we look at a polymer solution, we saw viscosity varying very drastically and if we now look at similar behavior for a dispersion, we see a very minor change.

So, clearly both of these systems are similar in qualitative response in the sense that there is Newtonian plateau at very low and high shear rates or stress and there is shear thinning in the intermediate, but what causes this extent of shear thinning and why is it much more in a polymer solution and why is it. So, low in a colloidal dispersion and so, this will force us to think in terms of the mechanisms that might be involved we had seen that in case of polymer solution the polymer itself has a tendency to stretch and orient.

And therefore, when at higher strain rates this orientation and stretching can lead to significant amount of shear thinning, in this case quite often, the colloidal system there is a clusters and breaking of those clusters or aligning of those clusters which leads to changes in the property of the material as a function of stress or strain rate. So, what can what we can clearly see is the clustering at lower stresses and at higher stresses is not very different and because the particle concentration is not significantly high enough for the clusters and percolated clusters to form.

And therefore what we see is a very little change in terms of viscosity, but clearly the timescales here which are associated with the overall stresses here are associated with the breakage of clusters or alignments of clusters depending on the type of particles and type of mechanisms we might have in the material when the volume fraction is increased further. Now, we can see that significant clustering of particles must be happening which leads to a very high viscosity.

Now, there is an order 2 orders of magnitude increase in viscosity with respect to the solvent viscosity itself and over the stress when its increased there is almost an order of magnitude decrease in the viscosity and what is very interesting in these cases is as one goes to higher stresses one can. In fact, observe slight increase in viscosity. So, therefore, this material is Newtonian plateau then shear thinning and then second Newtonian plateau and then it appears to have a shear thickening region.

So, this is a few of the class of materials which show both shear thinning and shear thickening region depending on the stresses or strain rates that the material is being subjected to now what is also interesting is if the volume fraction is increased further the lower Newtonian plateau Newtonian plateau at lower stresses completely disappears and it appears that viscosity diverges to very large values now we are talking about four orders of magnitude increase over the solvent viscosity and such a an increase is only possible.

If we have a percolated clusters and this is what we saw in terms of colloidal glasses or colloidal gels that if you have such percolated clusters then solvent can remain trapped in these and then therefore, a significant amount of stiffness and all the other properties can be expected. So, therefore, we have a percolated cluster which corresponds to very stiff properties or in this case very high viscosity and. So, when this kind of material is being sheared given that the particles are all attached to each other we will have to apply a significant amount of stresses for very little strain rate to be achieved and in consequently since stresses are high for low strain rates.

So, what we end up being is the ratio viscosity which is a ratio of stress to strain rate this tends to infinity and so that is what we see here that material is pretty much behaving as a solid material in which case there is no motion and therefore, the viscosity is in finite, but as the strain rate on the material is increased or the stress on the material is increased it is possible for the percolated structure to give way and therefore, it is possible that there will be some of these clusters would break down and therefore.

Now, we have a smaller clusters and which then can flow lit more easily. So, presumably what happens at higher stresses in this material is the fact that now we have isolated clusters and these clusters can, then flow because there is a solvent and then they are not percolated anymore and so, this leads to naturally and decreased in decrease in viscosity.

And we can see that over a small one order of magnitude change half an order of magnitude change in stress the viscosity undergoes almost 3 orders or 2 to 3 orders magnitude change and so, shear thinning is again observed because in most of such cases it would be a natural to expect the particulates to break up the clusters to break up and therefore, viscosity to go down significantly and again one observes a response in which over significant amount of stress or significant amount of strain rates the viscosity remains constant, but then beyond a certain stress or strain rate again a viscosity increases observed.

So, this would again imply that at higher strain rates or higher stresses there is again an tendency for particles to aggregate once more and form clusters and these could be due to hydrodynamic interactions these could be due to alignments these could be due to jamming. So, there are several features which are possible which can cause at higher strain rates the particle size and the again percolation to happen and then viscosity can increase again.

So, therefore, we again have a system in which we observe a response where the viscosity is observed to be higher again which implies that again there is either a percolated structure or a jammed structure in which case particles find it difficult to move about with respect to each other and this phenomenon is even stronger when higher concentration of particles almost fifty percent of particles in water are prepared you can see that up to 10 to the power minus 1 stress there is absolutely viscosity is very large or material is almost solid like.

So, clearly the stress here which is 10 to the power minus 1 can be thought to be the yield stress of this material. So, the idea here being that this material cannot flow below certain stress. So, cannot flow below a critical stress or strain rate and once this strain is crossed higher than these higher stress or strain rate the material flows or in other word it yields.

So, therefore, we can define yield stress or critical strain rate for yield for yielding from such data and this is quite essential in many of the products that we use either in personal care or in foodstuffs where we generally expect the material to be fairly rigid and solid like, but once given amount of stress or strain rate is applied on the material it flows very easily.

And so, material undergoes anneal process and therefore, it is then becomes very fluid like and in small number of cases it is possible that shear thickening may be observed and this system of styrene and ethyl; ethyl acrylate is one such system where shear thickening is also observed though we will largely speaking most of the materials that belong to this class may show anneal stress and the shear thinning behavior.

Now, we look at another example of a dispersion; dispersion in this case it is liquid and liquid and therefore, its water in oil emulsion and we are looking at oscillatory data in this case G prime and G double prime and what we can clearly see is a overall Maxwellian.

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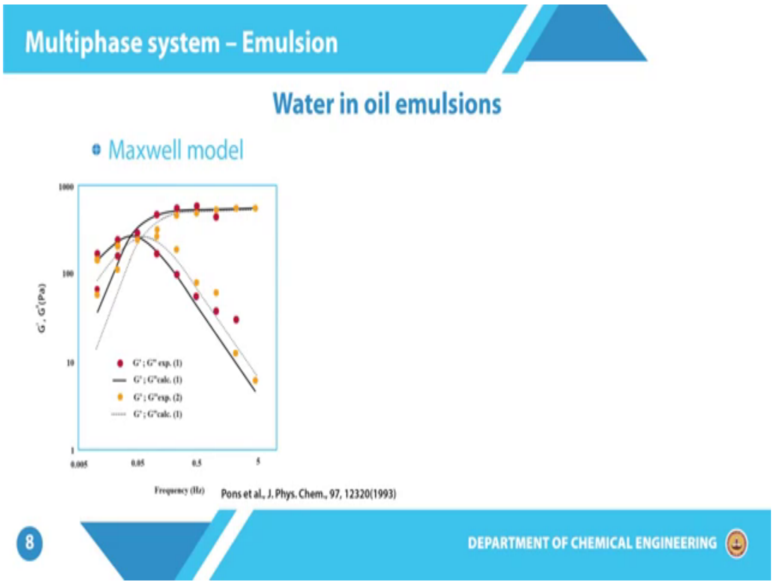

Multiphase system – Emulsion

Water in oil emulsions

- Maxwell model

Pons et al., J. Phys. Chem., 97, 12320(1993)

Response at low strain rates we can see that the G prime and G double prime are both increasing functions of frequency G prime seems to be lower and at higher frequencies we can see that G prime is almost constant and much higher than G double prime. So, this is a classical Maxwellian response and in this set of experimental data the first and second runs are based on the repeat.

So, after the first run in done given that this is a water in oil emulsion the droplets and their sizes can change because there can be coalescence event there can be breakup events and so, the first and the second run actually will give you a different overall rheological response depending on whether there was breakage and coalescence of droplets and.

So, we can use rheology as a tool to understand some of these coalescence and the breakup processes by characterizing the; such emulsions under different shearing conditions for example, we could also subject these materials to a very high strain amplitude and then again do this frequency sweep.

And if he is notice a difference then we know that subjecting the material to a very large strain actually causes significant changes in terms of droplet size distribution. So, this is one of the few examples where Maxwell model seems to do a reasonable job of describing with a single mode. So, there is a dominant relaxation process which can be used. So, what we can see is given that this is water and oil emulsion at very low frequencies it is easy for the water droplets to slip past each other and therefore, we see completely fluid like response when we have a very high frequency then basically the water droplets are as if they are attached to each other.

And therefore, it behaves almost like a frozen material where the G prime is relatively constant as a function of frequency and G double prime decreases even though this shows a glassy response in terms of what we observe here we should remember that the material need not be glassy in the sense it is not hard glassy material the way we usually think of a glass material. So, given that we are only probing the material to limited frequency range in this case 0.05 to 5 we see that in this frequency range the material seems to show frozen responses.

In this case, frozen response means that basically droplets are unable to move at most there is a small vibratory motion to the drops which is possible and therefore, the some amount of dissipation is there, but; however, the overall cluster of drops and the network of drops remains intact and does not is not very mobile in terms of giving us this glassy elastic response if you were to further subject this material to higher frequencies then we will see that some of the other dissipative modes which are available in water and oil itself will also be there.

So, the true glassy state where all the water and all the oil molecules are also frozen will be at much higher frequencies and of course, those frequencies may not be of great relevance from an application point of view because for example, even let us say pure water if we look at such oscillatory data we would find that if you go to very high frequencies it would again lead to a probing of water at lower and lower timescales and therefore, we would presumably start probing glassy modes in water at extremely high frequencies and similarly is the case for oil, but in this case we are only probing a limited range of frequency.

And so, glassy response in this case, therefore, only implies the response with respect to droplets and not really with respect to the individual phases and. So, this is something which we should always remember that whenever we do rheological analysis quite often we are only looking at the limited time or temperature or frequency range and therefore, the conclusions that we are drawing regarding its behavior is only valid for that range and beyond that there will be other relaxation processes which would be of interest and only.

When we do a time temperature superposition where we try to get data over significant orders of magnitude frequency or time then we can talk about the overall set of relaxation processes which are present in the material sometimes it would make sense to characterize the material to such an extent. So, that we get the whole relaxation time spectrum some other times it and it may not be very useful for example, in emulsion case we are mostly looking at probing it using it as a in lower frequency range.

So, therefore, this may suffice; however, a polymer melt on the other hand depending on the polymer processing method involved may have to be subjected to extremely high strain rate and therefore, low time scales are involved at the same time its long term steady response is also of interest. So, therefore, one can look at 7 or 8 orders of magnitude in terms of frequency or strain rates.

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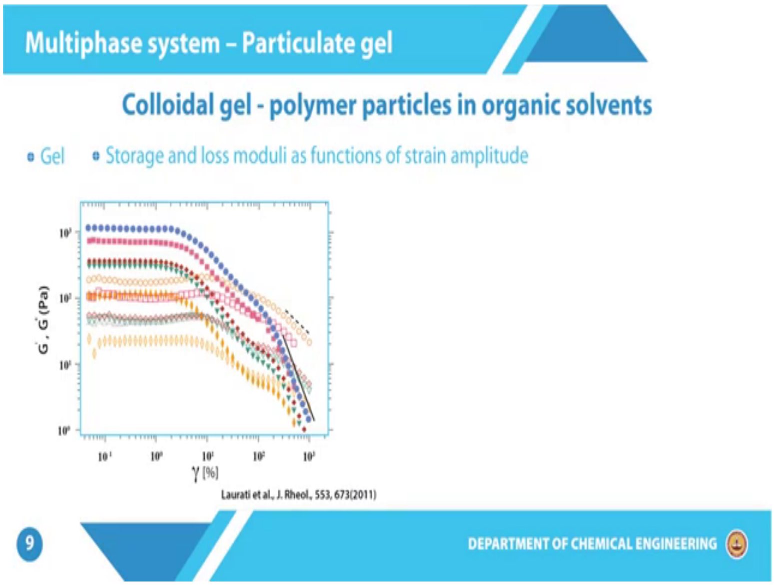

Multiphase system – Particulate gel

Colloidal gel - polymer particles in organic solvents

- Gel
- Storage and loss moduli as functions of strain amplitude

Laurati et al., J. Rheol., 553, 673(2011)

So, depending on the material and the engineering application one can choose broader or smaller range of time scales to probe the material with now continuing on the overall persuade the survey of materials.

Let us look at a colloidal gel system and in this case again we have a polymer par particles which are in an organic solvent and since this is again a percolated particle system the overall response is gel like which implies that both G prime and G double prime would be relatively independent of frequency and both of them will be significantly higher G prime being higher than G double prime and so, in this case also what is being shown is storage and loss modulus as a function of strain amplitude.

And what we can see is up to a certain strain amplitude both G prime and G double prime are constant implying that this is the linear range, if you recall, we had said that in the linear range the G prime will be only a function of frequency given that this data is being reported only at one frequency and at different strains for all these data points the frequency is the same and since frequency is the same G prime and G double prime are same and therefore, the data wherever G prime and G double prime are not dependent on frequency is likely to be the in the linear response however.

We can see that when strain amplitudes are higher which means we perturb the material with a significant deformation we see that both G prime and G double prime are functions of strain amplitude itself. So, in defining material functions we had also said that when G prime and G double prime are functions of frequency as well as strain amplitude that is the non-linear regime.

So, clearly in this data we can recognize the linear regime and the non-linear regime and over the last 10-15 years the investigation of non-linear properties of materials using the large amplitude oscillatory shear given that now amplitudes of 10 to thousand are being used is used quite often. So, there is a significant work being done related to large amplitude oscillatory shear to understand the material structure and overall signatures which are associated with the large amplitude oscillatory shear.

For our course purposes we will focus predominantly only on small amplitude shear to begin with or the linear response to begin with what we can see is as the particle concentration changes we can see that the G prime as well as G double prime changes for all the material systems.

G prime is greater than G double prime which means there is a percolated networks which leads to elasticity and therefore, dominant elastic mode and the difference between a colloidal gel and a colloidal glass is still a very active area of research in terms of what are the distinguishing features both in terms of microscopic structure as well as in terms of rheological response is being still actively pursued.

Going down further what we can see is the same data can be plotted what we have is G prime and in while measuring this G prime and G double prime we measure the stress in the material and we know that since gamma itself is a sinusoidal function stress also is a sinusoidal function. So, therefore, we can measure the stress amplitude and we can already applying a strain amplitude. So, we can plot stress amplitude as a function of strain.

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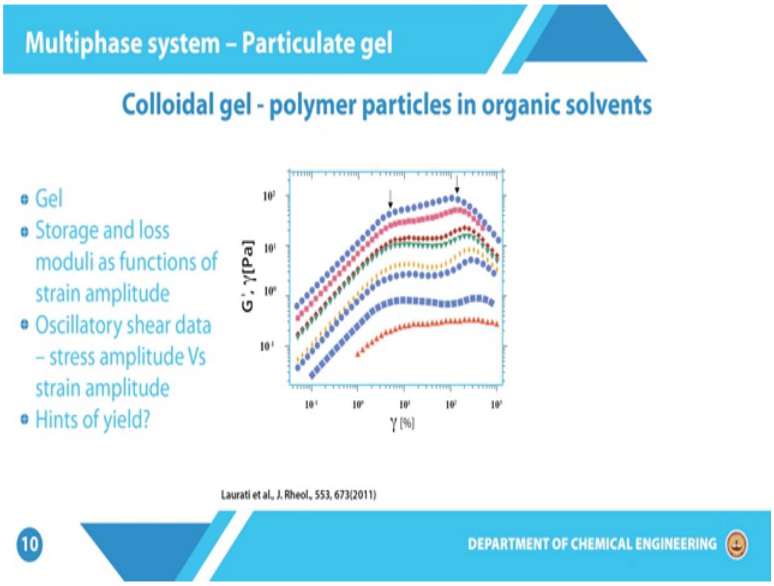

Multiphase system – Particulate gel

Colloidal gel - polymer particles in organic solvents

- Gel
- Storage and loss moduli as functions of strain amplitude
- Oscillatory shear data – stress amplitude Vs strain amplitude
- Hints of yield?

Laurati et al., J. Rheol., 553, 673(2011)

Amplitude in this case the stress amplitude which is in phase with the strain is being plotted. So, therefore, elastic part of the stress is being plotted with strain and what we can see is in the linear regime of course, whenever the strain increases the overall stress elastic stress increases and this is a linear increase.

So, as the strain is increased the lets say strain becomes 2 times the stress also becomes 2 times and naturally that is the reason why we have G prime being constant because between these 2 data points, if the strain is 10 times, we also has stress 10 times and therefore, G prime is actually independent of frequency, but when we go to independent of strain, but when we go to higher and higher strain we can clearly see there are transitions in the sense beyond a certain strain and now the stress increases, but it increases far more gradually and in fact, there is a decrease in stress beyond a certain strain.

So, these kind of transition points can be again possibly identified as yielding phenomena which are happening in the material as the material is being subjected to higher and higher strain.

So, the phenomena of yield and phenomena of the microstructure changing due to large deformations is one of the significant area in rheology today also where we try to understand what is the relationship between the micro structure and the rheology by trying to make a hypothesis of what is the microstructure and how does it change as a function of shearing and so, these are possibly hints of yield processes that are being observed in these polymeric saw particles in organic solvents.

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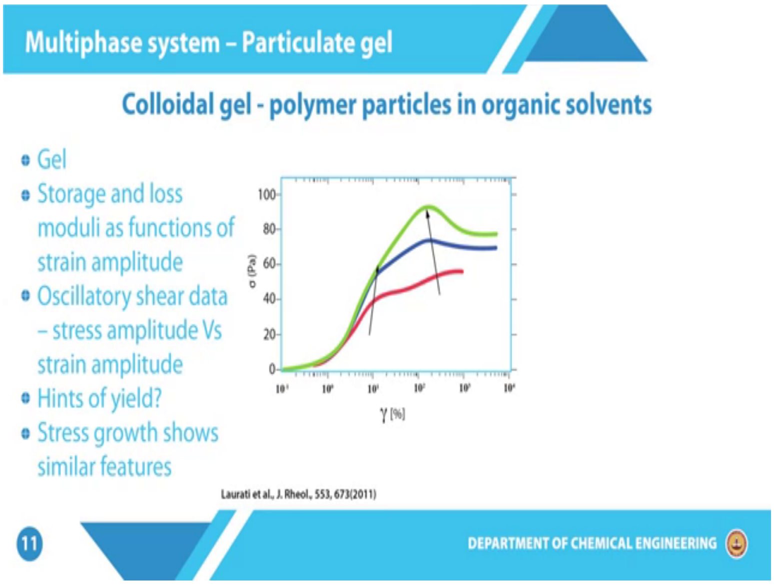

Multiphase system – Particulate gel

Colloidal gel - polymer particles in organic solvents

- Gel
- Storage and loss moduli as functions of strain amplitude
- Oscillatory shear data – stress amplitude Vs strain amplitude
- Hints of yield?
- Stress growth shows similar features

Laurati et al., J. Rheol., 553, 673(2011)

Now, the same colloidal gel we could also examine in terms of stress growth stress growth.

If you recall is an experiment in which constant strain rate is imposed on the material and then the stress is measured as a function of time and we know that for a Newtonian fluid stress will instantaneously become constant because strain rate is constant while for an elastic solid a Hokkien material the stress will continue to increase because strain rate constant implies strain increasing with time and therefore, stress will also continue to increase; So, clearly in this case for these systems.

We can see that when we look at stress as a function of strain or time remember that strain rate constant implies that strain is directly proportional to time. So, the x axis could be time or strain itself because gamma is equal to gamma dot times time. So, we could just summarize this by saying that if you have gamma dot yx.

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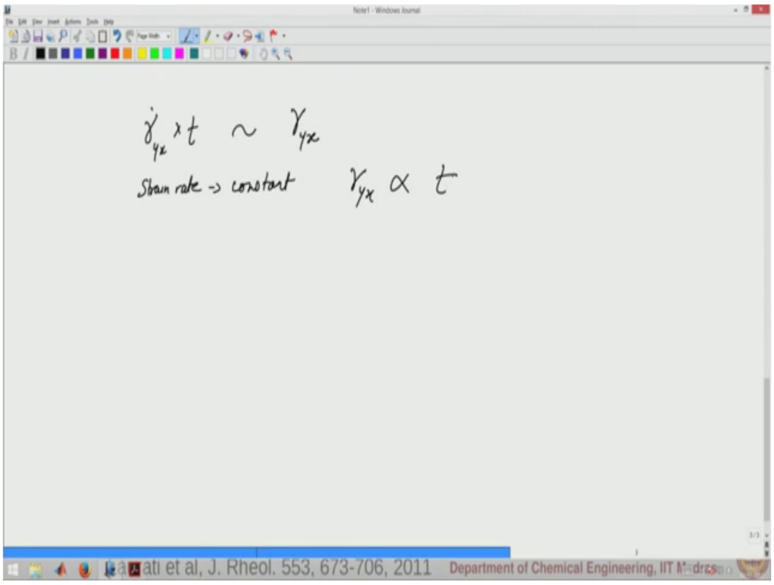

$\dot{\gamma}_{yx} \times t \sim \gamma_{yx}$

Strain rate -> constant $\gamma_{yx} \propto t$

Gamma dot yx that you multiplied by with time you will get gamma dot yx. So, strain rate constant implies gamma yx will be proportional to time and. So, therefore, the data in this plot is plotted where stress is varied as a function of strain and you can again see that there is a increase and then beyond a certain point again the same hints of yield processes can be seen in a stress growth experiment also and this is one of the best ways in terms of trying to understand the material in its microstructure by probing the material using two three different rheological modes.

So, in this case we saw that oscillatory shear is being done and stress growth is being done and given that we are probing the material slightly differently in the 2 cases can we try to understand and see signatures which arise due to micro structural change in both cases and using the same micro structural hypothesis if we are able to explain both the phenomena, then we have understood the material microstructure and its rheology very well.

So, with this what we have seen is look at the colloidal systems we looked at the particulate dispersions and emulsions and then glass and gels.

So, in closing we will also look at colloidal glass where the structural features of materials can be easily investigated by looking at again oscillatory shear and here what we are seeing is as the particle fraction changes and in this case these are polymeric particles in a solvent we can see that both G prime and G double prime are largely independent of frequency with G double prime with the slight function.

So, again if you look at the signature the colloidal glass and gel seem to have very similar frequency response, but its only because of knowing the material and the microstructure and the particles in terms of what is the inter particle attraction and repulsion we can try to guess the microstructure and therefore, we can try to see whether this is a signature of glassy like response or the real or the gel like response.

So, with this we have finished our review of colloidal systems and in the next segment we will look at some of the materials which are combinations of macromolecules and a colloidal system.