Rheology of Complex Materials
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Lecture - 05
Applications of rheology: some example material systems

In the previous few lectures we have got introduced to the idea of a rheology; in terms of what are the unusual flow phenomena and what are the micro structural features of a macromolecular and multi phase systems, which show very interesting flow behavior and therefore, a rheology of a these materials is of interest.

And so, in this lecture, what we will do is look at a some example material systems and we will also look at the class, several classes in the material systems belong to. And this is very helpful in terms of a when we work on rheology of a new material to start looking at and thinking about the overall mechanisms that are involved in the material by comparing it with what class of behavior does the material show.

So, we have already looked at these classes earlier polymer solutions.

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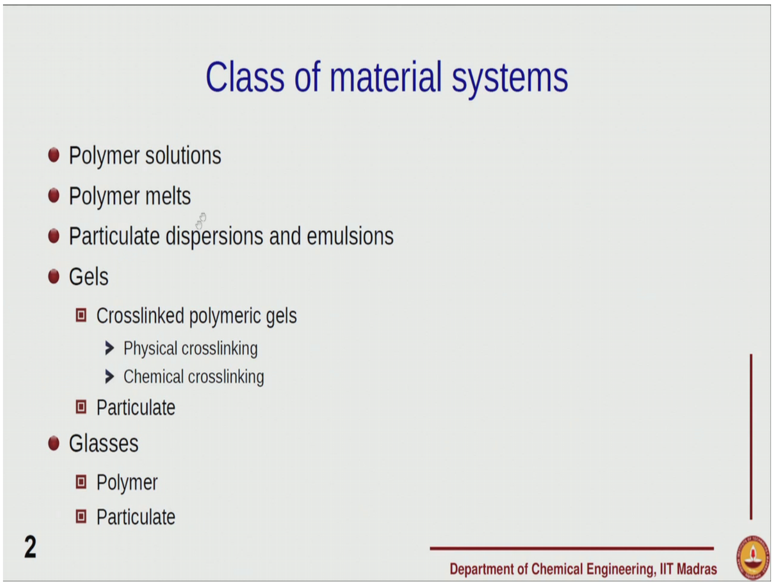

Class of material systems

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

A polymer melts particulate dispersions which would involve also emulsions which are liquid. In liquid we also have a gel which implies a more solid like response which could be polymeric or particulate and the glasses which is a harder solid like response a material which is more stiff and this could be based on a polymer or a particulate system. Therefore, in general we have systems which are a macromolecular or we have systems which are multiphase.

So, in this lecture, we will look at these examples of a material systems belonging to these and look at some key considerations involved in this material systems and also some details regarding what these systems are over and above these systems of course, we also have where the combinations of these exist. For example, we have a macromolecules as well as multiphase system together. So, at the end of the class, we will look at few examples of these systems as well.

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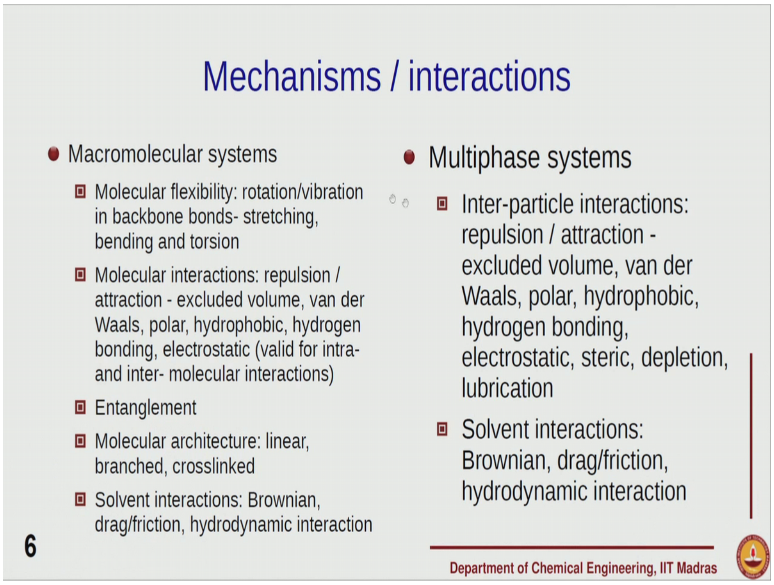

Mechanisms / interactions

- Macromolecular systems
  - Molecular flexibility: rotation/vibration in backbone bonds- stretching, bending and torsion
  - Molecular interactions: repulsion / attraction - excluded volume, van der Waals, polar, hydrophobic, hydrogen bonding, electrostatic (valid for intra- and inter- molecular interactions)
  - Entanglement
  - Molecular architecture: linear, branched, crosslinked
  - Solvent interactions: Brownian, drag/friction, hydrodynamic interaction
- Multiphase systems
  - Inter-particle interactions: repulsion / attraction - excluded volume, van der Waals, polar, hydrophobic, hydrogen bonding, electrostatic, steric, depletion, lubrication
  - Solvent interactions: Brownian, drag/friction, hydrodynamic interaction

So, going ahead we already have summarize; this in the previous class, the main mechanisms which are involved in a macromolecular systems as well as a multiphase systems interactions form in a very important part of the overall mechanisms which are there. And of course, in case of macromolecule entanglements are very important the molecular branching architecture is very important. And similarly in case of a multiphase systems interactions are very important as well as solvent interactions are quite important in both cases whenever we have solutions or a gel or a glass which is which has significant amount of a solvent in it.

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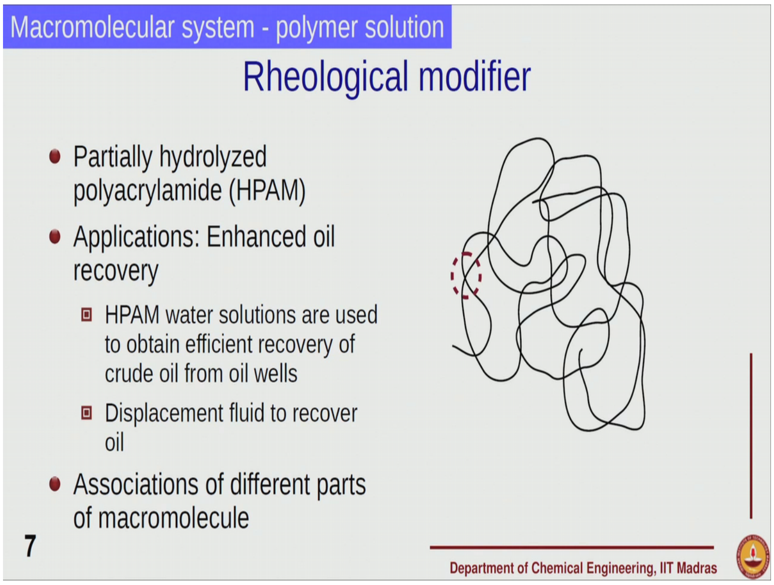

Macromolecular system - polymer solution

Rheological modifier

- Partially hydrolyzed polyacrylamide (HPAM)
- Applications: Enhanced oil recovery
  - HPAM water solutions are used to obtain efficient recovery of crude oil from oil wells
  - Displacement fluid to recover oil
- Associations of different parts of macromolecule

And this is the example that we had seen in the previous class which is related to partially hydrolyzed polyacrylamide. And this is an example of a polymer solution which is used in enhanced oil recovery to change the viscosity as well as in the end of course, to displacement of fluid effective displacement of fluid to recover oil.

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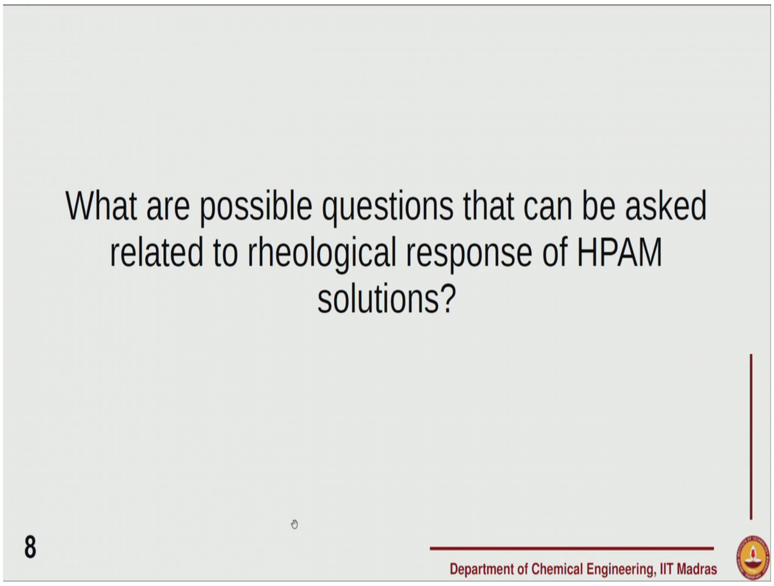

What are possible questions that can be asked related to rheological response of HPAM solutions?

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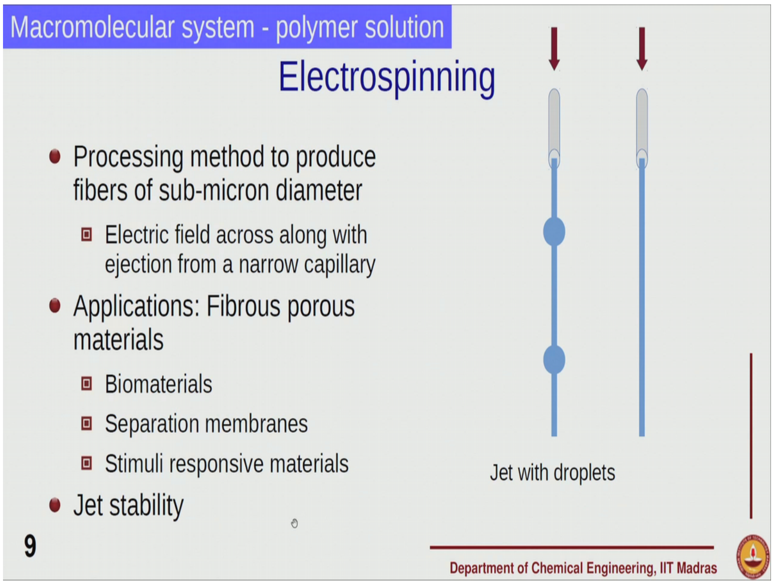

Macromolecular system - polymer solution

Electrospinning

- Processing method to produce fibers of sub-micron diameter
  - Electric field across along with ejection from a narrow capillary
- Applications: Fibrous porous materials
  - Biomaterials
  - Separation membranes
  - Stimuli responsive materials
- Jet stability

So, now, going on further, we will look at a few examples on each of these classes. So, the next example that I have got is related to what is called an electro spinning process.

So, rheology quite often is not just useful for determining the material properties and the performance of the material in the for example, a food which is served on a plate or a shampoo which is used in a bathroom, but quite often we are using a flow of the materials to process them. So, electro spinning is a processing method which is used to produce fibers of a fairly fine diameter nanometer sized diameter and the idea here is to apply an electric field and force a fluid through a very narrow capillary. And so, if we have a very fine capillary through which a fluid is injected and there is an electric field applied between the capillary from which the fluid is injected and the surface on which this fluid is going to fall.

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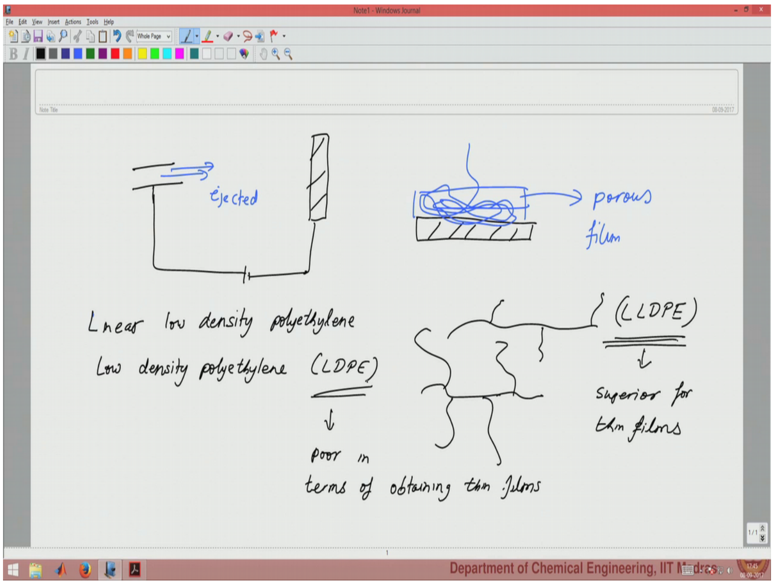

Linear low density polyethylene

Low density polyethylene (LDPE)

↓

poor in terms of obtaining thin films

(LLDPE)

↓

Superior for thin films

So, just to clarify this: so if we have a capillary from which we have a fluid being injected and so. Let us say we have a fluid which is being injected ejected and on the other side we have again a surface on which the fluid is going to go and in pinch. So, there is going to be an electric field between these two. So, that the fluid which is ejected will in addition to the force kappa forces due to the pressure and the Poiseuille flow and the jet formation which is these are the forces, but it will also have an electro electrical force.

And that is why the spinning which is nothing, but extruding a thin jet of fluid from us narrow opening and electro because the presence of the electric field. So, the applications of this of course, are getting fibrous porous materials these can be membranes these can be bio materials such as scaffold for tissue engineering. So, several examples of; so various materials can be constructed using these fibrous porous materials. So, what happens really is these jets which are impinged on this surface and if you look at what happens is if you have let us say the solid surface like this. And then what will happen is these jet which is coming will basically start depositing and we get this in the end this porous film.

So, this porous film is useful as I said in terms of a various applications is biomaterials and filtration and so on. So, in this kind of a problem flow and rheology is extremely important because our idea is to get a very uniform size of a diameter of the jet that comes depending on the stability of the jet there might be a regime in which the jet will actually have a few places where there is a diameter is large. So, basically bead formation or these spherical regions are formed in otherwise a cylindrical jet. And clearly this will modify the nature of the porous membrane that is made later on and also this number of these. And if they are not well controlled then basically electro spinning as a method is yielding a material which is not a very well controlled.

So, in general it is of interest to be in this regime and the a possibility of this regime depends on several factors and rheology is one of those for example, of course, it may depend on the flow rate which is used it may also depend on the surface tension of the fluid with respect to the surrounding medium. And so, based on all these and rheology of the material will determine; what is the regime we are in the other important feature that we have to remember is in such flows extensional flow is involved, because we have a fluid being forced through a very narrow opening and then it is because of electric field, it is getting impinge towards the substrate with electric field we have extensional flow and therefore, not only shear properties of the fluid, but also extensional properties of the fluid are of interest.

So, in these cases quite often polymer solutions are used it will be difficult polymer melt viscosity is very high. So, therefore, generally as a solution spinning is used and so polymer solutions are electro spun into these porous membranes now the next example that we have is of a polymer melt we use these days. Of course, packaging films and grocery bags and plastic bags all throughout for all kinds of a day to day applications; and all of these films are made using a process which is called film blowing and in film blowing what you have is a cylindrical sheet is made.

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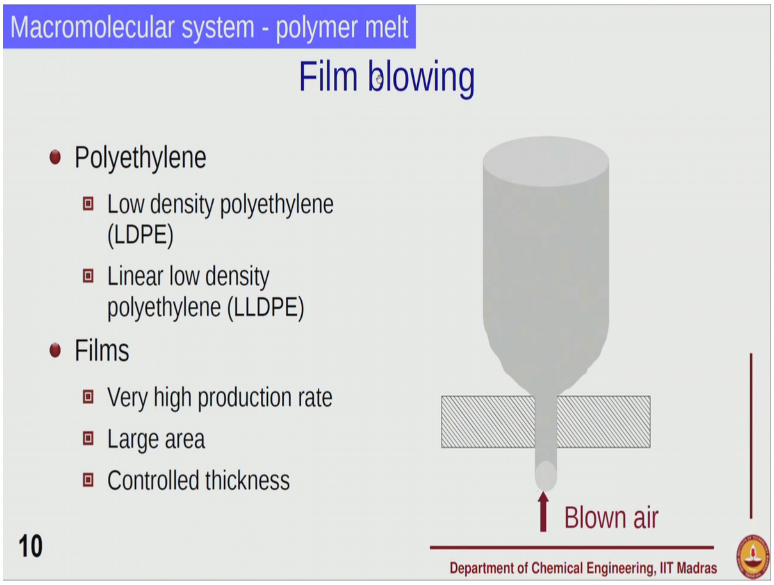

Macromolecular system - polymer melt

Film blowing

- Polyethylene
  - Low density polyethylene (LDPE)
  - Linear low density polyethylene (LLDPE)
- Films
  - Very high production rate
  - Large area
  - Controlled thickness

So, basically an annular sheet is made of plastic and in the center of it air is blown and because it comes out of an opening and air is blown at a high velocity the cylindrical sheet actually extends and bulges out. And therefore, it increases in diameter and it decreases in thickness. So, that is how from a sheet we get a thin film and of course, the higher the stretching here thinner will be the sheet that we obtain. And of course, to use it we can cut it here and then we have a very large polymer film which is available this is of course, we know polythene is what we usually call these bags also.

So, they made of polyethylene and this could be based on a low density polyethylene or a linear low density polyethylene and why these 2 materials are used is because of the extensional properties that they have during such a extensional flows. So, linear low density polyethylene is basically largely linear with some control branches and this is called LLDPE low density polyethylene. On the other hand which is called LDPE is very heavily branched very long branches and also uncontrolled branches. Therefore, in extensional flow it has been found that LDPE is poor in terms of obtaining thin films while LLDPE has a superior performance.

And so clearly for getting thin films; so clearly it is better to use a LLDPE in such applications as opposed to LDPE. So, many of the better quality grocery bags will be made of a LLDPE while the other thin bags may be made of LDPE. And so, these case what is required is a very high production rate which means we would like a controlled thickness and a very large area at a very high rate and so extensional flow behavior of a polymer melt is of a great interest in such kind of applications. And again this is an example of a material processing.

So, the final product that is being used as a polyethylene bag, but film blowing as an operation is being used to produce these bags at a very high production rate. And historically the importance of extensional flow was also because of the analysis of such operations and trying to get higher and higher production rates.

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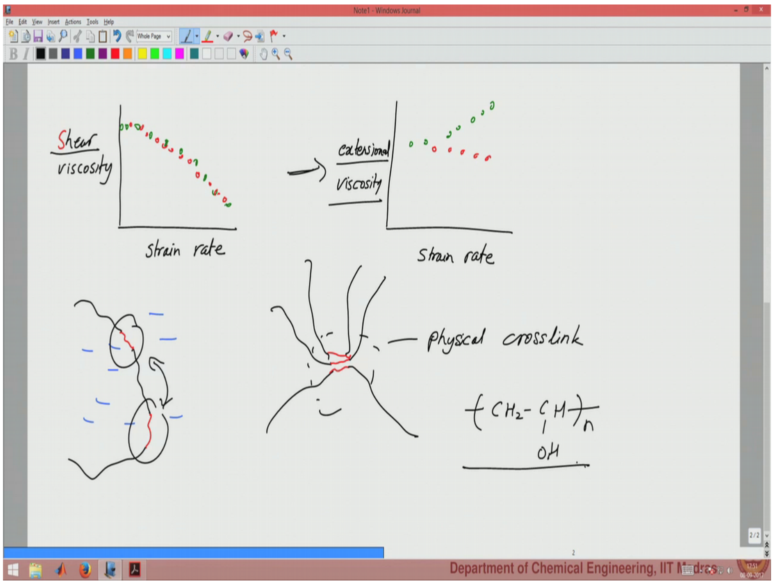

For example, it has been observed earlier that let us say if you have 2 different materials and you are looking at their viscosity the viscosity may be very similar for 2 different materials. So, for example, this is viscosity which is in shear mode which we will define later on. And so let us just right now say shear viscosity as a function of strain rate.

So, these 2 polymer seem to show very similar viscosity, but if you look at the same 2 polymers and look at extensional viscosity and this is something we will define in our course. So, clearly there will be different behavior in extension and in shear. And so, what can be sometimes depending on the material system that is involved we may have a behavior where there is a one of the material shows responds like this while the other material shows a different behavior. Therefore, the 2 materials even though they are identical in one case, but when you look at how their behavior is in extensional behavior it is very different.

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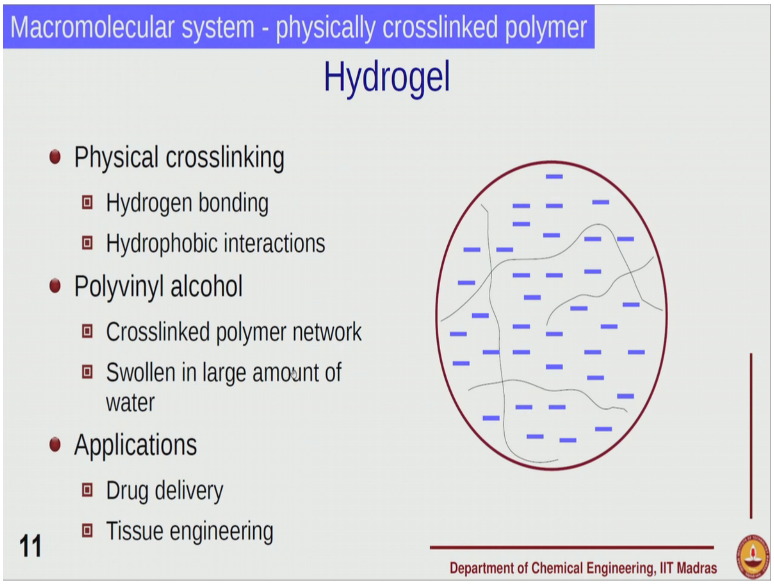

Macromolecular system - physically crosslinked polymer

Hydrogel

- Physical crosslinking
  - Hydrogen bonding
  - Hydrophobic interactions
- Polyvinyl alcohol
  - Crosslinked polymer network
  - Swollen in large amount of water
- Applications
  - Drug delivery
  - Tissue engineering

So, therefore, it is of interest to know the polymer melt rheology in shear as well as extension to understand and optimize the performance for very high production rate the next example that we will take is what are called gel materials. So, in gels we have 2 different kinds of cross linking we have a physically cross linked polymer or a chemically cross linked polymer we are still looking at a macromolecular system. So, in this case the polymers are physically bonded this physical bonding could be hydrogen bonding or it could be hydrophobic interaction.

So, for example, if all along the polymer we have some small patches which are hydrophobic then these hydrophobic ends which come together. So, these are polymers sometimes are also called sticky polymers as. So, what you have is a polymer and then on that periodically there is let us say a hydrophobic patch. And so because when you have a these kind of polymer in a solution what happens is these hydrophobic patches would like to come together. So, this patch and this patch would like to come together. And so, in the end what happens you would end up getting our structure like this where there is this the hydro phobic patch of a one polymer is coming together and the other polymer also hydrophobic patch comes together.

And. So, you have several such hydrophobic patches coming together and this is then what is called a cross linked. So, therefore, this is a physical cross linked because its effectively linking several molecules. And therefore, this is also a sticking point which connects. So, generally we will have cross linking points which are based on a interactions such as hydro oxygen bonding or a hydrophobic interactions and these are depicted by these points here and polyvinyl alcohol is a common example of a hydrogel material a polyvinyl alcohol is nothing but CH 2; CH OH. So, this is the vinyl alcohol group.

And the same repeating unit keeps on repeating and this is a very hydrophilic polymer. So, it is soluble in water, but depending on the conditions under which we create the material strong hydrogen bonding between different parts of polyvinyl alcohol can create these cross linked points. Therefore, cross linking is due to these and these are the cross linking points and between two cross linking points we have the free chains the giant chains which are daggling or the segments of a polymer which are there in applications of such materials which can actually contain large amounts of water. And therefore, they are called hydrogel.

And therefore, they can use in a drug delivery or tissue engineering and several other bio biology logical applications. So, the key characteristic they have is they have; they swell in water and they have large amount of water when they swell. And therefore, then their diffusion within these hydrogels is quite fast because the quite a few properties are almost bulk water like because of the large amount of water. And therefore, which is ideal for example, in biology also several cases we have large amount of water in either plant cell walls or a human body and such.

Therefore, generally you would want a solid material which is structurally integrated which is in terms of because of this physical cross linked material, and therefore it is called a gel, but at the same time it contains fairly large amount of water for diffusion of a several molecules to take place reactions to take place a; and so, the biochemical phenomena could happen the other example of a cross linked material is due to chemical cross linking.

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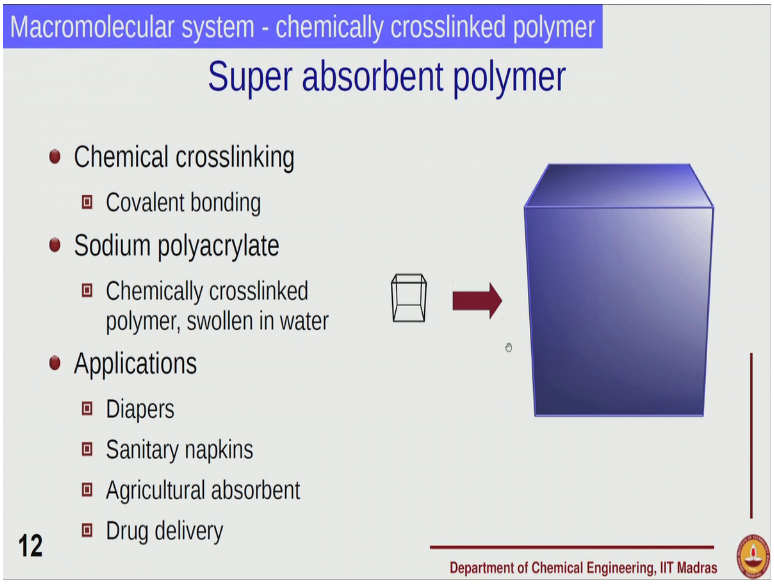

Macromolecular system - chemically crosslinked polymer

Super absorbent polymer

- Chemical crosslinking
  - Covalent bonding
- Sodium polyacrylate
  - Chemically crosslinked polymer, swollen in water
- Applications
  - Diapers
  - Sanitary napkins
  - Agricultural absorbent
  - Drug delivery

So, in this case what we have is a covalent bonding that actually bonds the material. So, in this case the 2 chains of polymer a linked with each other due to a covalent bond and sodium polyacrylate is one common example this is a chemically cross linked water and it can swell. So, it can absorb very large amount of water a few times it is actually its own weight. So, this increase can be five times or eight times and that is why it is used in applications like a diapers and sanitary napkins and absorbent material and so on.

So, these gel like materials are very important from the point of view of their mechanical performance and their properties in terms of strength itself. So, the load at which let us say they tear is important, but also there are properties in terms of what happens to them when we shear them or when we apply a tensile deformation on them and these deformations may not be very small deformations. So, what happens to these materials at large deformations and how; what kind of viscous and elastic response do they have is of great interest for applications of different kinds.

And the key feature in these cases cross linking and the degree of cross linking and then the molecular weight of macromolecules between these cross linking is a fairly important feature.

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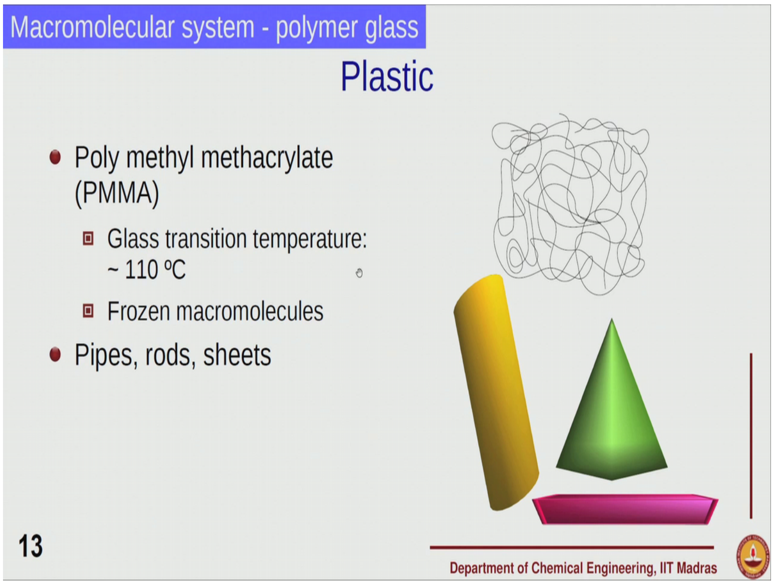

Macromolecular system - polymer glass

Plastic

- Poly methyl methacrylate (PMMA)
  - Glass transition temperature: ~ 110 °C
  - Frozen macromolecules
- Pipes, rods, sheets

So, the next class of material which is again macromolecular, but is related to a frozen sort of a material because it is below the glass transition; so an example is poly methyl methacrylate and glass transition temperature for this is around a 110 degree Celsius.

So, at room temperature, it is basically a glass and as we know glasses we learn during our earlier courses also that silica glass is a super cooled liquid. So, if you look at the overall arrangement of molecules and in this case macromolecules the arrangement is a random, but there is a molecular mobility is practically absent below glass transition temperature. So, therefore a macromolecules are frozen.

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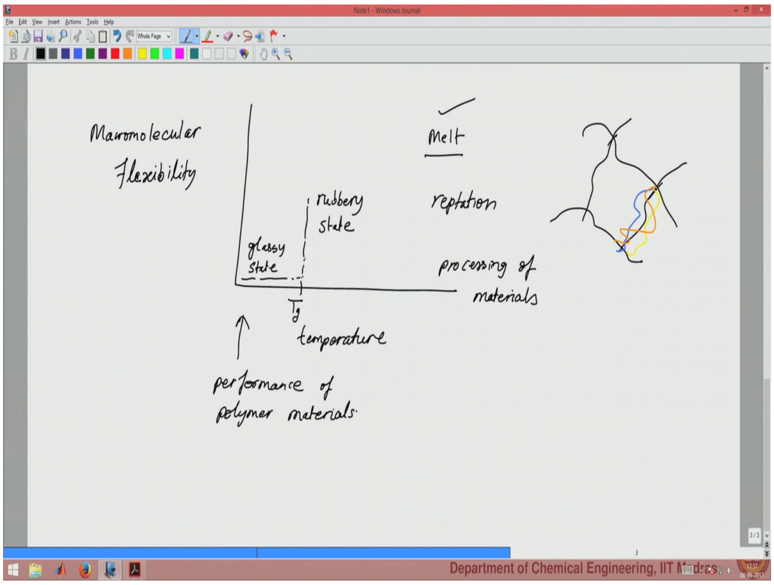

In fact, when we go and look at the macromolecular flexibility as a function of temperature as a function of temperature we have a several distinguishing feature a macromolecular mobility is very low in the glassy state, because the thermal energy which is available is not sufficient for a segment to move at most maybe a side group may be able to rotate of course, the bond vibrations may be present just like in a crystal also atomic vibrations are present.

However, any motion of a macromolecular segment for example, a part of macromolecule is not possible then beyond a certain temperature which is called the glass transition temperature there is a; what is called the rubbery state. So, in this case because the polymer molecules are, of course entangled between a cross links the polymer chains are free to move. Therefore, a polymer chain may explore different conformations as the time goes by. And therefore, there is molecular flexibility. However, the whole molecule may be it will not does not have sufficient thermal energy for it to move.

Now, beyond a certain point we go to the melt state where the overall molecule can also move through repetition in case of a polymer melt. So, the earlier examples of a polymer melt we saw related to film blowing or a in case of a; so, any processing operation like injection molding a polymer melt is involved. So, this is where processing of material happens and this is where the performance of a many structural material structural polymer material happens.

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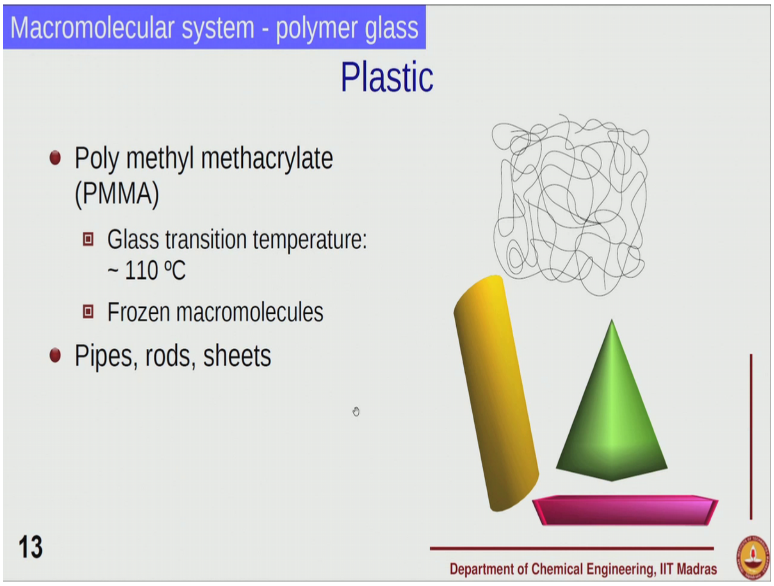

Macromolecular system - polymer glass

Plastic

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- Pipes, rods, sheets

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So, PMMA which is used as a glass; as a rod or a sheet is of course used under its glassy state; so these materials are largely solid like, but they have a depending on the time scale of interest several visco elastic features and so. And given that the molecular arrangements and the basic mechanisms which are present are similar in the rubbery and melt state only thing is the timescales are very different. So, later on in the course, we will define something called a relaxation time. And we will see that the one characteristic of glass transition temperature is the relaxation times are extremely large while in the rubbery and the melt state the relaxation times are lower.

However, one can look at these transitions from melt to rubbery state and rubbery state to plastic state or rubbery state to the glassy state and in terms of these relaxation times by doing real logical analysis and especially when it comes to a long term property prediction when we design a product for let us say 10 years of service life a many times its not feasible to do the test of over long term even let us say few months. So, in that case what we do is we do accelerated tests and one key idea there is a time temperature superposition which is used to obtain. So, the tests are done at different temperatures over short duration maybe just a few days or even hours and then the data is extrapolated to at one particular temperature for over years.

So, in in these kind of things also therefore, we can get an idea of the response of a poly methyl methacrylate in the glassy state at let us say at a room temperature which is depending on the geographical location could be from a 0 degrees to let us say 50 degree Celsius; what we could do in the lab is do the tests at PM on PMMA from 0 degrees. All the way till maybe 150 degree Celsius and then use this kind of data to see what happens to this material at room temperature over maybe years couple of years or 10 years depending on whatever the product life of this kind of products is.

Therefore, rheology of a polymer glasses is very important and given that they are frozen macromolecular systems the relaxation times and the analysis of relaxation times in the glassy state is a very important investigation that still goes on.

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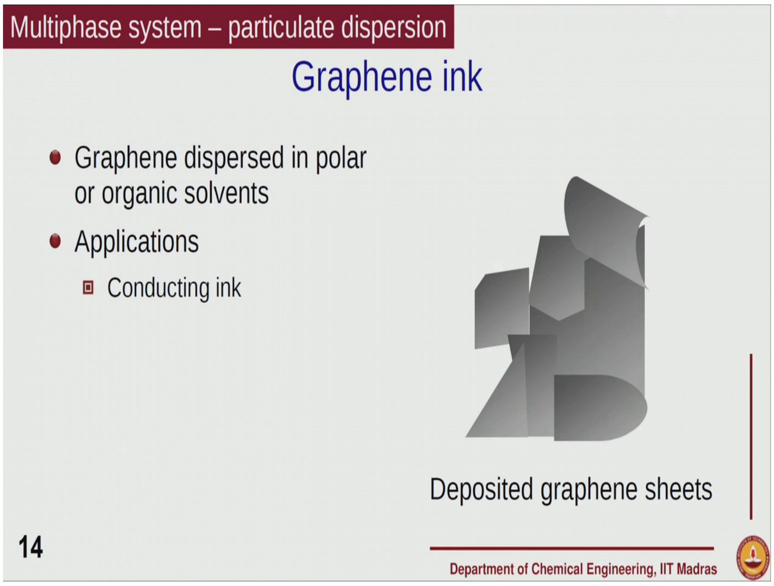

Multiphase system – particulate dispersion

Graphene ink

- Graphene dispersed in polar or organic solvents
- Applications
    - Conducting ink

Deposited graphene sheets

Now, having looked at the macromolecular materials and the materials which both belong to the class of a either solution or a melt or a glass. Now we will go on and look at similar materials in terms of particulate materials which are multi phase systems.

So, in the next segment of the course, we will look at we will start with graphene ink and then look at a several other materials which are particulate.