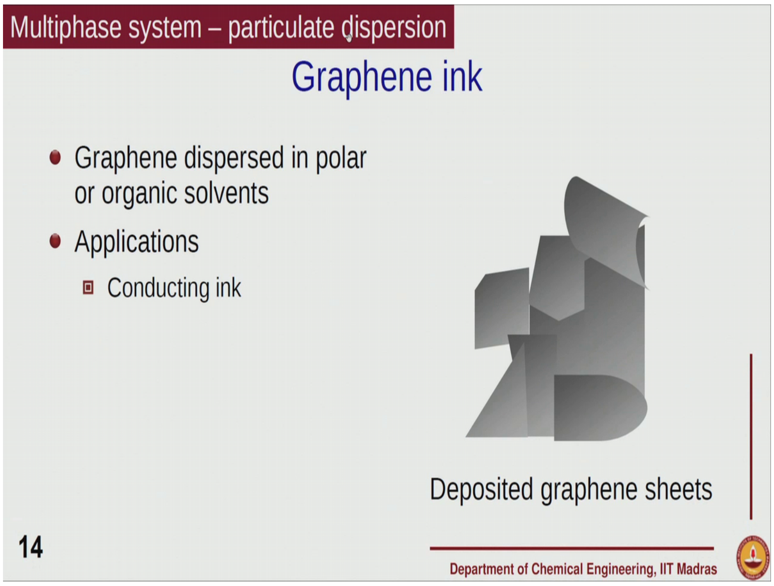
Rheology of Complex Materials

Prof. Abhijit P Deshpande
Department of Chemical Engineering
Indian Institute of Technology, Madras

Lecture - 06
Applications of rheology: some example material systems

So in the previous lecture we looked at the macro molecular systems. Now continuing on, we will look at some of the prominent classes of materials which are multi phase system. And we begin with a particulate dispersion.

(Refer Slide Time: 00:27)

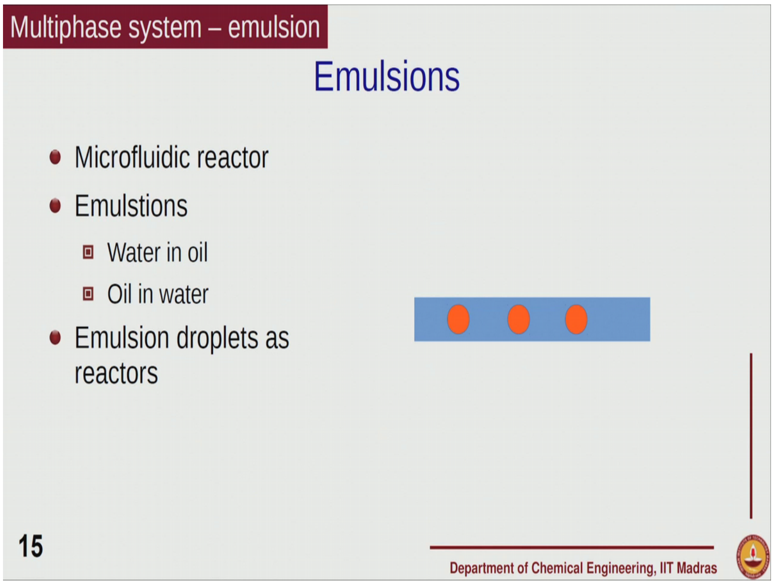


By this we mean, the amount of particulate material in this case this is graphene let us say is small. So, generally the consistency of these kind of materials will be solve may viscosity will be of course more than the solvent itself which is used. However, it will not be very high a. So, unlike a polymer melt or unlike some particulate dispersion at very high concentration these are likely to be very well flow materials which flow easily.

For example, if it has to be used as an ink then usually we the ink will be fed into a cartridge if let us say, we are using printing such as inkjet printing to deposit this ink then. And therefore, it has to flow through narrow openings and then impinge on the substrate and then provide the let us say either a conducting link or it could also be part of a overall device transistor which is being made using organic materials. So, there are several applications in which graphene ink, because it graphene is conducting material and it has very interesting properties as a sheet like material. And therefore, when it deposits, it can form contacts and therefore, lead to high conductivity and during again the rheology of conducting ink material such as conducting ink will be very important during processing stage.

In the sense when device is being made with deposition of these graphene sheets the ink has to flow out of whatever may be the printing device that is being used or whatever may be the coating device that is being used.

(Refer Slide Time: 02:18)

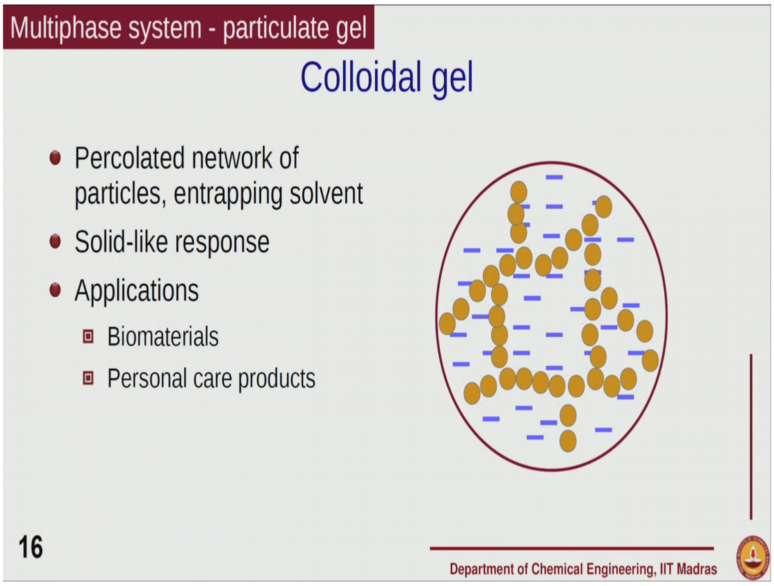


So, the flow ability and overall rheology of conducting ink is a very important in such applications the other types of a multi phase system where we have one liquid and another liquid and the example here is of course, of a microfluidic reactor in this case you have emulsions which are could be either water in oil or oil in water and the idea is to get very controlled size droplets and these droplets, then are used as reactors. For example: you could have let us say the water phase which is the continuous phase and there is a monomer and initiator and cross linker which are in the oil phase.

And so, these then can start reacting and once the reaction is over the final particle that you get let us say of a polymer will exactly be the shape of this drop itself and since all the drops are sim same the overall size of the particle that you get in the end they will also be exactly same. So, as you can see therefore, this is being used as a reactor and each and every drop is being used as a reactor.

And so, in these cases generally the flow behavior of the emulsion systems is of importance because that will determine how the droplets will flow what kind of shapes will they acquire and so on. Of course, emulsions are also involved in various other applications such as creams and day to the personal care products. And therefore, emulsions are generally very useful in terms of applications in which we make them flow and then achieve the performance that is required.

(Refer Slide Time: 04:08)



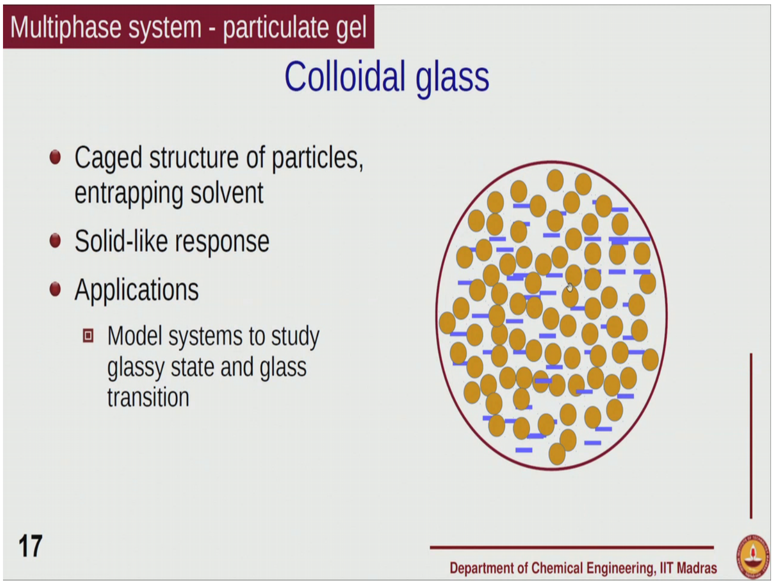
Now the other example of a multi-phase system which is important is a colloidal gel system in this case very similar to the macro molecular case, we have a chain of particles which actually is present and the chains are actually linked with each other through a network. So, therefore, there is a percolated network of particles and this percolated network in it contains large quantities of solvent. And therefore, this is again a solid like material because of these the network that is present. And the applications of this again could be in biomaterials or personal care products many of creams that we use actually belong to this class because we generally have a crystalline. Let us say a triglyceride wax which is deposited out in terms of these particles and then they form the network in which the fluid is also entrapped and then this material is applied on the body and does its job of cold cream or several other such applications.

So, these materials are solid like in their response which means that from in common parlance if we place this material, we have to cut it through a knife is what is generally said in terms of or if we take a small piece of it and put it, it will retain that shape at least for a significant amount of time and so. But these materials are not necessarily they are not hard like the glassy materials. And therefore, they belong at different class we will also see as opposed to the glassy state. Here, actually the particles are joined with each other due to some attractive interactions between them, but you can see that this set of particles here can actually do a little bit of dangling.

So, just the way in a macro molecular network which was a height hydrogel the chain between 2 cross linked point can actually move about, but because of these overall cross links the material itself as an overall rigidity and therefore, it is called gel. Similarly in case of a colloidal gel also, we have these chains of particles and the chain itself is not completely rigid and therefore, some amount of soft solid nature is there in these systems, because of the flexibility of these chains. And of course, over and above the colloidal gel are also different from macro molecular gels in the sense that these cross linking points are physical.

So, therefore, it is like a physical macro molecular gel and not a cross linked macro molecule gel. And so, these cross link points can also form and break. So, therefore, the colloidal gel system response will be quite soft solid like. And so, the relaxation time that are there for these materials though the largest relaxation time we will see can be high, but we will also see the presence of several smaller relaxation times.

(Refer Slide Time: 07:25)

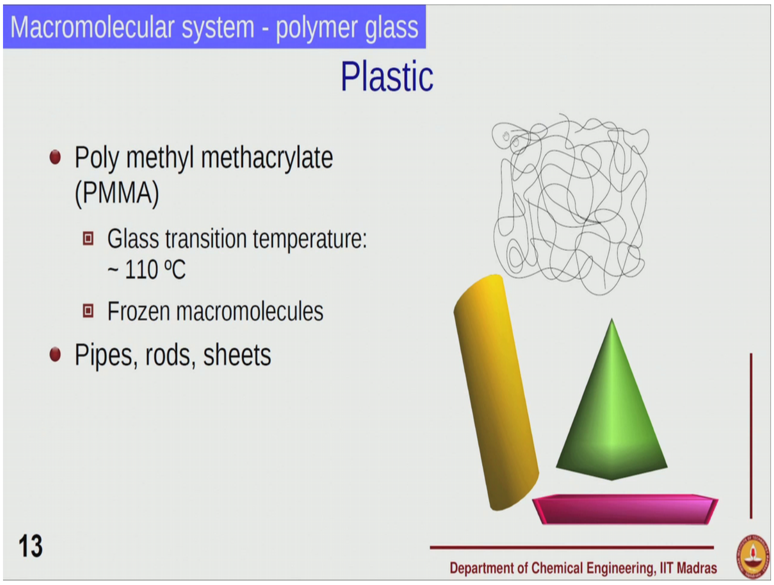


Colloidal glass on the other hand is a caged structure of particles, here each particle is not able to move out because of the cage that is built by several particles which are surrounding it and thermal energy is not sufficient for these particles to move about freely. So, that this particle can escape once in a while of course, due to thermal events particle motion is possible, but in general the case structure of particles lead to entrapping solvent as well as the limited mobility of each and every particle and so.

Again there we have a solid like response and generally these colloidal glasses are being used as model systems to study the glassy state because many times it is more difficult to analyze in a molecular glass in terms of what kind of arrangements it has and in terms of simulating the realistic behavior. On the other hand colloidal particles are far more easy to visualize and also manipulation of interactions between different colloidal particles can be done by tuning the either the surface of the particles or maybe the conditions of the solvent. And therefore, they become a model system to study the glassy state and the glass transition. And so, the glass transition can happen also may be by changing the interactions.

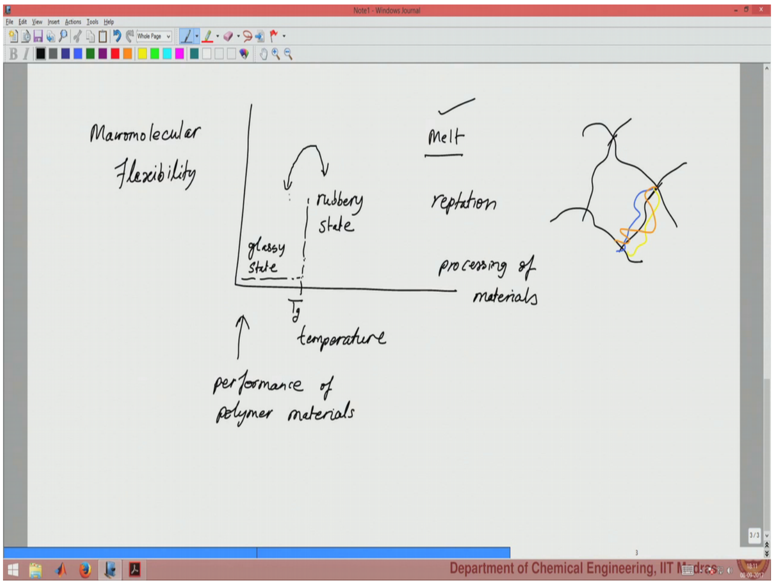
So, under one condition the particles are relatively mobile and under some condition the particle becomes frozen and so again.

(Refer Slide Time: 08:49)



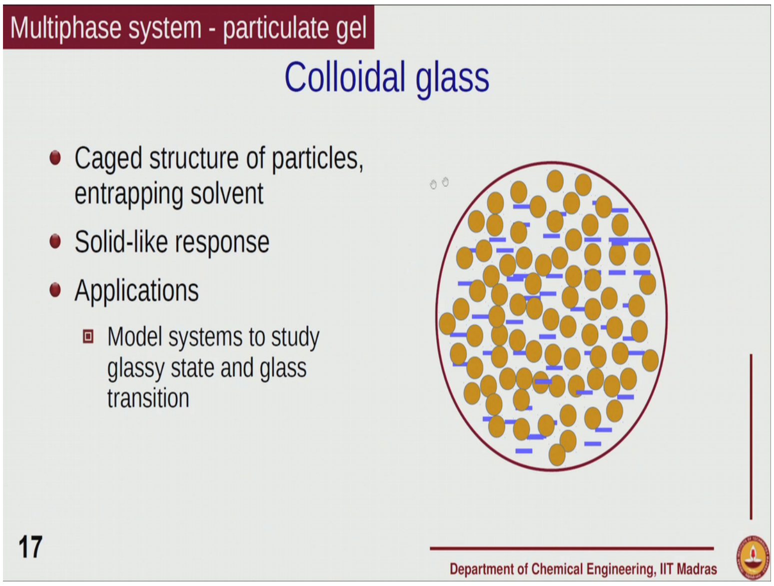
So, this situation is very analogous to what I described where the molecules as a function of temperature are frozen.

(Refer Slide Time: 08:55)



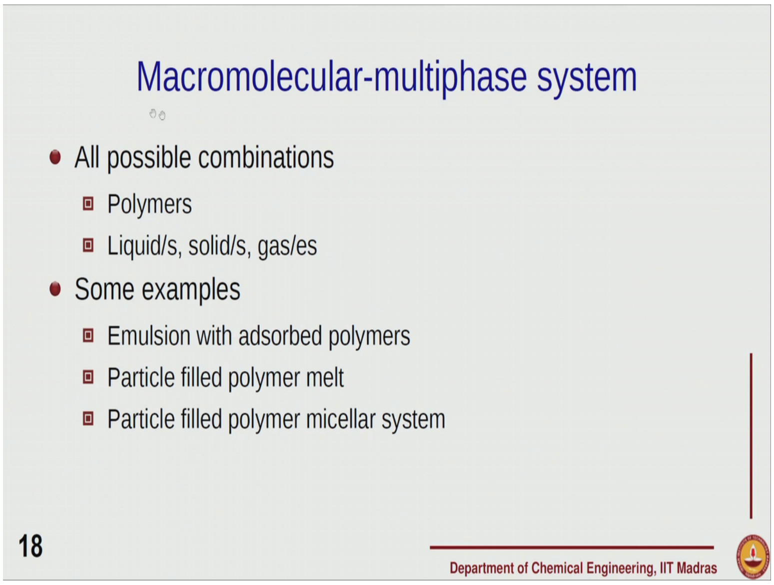
So, in case of macromolecule also, we have this glassy too rubbery transition where there is segmental mobility, and then there is glassy state where all the motion is frozen.

(Refer Slide Time: 09:09)



So, similarly in case of colloidal glass also, we will go through such transitions and so approach to glass transition and the glassy state can be investigated; if we effectively manipulate the interactions and try to understand their role on the overall behavior of the system.

(Refer Slide Time: 09:39)



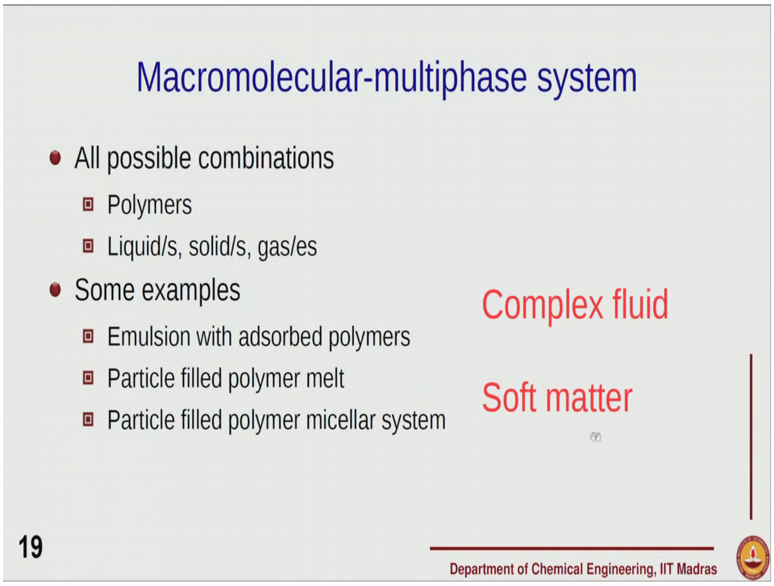
So, in general after having reviewed the macromolecule and multi-phase systems by themselves all possible combinations of these is also there. In fact, more often than not the commercial systems are available. Actually, we will combine both macromolecules and multiple phases in an overall systems.

So, polymers and then liquid may be 2 liquids may be different solids and gas. So, for example, foam is a very form is a mixture of gas and liquid and to modify the properties of the interface material such as protein or some other polymers can be used. And therefore, foam actually will contain liquid gas and polymer. So, generally multiple phases as well as macromolecules are incorporated in several systems and these are some examples for we having an emulsion where polymer adsorbed polymer is used to improve the stability of the emulsion polymer melts are used. As we already said to process the materials which could be used in structural application or applications such as chairs and instrument covers and so on. And if you want better properties from these polymers then we actually fill it with particles

So, these are reinforcing particles. And so, when we process this material the rheology of polymer melt is not so much of interest, but we what we should really understand is what is the rheology of polymer melt with the particles there and the particles interact with the polymer melt the particles interact with each other. And if we have particles which are let us say rod like then these particles may also orient due to deformation. And therefore, one needs to understand the rheology and flow behavior of particle filled polymer melts for quite a few engineering applications.

Similarly, we also have a micelle system in which case let us say if nano particle is being used as part of a drug delivery system then we have a micelle which is formed with polymer and then there is a particle also there. So, these are all examples of material where there are macromolecules and there are multiple phases.

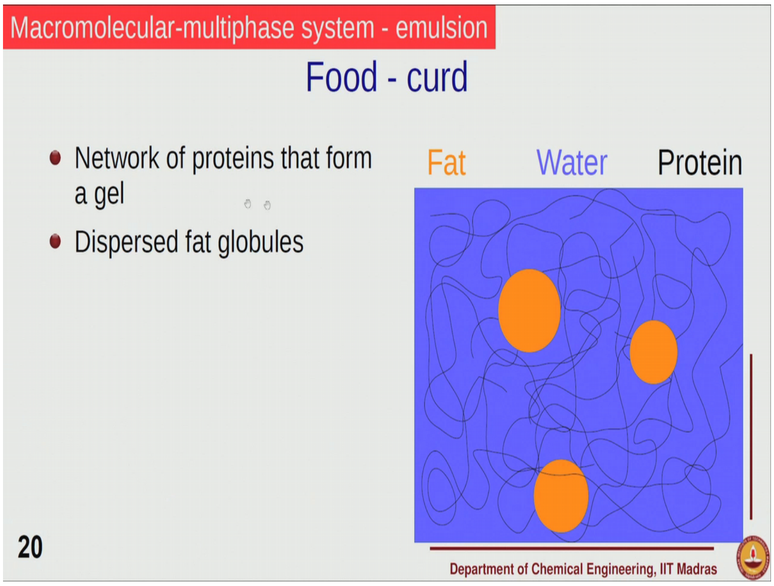
(Refer Slide Time: 12:06)



So, in the next few examples that we will look at belong to these class and because of their inherent complexity most of the rheology these days is done for materials which are for is called complex fluid or soft matter.

So, these are the materials where thermal energy is sufficiently high for molecular and particle motion flexibility at the same time they are composed of multiple length scale and time scale response because of their complex makeup. And so, when we say rheology of complex flow materials we mean that we are in this course we are going to look at rheology of complex fluids or rheology of soft matter. And so, the examples that we look at will start with a material which is quite commonly used of curd and curd is again a solid like material we would like it to be less runny when it is consumed for us to give a good feel about its richness and texture and curd is basically formed by a network of proteins which are which is casein which comes from milk. Of course, and milk also has these of course, fat and water and so. In curd what we have is a network of these proteins has formed which gives us this gel like structure it gives us the solid like response. And then in that these flat globules are actually fat globules are entrapped. And of course, there is overall aqueous medium also which is part of the milk.

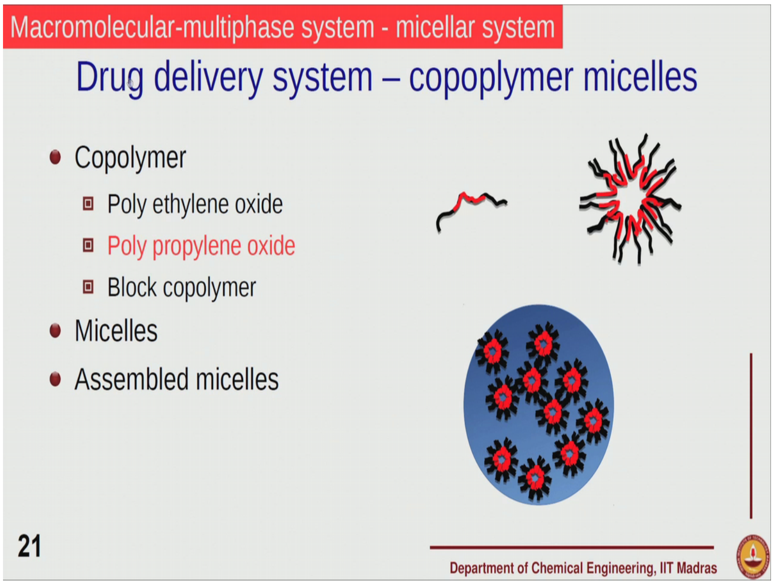
(Refer Slide Time: 13:11)



So, curdling process is basically the formation of the network of the protein and formation of these entrapments of these fat globules in an otherwise continuous medium of water. And so, clearly in terms of eating of the curd rheology is important because the way it appears in a dish or the way it appears when we take it in spoon or take it by hand it is very important how it feels, we first impression of how it is based on the rheological properties in the plate or while we are in the process of eating it.

The next set of rheological in features which are very important is when we eat it. So, how it feels when it is being chewed on or and when it is been manipulated in our mouths and what kind of feeling does it lead to. So, in both cases what happens is this network of proteins and the fat globule. So, this is all responding to the deformation that is being imposed on it. And therefore, rheology of such a system is very important in terms of understanding and trying to get the right type of rheology especially given that now we have multiple products which come in a commercial large scale production. And so, the companies which are making curd will be inherently looking at rheological response of it under different conditions.

(Refer Slide Time: 15:20)



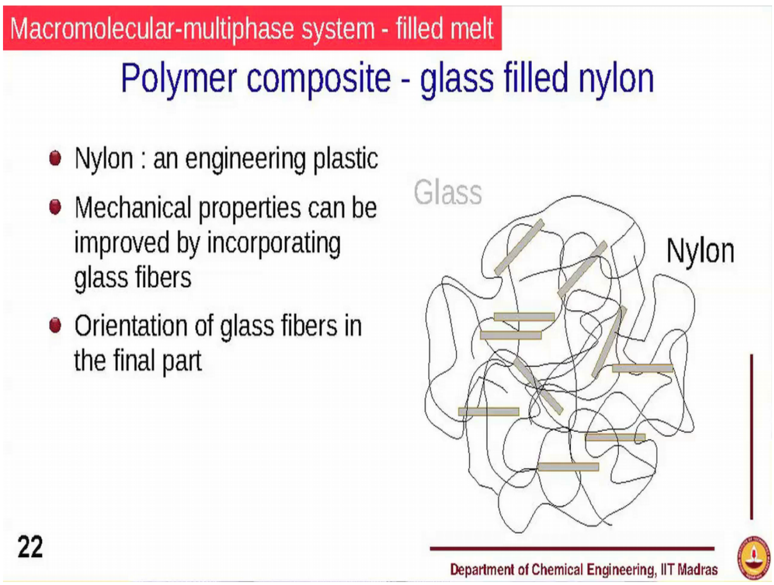
The other example of a multi phase multi component and micelles system is a copolymer micelle this is a copolymer which is called a block copolymer because there is a block of polyethylene oxide which is depicted in black here and poly propylene oxide. And so, we have basically 2 blocks of polyethylene oxide on the 2 sides. And in the center, there is poly propylene oxide and polyethylene oxide is hydrophilic while poly propylene oxide is not as hydrophilic, it is hydrophobic relatively more hydrophobic. So, if we put this molecule in water and several such molecules are there then what happens is all the hydrophobic domains of poly propylene oxide would come together and therefore, a micelle is formed.

So, when this copolymer is put in water we get micelle where all the hydrophilic domains of polyethylene oxide are exposed to the solvent and while the; a poly propylene oxide are sort of exposed to each other in terms of and create a hydrophobic core. So, we basically have a hydrophobic core surrounded by a hydrophilic shell and when these concentration and temperature are appropriate these micelles actually assemble themselves into different arrangements and therefore, this again leads to a gel like material. So, this kind of a micellar system can be used very effectively; let us say for drug delivery because depending on if a drug is hydrophobic and quite often drugs are. So, it could be encased in this kind of a micelle and the overall formulation could incorporate a gel like this and when it goes to the target organ then depending on the conditions. There the overall gel could break up into individual micelles and even individual micelles could break up and therefore, the drug then can be released at a very targeted location under targeted conditions.

So, therefore, these kind of copolymer micelles are as one among several materials which are being investigated for drug delivery applications again this is an example where I have tried to emphasize the macro molecular nature of the polymer because these are block copolymers, but the way they assemble themselves its essential to look at their response through the micelle and in fact arrangement of micelles. So, even though in this case effectively no new phase is being added the overall analysis of this system has to be done in the context of the micelle and it is the arrangement of these micelles in a solvent.

Therefore, we are looking at if it as if a multi phase system, but given that the; this is not a really a droplet or a solid particle. In fact, these are polymer dangling chains. And so, the interaction between different micelles or how the micelle breaks up or how the micelle forms the macro molecular nature of the entity which is making up the micelles and also the micelles which make up the gel micro molecular nature is not cannot be ignored.

(Refer Slide Time: 18:55)



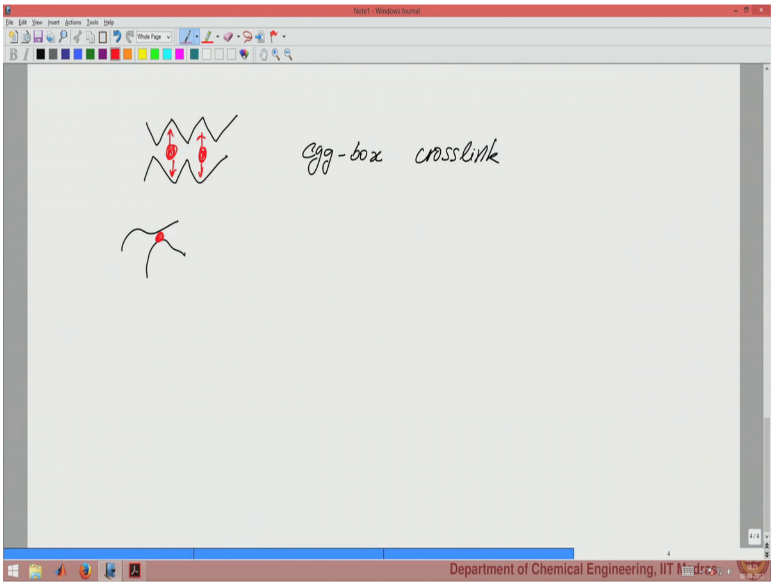
So, therefore, this is also another example of a macro molecular multi-phase system, now the next example that we will look at is a filled melt as I mentioned earlier that many of the application a composite is used a polymer composite where a reinforcement like a glass fiber is added on to nylon. Let us say which is a polymer which is quite often used for several application. And so, what we have in this case is the macro molecules of nylon which are entangled mass and in this we have these glass fibers and this overall system has to be processed in injection molding or whichever process is being used for processing the material, and because of these glass material are usually in a fibrous form the glass fiber can orient itself also. So, the processing not only is important from the point of view of making sure that we get a final part which is free of defects and so on depending on the processing condition we may end up having these glass fibers orienting themselves.

So, the properties of the final part will depend on what type of processing was done on it. So, in this kind of case not only are we interested in rheology for just ensuring that we get a product which is free of defect in this case we use the rheology also to get manipulate the processing condition in such a way that we get an optimum orientation of glass fibers at the end. So, that we get a part which performs appropriately. So, it is not uncommon to manipulate the overall geometry of the part in such a way that glass orients in certain sections much more wherever let us say there is a higher stiffness required in one particular direction and some other parts where the glass fibers may be randomly oriented.

Therefore, rheology of such filled materials is very important. So, we have to consider the macro molecular mechanisms that are involved we also have to consider the interactions between macro molecule and the glass particle a glass fiber and also we have to consider the orientation of glass fiber itself. And if let us say the glass is being used at high concentration then the interaction between glass one glass fiber with other glass fiber will also have to be considered. Therefore, in this case we have to incorporate interactions and mechanisms based on macromolecules as well as the particle eight systems in. So, rheology of these systems is of great interest.

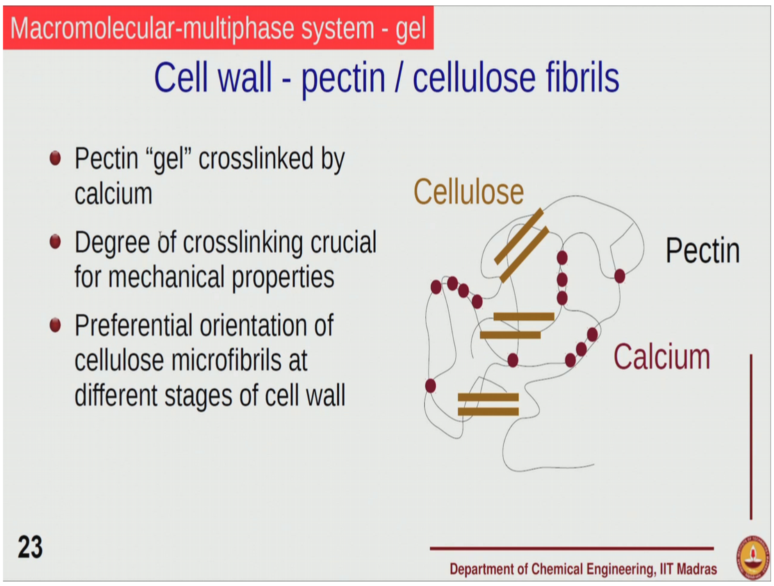
The final system that we will look at is from a plant cell wall where actually what we have is again a network of pectin; pectin is a polysaccharide which is part of all the plant cell wall and in this case the calcium is there as a cross linker. In fact, there are certain 2 different types of cross linking's one set of cross link where actually there is a calcium bonding the subsequent neighboring portions of the pectin molecules. And this is kind of a cross linking point is called an egg box kind of a cross linking because in this case what happens is we have basically pectin molecule.

(Refer Slide Time: 22:26)



So, different pectin molecules are basically aligned like this and then the calcium which is there is there as a cross linker. So, it is acting a cross linker between different back pectin chains. And therefore, this is called an egg box cross linking while we also have on the other hand a single cross link point. So, both of these cross link points are there.

(Refer Slide Time: 23:06)

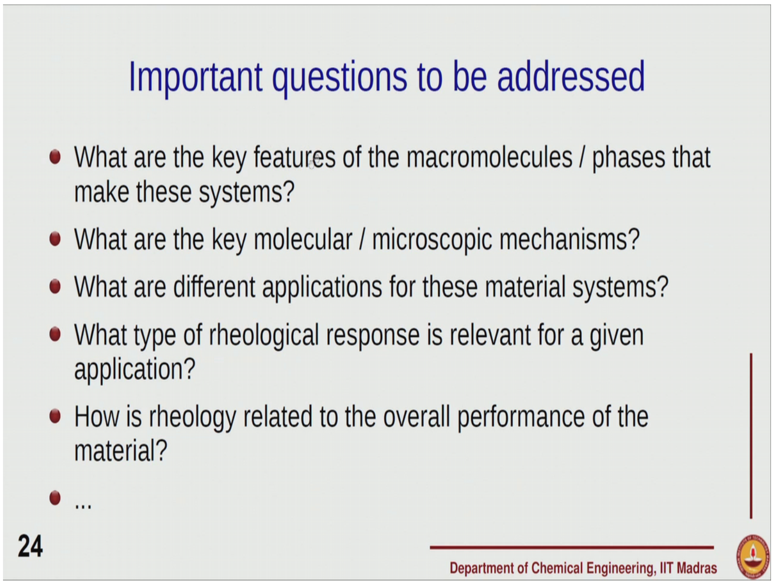


And the relative distribution of these fire cross link points of course, determines what is the overall behavior the cross linking also gets affected based on the nature of the pectin and so. In fact, there are enzymes in the plant cell wall which control how much what is the type of pectin is there and how much hydrophobic and hydrophilic group that are there. And so, methylated pectin for example, is more hydrophobic and therefore, the properties are very different methylated pectins cannot be cross linked as much because calcium requires a hydrophilic group for cross linking.

So, pectin itself determines some properties of this plant cell wall, but what is also important equally important is the cellulose micro fibrils which are there and the mechanical properties of this overall system which is the plant cell wall is very important during the growth phases. So, when a plant is growing and it is adding on cells. So, in those cases which direction does the cell growth happen what are the properties of cells when the growth is happening all this is determined based on biochemistry of this system. So, it involves a macro molecular cross linked system and it involves particulate micro fibrils. And of course, there are other components such as hemi cellulose which are also there which I have left out in this somewhat simplified picture and what is important again is preferential orientation of cellulose micro fibrils.

So, for example, if plant cell wall needs to be stronger in one particular direction then the cellulose micro fibrils will all be oriented in that particular direction. So, what we have seen. So, far are examples of macro molecular multi phase systems which are fairly complicated, because we have to incorporate mechanisms of both macro molecule and multi phases. And of course, all the systems we saw rheology is extremely important, because the material behavior under deformation is a key concern either for processing of the material or for its performance.

(Refer Slide Time: 25:34)

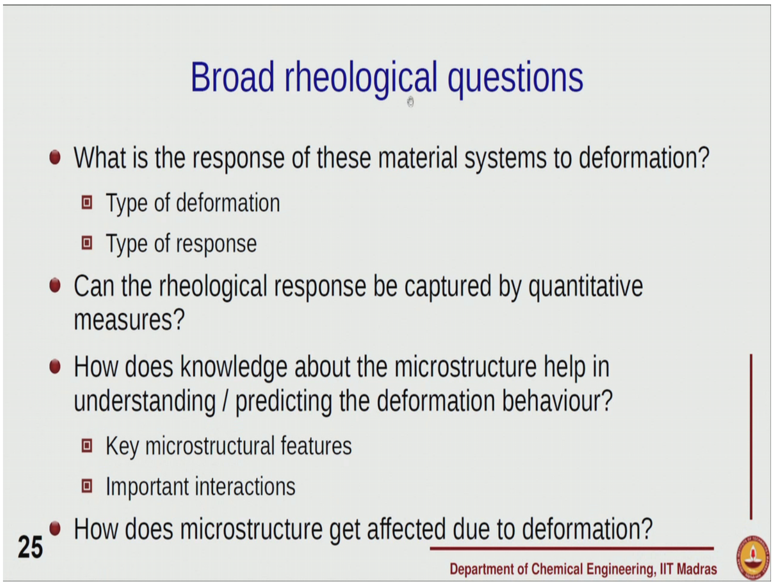


Generally when we are looking at from a rheological view point and we are looking at let us say a material system the key question that have to be addressed are we should have an idea of what are the key features I tried mentioning several such features depending on what the material system was. So, in case of polyvinyl alcohol, there was hydrogen bonding cross links in case of let us say a glass fiber filled melt there was also orientation of glass fibers. So, there are several key features of a macromolecules or the dispersed phases that are important for analyzing the rheological responses.

These features lead us to sort of conclude what might be the mechanisms at a molecular or a microscopic scale and of course, we need to be very aware of what may be the applications. If it is a new material then what is the target application if it is a replacement material then we know what the application is like is going to be. And so, one other key question that we need to know is what type of rheological response is relevant for a given application and this material. As I have highlighted during the introductory lecture also that it is possible sometimes to look at sheer flow alone some other times we need to look at extensional flow at some times steady response of material is sufficient some other time dependent response of the material is required.

So, therefore, what type of rheological response is relevant is a key question and of course, one important feature is doing rheology under controlled condition in a laboratory setup how is it useful and how can we relate this rheology to overall performance of a material if it is a product or overall performance of a material in terms of processing is equally important. So, once we have come to some of the answers to the previous set of questions the next set of questions that we need to answer.

(Refer Slide Time: 27:26)

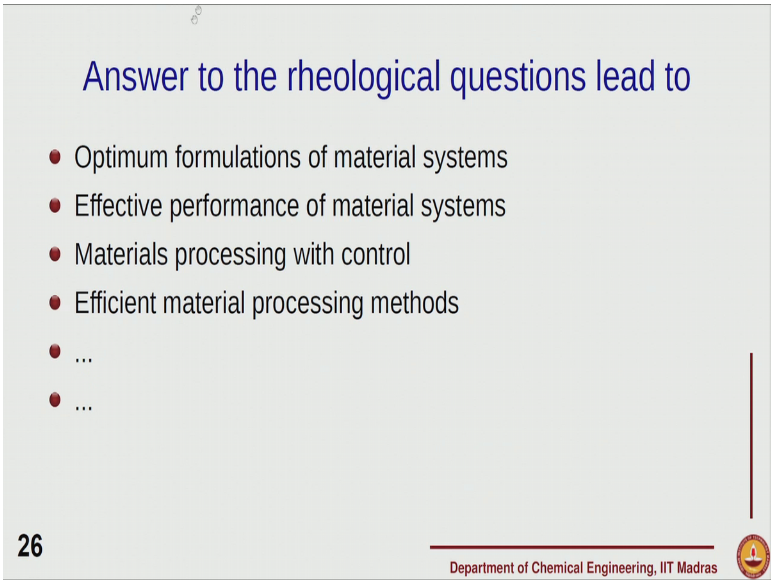


So, that we can do our rheology more effectively is what is the type of deformation that we should investigate what is the type of deformation what is the type of response and as rheologyst; one important feature is to capture the rheological response using quantitative measures.

So, we will see that we will define material functions which are very useful for quantifying the rheological response as opposed to a Newtonian fluid where a viscosity as a single constant characterizes the overall flow behavior we will see that there are several quantitative measures which are possible to be used for a complex materials such as macro molecular and multi-phase systems and so the next question set of questions are related to how can we use the micro structural knowledge in understanding and predicting the deformation behavior also importantly. Because for example when we talk about eating of curd due to the deformation being imposed either while manipulate using it serving it or in terms of eating it the microstructure is continuously getting modified.

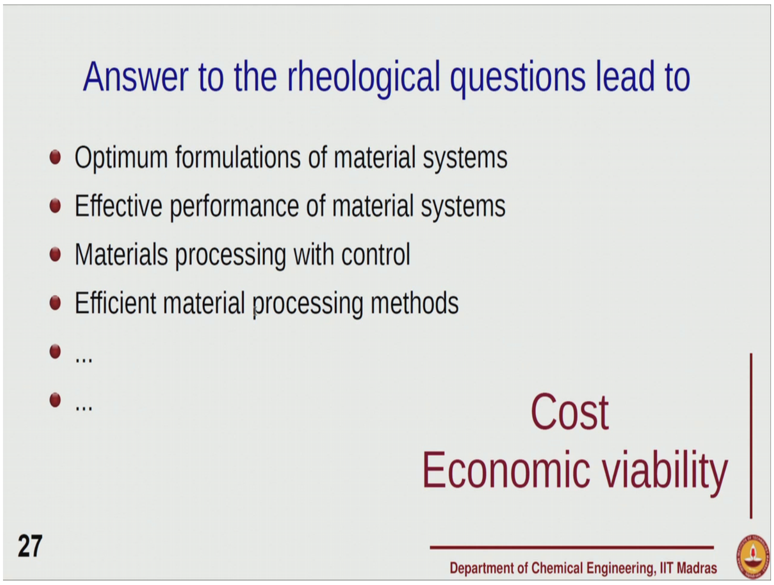
And therefore, in the end what we feel as its mouth feel depends not just on the deformation, but also since the microstructure is getting affected by deformation these are closely linked.

(Refer Slide Time: 28:57)



So, we need to know microstructure under rest, but we also need to know microstructure under deformation and so of course, the hope of a rheologist is that if we are able to answer the questions related to the previous 2 slides. Then hopefully, we will lead to an option or optimum formulation of material systems hopefully these materials will have an effective performance processing is more effective. And so that the thickness of the film that is being obtained or the consistency of a product which is being obtained is consistent and also the processing itself is a efficient. And of course, all of these effectively done along with the general cost an economic viability issues which are there for any product or process will eventually lead to sort of rheology playing an important role in determining the overall application of the material system for a particular case.

(Refer Slide Time: 29:33)



So, with this we have now laid the stage in terms of introductory material which we should be aware while we go on to look at the rheological performance and rheological properties of materials in the next set of lectures.

Now we will start looking at first some preliminary descriptions of the flow of materials and deformation of materials and the stresses which are rise in the material. So, once we discuss the stress strain and strain rate in the material. Then we will be in a position to start looking at the rheological response of the material systems.