

**Rheology of Complex Materials**  
**Prof. Abhijit P Deshpande**  
**Department of Chemical Engineering**  
**Indian Institute of Technology, Madras**

**Lecture – 55**  
**Survey of Material Functions: Multiphase Systems and**  
**Macromolecular/Multiphase Systems**

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So, continuing on our journey of survey of material function for selected materials. In the section on polymers and related materials; we saw largely textbook data from which is classical, and then for multi phase systems we took a look at data which is a mixture of from some classical data from textbooks as well as some recent data which is published in recent literature.

We will continue our journey in terms of looking at some example material systems and material functions for them. And many of these materials of systems are very complex, because they are combinations of macromolecules and multiple phases. And the macromolecules themselves may be multiple and multi phases also could be combinations of two or three liquid phases or gas and liquid phases and so on. So, these are the material systems which are being used in personal care, foods and they are relevant in biology.

So, several material systems that we want to probe in for today's applications belong to this class of materials, where both macromolecules are there as well as multiple phases are there.

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### Class of material systems

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

**MACROMOLECULAR SYSTEM**

**MULTIPHASE SYSTEM**

**MACROMOLECULAR MULTIPHASE SYSTEM**

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And so, the examples that we will look at for the in this case are all belonging to macro molecule as well as multi phase system.

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### Macromolecular-multiphase system - emulsion

#### Food – curd / yogurt

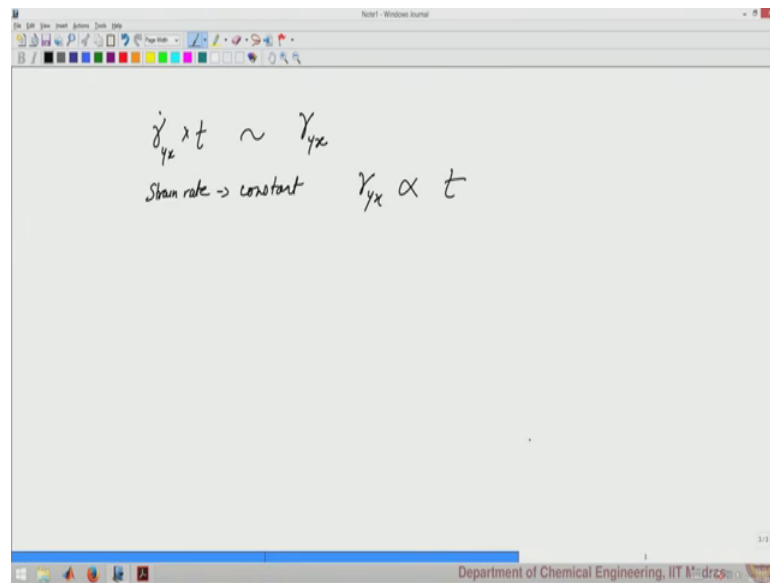
- Stress growth
- Constant strain rate : strain ~ time
- Stress growth depends on protein fortification

Pang et al., J. Food Sci, 74, 9(2009)

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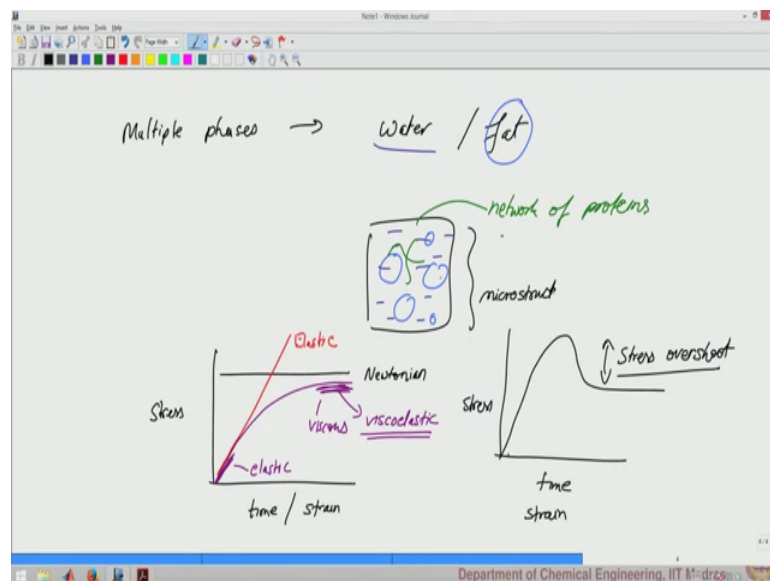
So, let us start with the material, which we are quite familiar with, which is curd and again curd is a fairly complex material in terms of its makeup.

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It has both multi phases.

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And the; so, the multiple phases are in terms of water of course, and then fat. So, there are fat globules which are present in. So, fat globules which are present in water. So, what we have is if you have if you take the overall curd system, what you will have is water molecules present and you also have the fat clusters. And of course, over and above this there is a set of proteins and the network of proteins, which is essential part of milk also and these are macro molecular systems and so you have again a multi phase

and macro molecular system together. And we know that in terms of the overall appreciation of curd as a material and its consumption is very strongly related to its mechanical response.

In the sense that if we observe on a bowl of curd and if it is very runny and very fluidy and whenever its broken pieces, then we do not feel that it is as good curd if it comes out as a more solid like material. So, the way the fat globules and the water molecules surrounding water phase surrounding it and the presence of network of proteins, how effective network it forms to give a solid like response is a very important con factor in determining the rheology of curd or yogurt. Of course, we also given that it is a product which is available in industrial form today, we can have different proteins added by way of providing more nutrition.

So, it re it is of interest to device newer and newer curd or yogurt products with either different flavor or different type of nutrients which are available in them. And so for all these different formulations it is important for us to have the rheology well understood and so given that it is a complex mixture of multiple phases and the network of proteins more often than not we have a non-linear rheology playing a more significant role in terms of its overall rheological response.

If you were to look at the linear response, you would again see a more gel like response which is what we know the curd to be. It is basically a more material which has significant amount of elasticity and therefore, it we can scoop it out using a spoon. If the curd on the other hand has been sheared quite, a bit then it breaks down and then it gives a more predominant fluid like response. In that case the network of this protein as well as the fat globules has been broken down and then we get the overall fluid like response. So, clearly in this case the microstructure depends on the amount of shearing that has been given in the material.

So, clearly a thixotropic kind of response may also be able to explain some of the behavior that is seen in foodstuffs in general and also materials like curd more specifically. So, the one example set of data that we are looking here is a first stress growth and again stress growth is an experiment just to remind ourselves is where we apply a constant strain rate and observe the stress as a function of time in the material. What we have seen earlier was if its a linear viscoelastic material, we would see an

exponential increase in stress. So, just to remind ourselves what we had seen was in a stress growth experiment if it is a Newtonian material.

So, either time or strain could be used for plotting, and if it is a Newtonian material then since strain rate is fixed we would have stress also to be fixed. And given that if it is an elastic material then stress will continue to increase and as the strain is increasing. So, most of the linear viscoelastic materials will show a response which is in between. So, you would observe something like this. So, this is a viscoelastic material and this viscoelastic material basically what it says is at lower times, we see elastic response and at higher times we see viscous response.

So, at lower times since the overall relaxation process gives us an elastic response because we are probing the material at very low timescales, we get a response which is similar to a hook and elastic material. At very large time stress the relaxation process can completely dissipate. And therefore, we get largely fluid like response. So, what we see in large class of materials which are non-linear and this we have seen before that there is a stress overshoot observed. So, we see stress overshoot and so by knowing this stress overshoot, we can find out time or strain we can knowing this stress overshoot we can find out what is the underlying microstructure in the material.

So, the example data that we are looking at here for curd are different set of protein fortifications were used. So, in the end in the since that formulation of the curd or yogurt has changed and then we want to understand what happens to if we use different set of proteins and we can clearly see that proteins have a very significant influence on the overall non-linear viscoelasticity of the material, the stress overshoot is three to four times when we use one protein material as opposed to the other. We can also see that the initial slope, which is an indicator of initial elasticity of the material is very different in the four cases.

You can also see that in one case the overall time required to reach steady state is much larger at much larger strains or strain rate at times the overall steady state is observed, while for some other proteins the it is much lower. So, there is about a difference between 60 70 to about 80 90 is where the steady state is observed. One other thing of course, one can also notice is by changing the proteins the overall viscosity of the

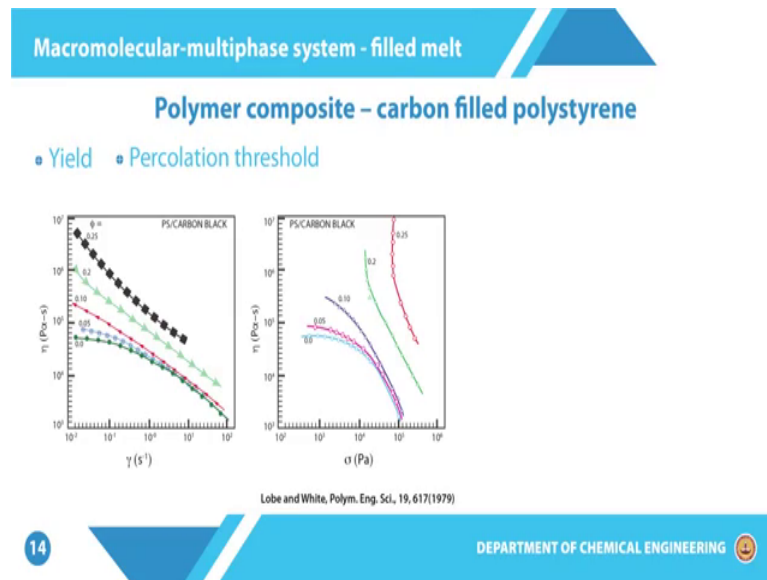
material itself is different. Remember that viscosity can be obtained by knowing what the strain rate at which this material is being subjected and the steady value of stress.

So, clearly this particular protein fortification leads to higher viscosity and it also leads to higher stress overshoot. So, clearly the network in this case which is formed by the proteins and the fat globules is much stronger at steady state and it is much stronger at short timescales also, which means it leads to a very strong elastic contributions at short timescales leading to a very significant stress overshoot. And given that there is a large decrease after the stress overshoot it implies that as shearing goes on the material structure gives way, which could either be due to breakage of networking points, it could also be due to alignment of chains.

So, various such mechanisms can lead to overall decrease in the stress. We can continue looking at again systems which are combinations, this is an example of polystyrene material which is melt and it is filled with the carbon. And in this case carbon black particles and what we can again see here is how does viscosity change as a function of strain rate. So, when we see again a shear thinning response of the polystyrene melt itself.

So, earlier whenever we have looked at the dispersions or particulate systems, we were looking at solvents predominantly in terms of a Newtonian fluid either water or organic solvent; in this case now we have a carbon black which is the dispersed phase and its being dispersed in a polystyrene melt which itself is viscoelastic or which itself has shear thinning response in this case.

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So, the polymer viscosity is around 6 into 10 to the power 4 and it decreases gradually as the strain rate is increased and leading to overall shear thinning response. Now when we start adding more and more carbon black in this material again we can see that there is a qualitative change. The Newtonian plateau which is observed at low strain rates is no longer observed and it appears that at higher and higher volume fractions of carbon black in fact, there is a divergence and the velocity viscosity would appear to be going to infinity.

The same data if you plot in terms of stress, what we can see is when there is no carbon black added for some values of stress viscosity is constant and again that is the Newtonian plateau and as the stress increases there is shear thinning observed in the material. But what we can see is there are at higher volume fractions of carbon black we can clearly see a critical stress or the yield stress, which we already discussed before when we were discussing colloidal gels and colloidal glasses.

So, similarly in this case the carbon black dispersed particles form a percolated network in polystyrene melt. Tnd therefore, the percolated network is intact up to certain amount of stress and therefore, it is not yielded. Beyond a certain yield then the percolated network gives way and there is a structural change and breakdown of clusters and therefore, viscosity decrease is observed and overall shear thinning is observed. What is interesting to observe in such data is also the fact that the extent of shear thinning in let

us say 1 to 10 range is almost identical. In other words the slope of these curves is identical regardless of whatever is the volume fraction. So, clearly what we have is most probably identical types and sets of clusters in this range and given that we just have more number of them the overall viscosity is higher.

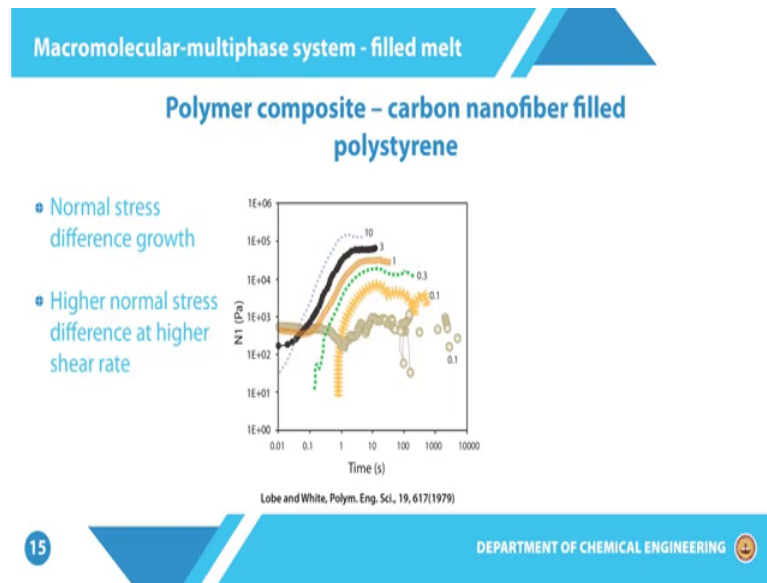
However, the slope or the rate at which they change, when progressively higher strain rate is applied is same. So, the effect of shearing in carbon black dispersion is very similar at these strain rates. But at low strain rates we have a very different effect, the clusters that are available at 0.05 and 0.1 are not affected as significantly as the clusters which are there at 0.25 and this is what is seen here also.

So, there is a semblance of an yield stress in these cases also given that the overall decrease is much higher in the low stress, but still you do not see overall divergence of viscosity at the same stress value. So, therefore, yield stress is observed for these and yield stress this is where if there is a Newtonian plateau and in between there is a transition region. We can continue looking at the same composite system which is where a filler has been added to a melt and in this case it says: now a carbon nano fiber and in nano fibers are again very thin and long objects with respect to their aspect ratio and they are being used in a polystyrene melt and in this case we are looking at normal stress as a function of time.

So, just the way when we apply a constant strain rate, stress growth is observed the normal stress of the material also changes as a function of time. Only at steady state we will obtain a constant shear stress and a constant normal stress difference. But by looking at the growth of normal stresses. Again we can get an idea about what kind of non-linear viscoelasticity this present in the material.



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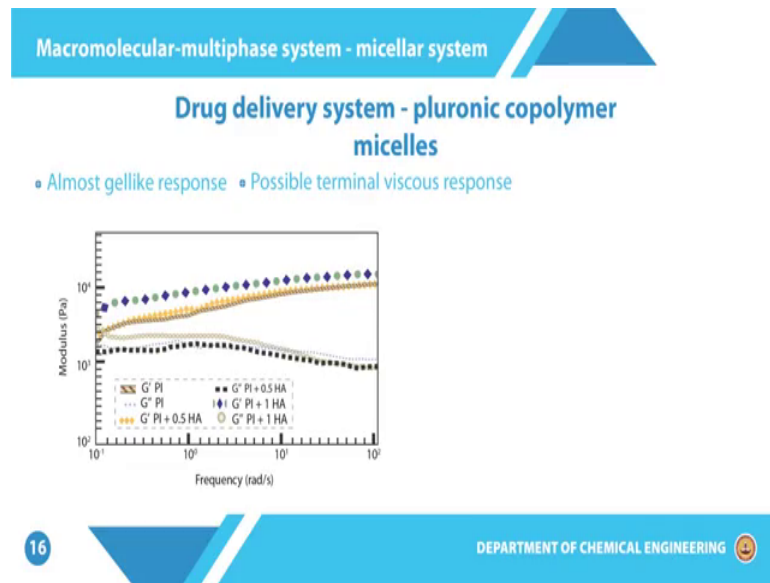


So, in this case we can see that when material is subjected to different strain rates, the normal stress difference is different. More specifically as the strain rate is increased the normal stress is higher and higher and one can also get an idea about the timescales of processes involved by looking at over what timescales these happen. We can also see a presence of small overshoot. In many of the material systems we may see that the stress growth and normal stress growth may happen at different time scales. The same relaxation time may not be possible when we measure it using experiments the same relaxation time may not be valid in both the stress relaxation for shear stress and stress relaxation for normal stress.

Similarly in stress growth experiment the material response in the two cases for shear stress growth and normal stress growth may not be entirely identical in terms of relaxation times. What this indicates is the presence of relaxation processes in the material, and the fact that non-linear viscoelasticity is involved large deformation gives different response for elasticity and shear.

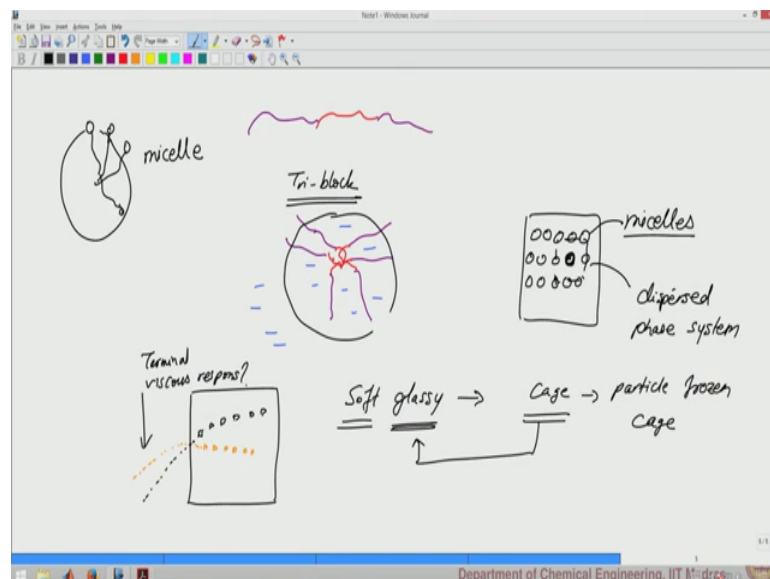
So, many of the non-linear models which are used actually incorporate terms so, that we can get different responses in shear and in normal stresses, in terms of the either growth or steady responses. Now we will look at another complicated example of material system in this case this is a polymeric material system which is a copolymer.

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And these are being investigated for drug delivery or various other applications and given that these are copolymer systems they in when in they are put in a solvent, they actually form micelles and the copolymer blocks, which are similar to each other will come together and form a micelle. So, this is very much like what happens in case of a surfactant and where we have the heads and tails.

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So, the heads and tails in case of surfactant basically form a micelle. So, micelle of surfactant is formed. So, very similar to this in case of a block copolymer, where we

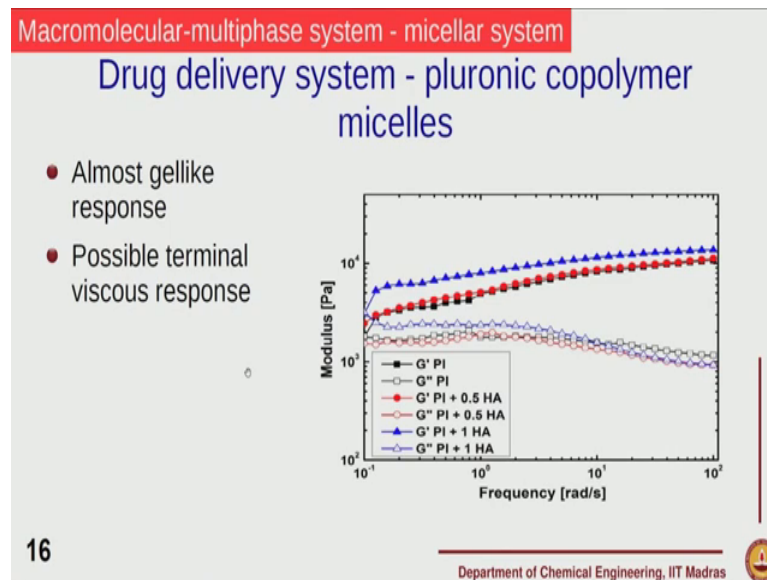
have one block and then another block and then. So, this is a triblock copolymer. So, what happens in this case is for example, all the red part one of the blocks will all come together and then we will have the other. So, again we have a micelle form and. So, this micelle is basically an object using techniques such as light scattering, we can actually probe these micelles. Because the refractive index of the medium in which polymer is there is different compared to the overall solvent which is surrounding.

So, therefore, this micelle has a distinct identity and it naturally leads to different rheological response depending on what is the number of these micelles as well as the arrangement of these micelles. So, in these block copolymers it is known that these micelles arrange themselves in an ordered fashion. So, they form a crystal like structure where all the micelles are arranged in a cubic or some arrangement. And so this material therefore, has an example of a dispersed phase system, because it appears as if these micelles are dispersed in solvent water, on the other hand each and every micelle is made up of polymer molecules.

So, therefore, again a combination of macro molecule and multi phase though the multi phase in this case are formed by the mac polymers themselves or the macro molecular domains themselves. And if we look at the overall frequency response, we are looking at oscillatory shear of these materials where we are looking at  $G'$  and  $G''$  and what we see is predominantly a gel like response. So,  $G'$  is almost independent or its varying about half an order of magnitude in terms of frequency, when we goes from 10 to the power minus 1 to 100, there is a half an order magnitude change in  $G'$  as well as  $G''$  largely seems to be constant, but there is a small decrease.

And so, one can say that these are pluronic gels that are being studied, because in the gel like responses because there is a definitive arrangement of these micelles and they form a mass which cannot be easily sheared and therefore, a gel like response. But if you see the data little more closely, what you can see is the fact that the  $G'$  is increasing somewhat gradually and it appears that if you what could do the experiments below maybe you could observe the  $G'$  going down much further similarly the  $G''$  data seem to be decreasing slightly, and so it is presumably possible that if you do experiments you might see. So, therefore, you can possibly see your terminal viscous response. So, of the material if we probe them at much lower.

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So, is it possible that what we are seeing as a gel like response is it predominantly because we are only probing a smaller range of frequencies. So, these are questions which are very much valid whenever we are looking at a new material systems and to begin with we always look at new material systems, in a limited frequency range.

So, in this case also looking at just this, it may be easier for somebody to just conclude that or these are gel like systems and there is a small dependence of frequencies, but that could be ignored and we could say that these are gels; which basically have a frequency independent response and  $G'$  is greater than  $G''$ . But one of the ways to actually look at the material far more closely is to try to expand in some way can we probe either higher frequencies or lower frequencies.

And of course, one way to do that is to do time temperature superposition which may or may not be always possible to do given the limited type of the material systems for example, this is water in this case and so this is room temperature data, but at zero degrees the water will freeze and similarly if we go to higher temperature water evaporation may be a significant factor. So, therefore, to do time temperature superposition may not be always feasible in many material systems; so one other probe, which can be used in such kind of systems which are also called soft glassy materials. So, soft because the overall modulus of the material is not very high they are not very stiff material, but at the same time they seem to have a glassy response in terms of a cage

of particle confined in a cage. So, in this case the hypothesis is that this micelle is confined in a cage which is formed by all the other particles.

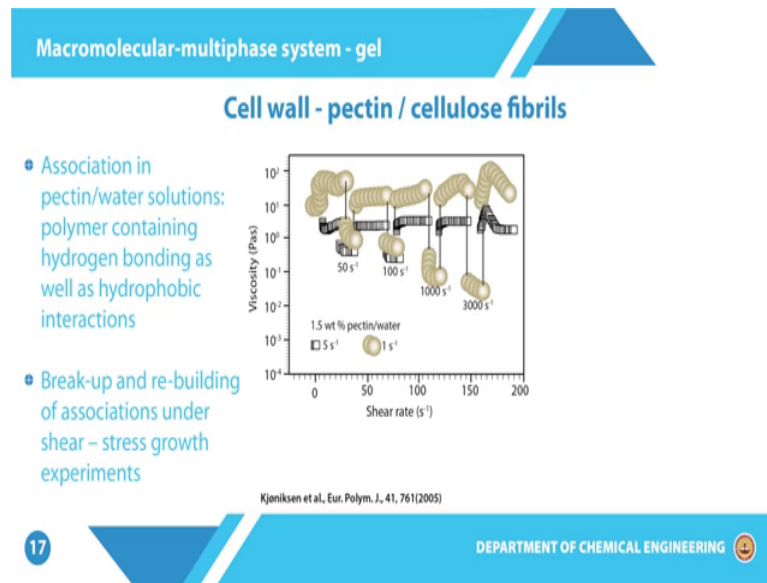
So, given that there are cage like responses and the particle is frozen because of this cage, this is similar to no molecular flexibility at all in the glassy state of macromolecule or for a colloidal glass the particle being frozen because it is in a cage. So, we can say that because of the presence of this could be a soft glassy material.

So, if to probe this further and to get response at other frequencies, we come up with newer and newer techniques in terms of is it possible to probe. So, given that these materials it appears that if you probe them at lower, and lower frequencies then maybe you can see the terminal viscous response. A problem with that, usually is also that given that their overall modulus is low the talks required in the instrument are reasonably low.

So, if you go to still further lower frequencies you may not be able to get good signal to noise ratio or you may not be able to get reliable data. So, one way to look at therefore, these kind of materials is a new technique proposed which is called strain rate frequency superposition. So, just the way we talked about time temperature superposition or frequency temperature superposition in this case we conduct the experiment at different strain rates and then we use shifting to actually construct a master curve and therefore, we have a strain rate and frequency superposition.

So, those of you who are interested can look at this in the current tilted literature, this is not a very old technique or in other words it server one of the relatively new techniques and it is used quite often these days to probe soft glassy materials. So, as the material systems are more complex and more and more non-linear rheological response is important, we can see that the material functions that we look at are more varied and we have to use new tools to start probing them more closely. So, one of the materials which is of great relevance from the point of view of mechanics in plants is the cell wall of plants.

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And we know that the cell wall consists of polymeric materials in fact, cellulose is also polymer; however, it crystallizes and forms fibrils. So, therefore, its more like a rod like particle present in a network of pectin, which is a polysaccharide or a polymer with sugar as the basic monomer units. And so this composite material is very essential in terms of giving the rigidity to the cell wall of plants and the mechanical properties of the cell wall are very essential in terms of the growth of plants as well as in terms of properties of the plant itself. For example, the stem needs to be stronger and therefore, the cell wall properties will have to be stronger. A fruit when its ra very raw usually has a stiffer cell wall and when the fruit ripens the cell wall actually becomes softer.

Therefore, how the pectin cellulose fibrils together act and what kind of mechanical performs do they give is very important in terms of looking at the cell wall mechanics which is present involves. Of course, pectin by itself is also an interesting polymer it is also used quite heavily in food industries as an additive as a gelatin agent, because of the hydrogen bonding and hydrophobic interactions which are possible in pectin it forms nice gel networks. And therefore, it can lead to shear very high viscosity with low amount of pectin added. So, therefore, it is used as a jellifying agent in the systems and because of this there we know that there are strong associations in pectin water resolutions.

So, this is a study the data that we are looking at, is again rheological test which is an modification of what we have seen so far. So, generally we have seen that viscosity as a function of strain rate is studied and what we look at is basically we subject the material in between to a very high strain rate and then again look at what happens to the material response, when we again test them at constant strain rates. So, in this case we are looking at data which is at 5 or 1.

So, therefore, we can see that at five the viscosity is lower and at one the viscosity is slightly higher and as soon as we subjected to a strain rate which is 50 immediately viscosity drops. So, the associations which are present in pectin and water solution can be affected and more often than not broken whenever we subject them to higher and higher strain rates.

So, as we subject the material to higher and higher strain rate, we can see that the drop from this initial value is much more significant, which means there is a more significant breakage of the associations. But of course, once we remove this very high strain rates and bring the material back to low strain rate we can see that again viscosity builds up or the associations have started to again form. Of course, the overall viscosity that is reached may not be the same as unshared samples. So, indicating that the association the formation and breakage of associations are time dependent they depend on sheer as well as the amount of time available. So, such measurements where we are cycling the material at different strain rates are quite useful to look at breakup and rebuilding.

So, in effect what we are doing is, we are combining stress growth experiments with periodic excursions to different strain rates to break or reform of these associations. Further looking at the same material with cellulose micro fibrils itself, when we form gel calcium actually cross links pectin. And therefore, in the presence of cellulose micro fibrils and calcium we can form a gel and we can see that the overall response is pretty much gel like.

In the sense that  $G'$  is higher than  $G''$  and in this case we can see that if only carbon cellulose micro fibrils are their properties are lower. Similarly if only pectin is there then properties are lower, but when both of them are together in the case where there is cellulose as well as calcium, the properties of cell wall is properties of this pectin cellulose composite is higher and the other thing to notice is that when the both cellulose

and micro fibrils are there, there is a more stronger percolated network which is formed of the pectin and cellulose together to give us a more perfect gel like response where moduli are not dependent on frequency. While in the other two cases there are relaxation processes, which make both the moduli functions of frequency.

So, with this overall review we started with polymers then we looked at multi phase systems. And then finally, we have looked at a class of materials which are far more complicated and on which research is being done in recent years and so in each. And every case, we could see that the materials functions were very useful in terms of understanding the microstructure of the materials and different types of material functions could be measured and each of these material functions we have to understand using a micro structural hypothesis. And it is our hope that using one micro structural hypothesis we can explain different material functions which are measured for a material system.

So, with this review we have learnt about the variation of material system for some few class of materials, in the through the assignments in the course and through the problem solving we hope that we can extend this understanding to some of the material which are unknown to us.