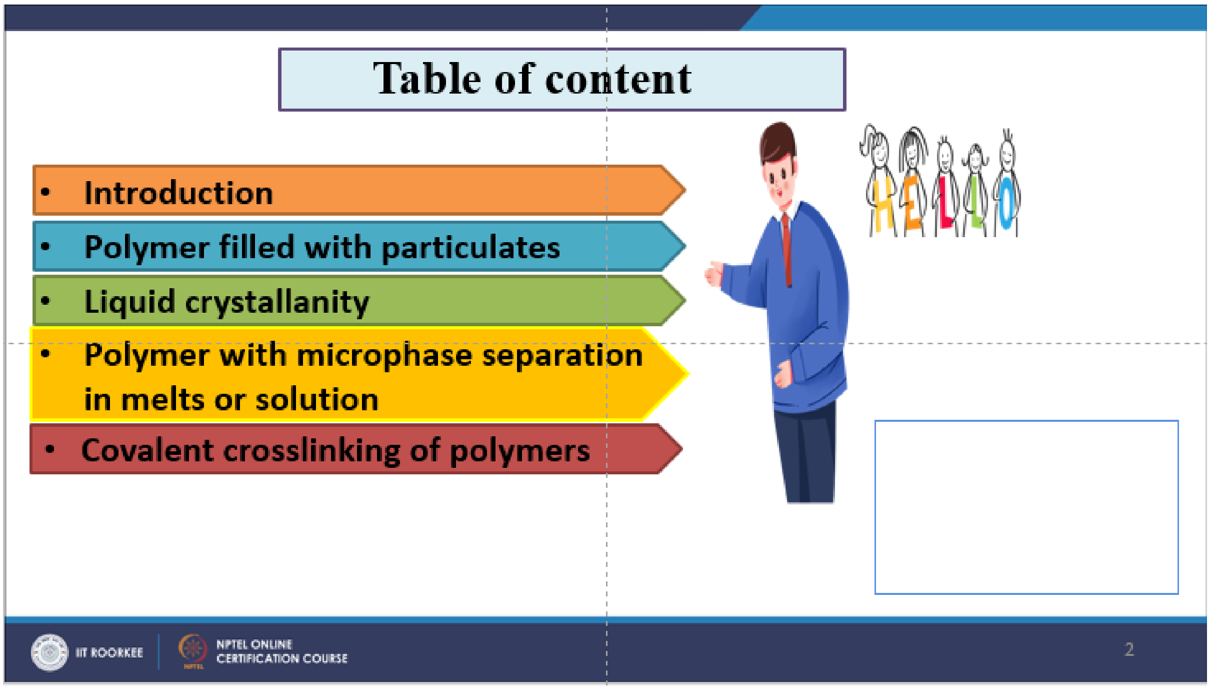
Polymer Process Engineering
Prof. Shishir Sinha
Department of Chemical Engineering
Indian Institute of Technology-Roorkee
Lecture – 13
Applied polymer rheology: Flow of modified polymers and polymer with super molecular structure

Hello friends, welcome to the applied polymer rheology of polymer process engineering. In this particular segment, we will have a brief outlook about the flow of modified polymers and polymer with the super molecular structure. Let us have a look about that the table of content what we are going to discuss. We will have a brief introduction, then we will discuss about the polymers filled with particulates. We will discuss about the liquid crystallinity, we will discuss about the polymer with the micro phase separation in melt source solution. Apart from this, we will discuss about the covalent cross linking of polymers.



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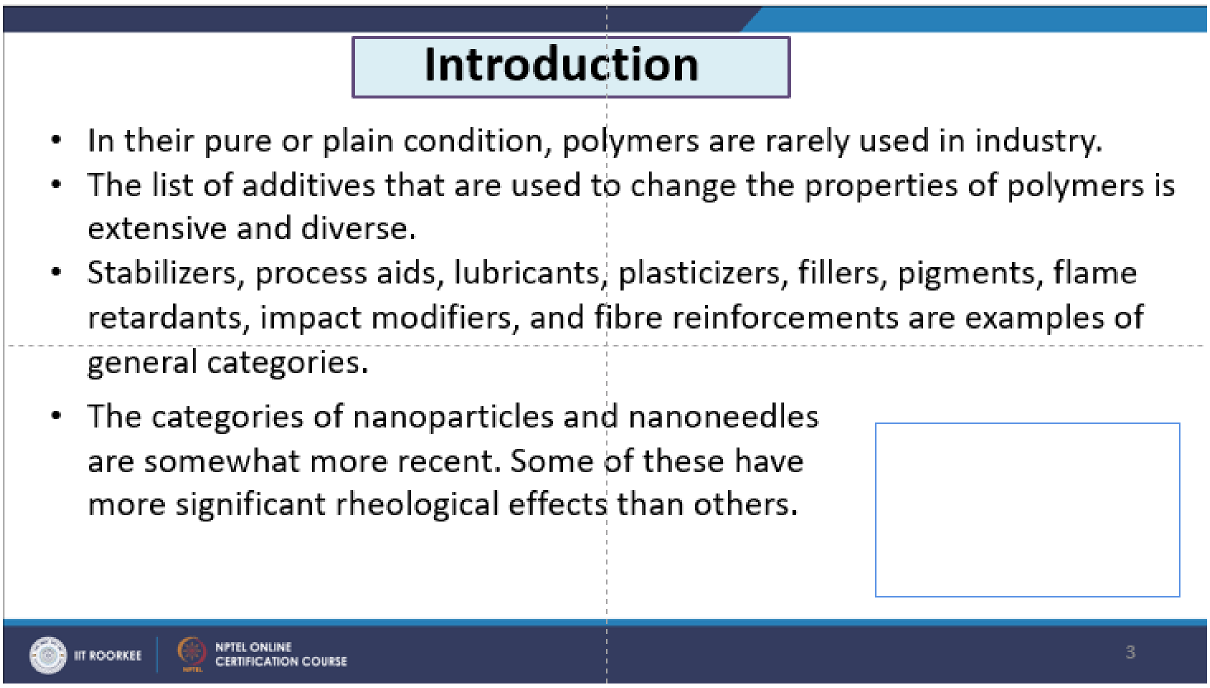
Now, in the pure or plain conditions, the polymers are rarely used in industry. So, because to improvise the properties, because to improvise the certain speciality aspects in those polymers, they are often mixed with different type of additives or different type of fillers. So, the list of additives that are used to change the properties of the polymer is extensive and it diverts in nature. So, when we are having this kind of additives or fillers, then a lot of things need to be addressed.



Introduction

- In their pure or plain condition, polymers are rarely used in industry.
- The list of additives that are used to change the properties of polymers is extensive and diverse.
- Stabilizers, process aids, lubricants, plasticizers, fillers, pigments, flame retardants, impact modifiers, and fibre reinforcements are examples of general categories.
- The categories of nanoparticles and nanoneedles are somewhat more recent. Some of these have more significant rheological effects than others.

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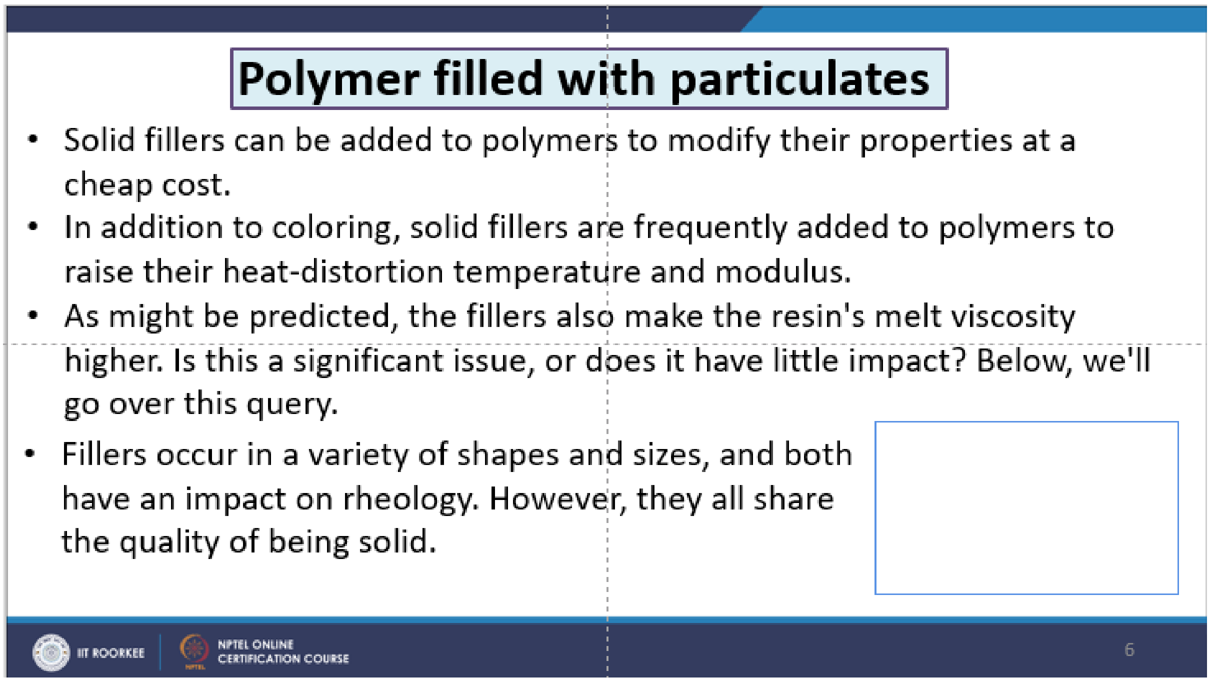
One thing is that what is the affinity between the additives and the polymeric chains? What is the synchronization of the chain? How do they impart with the other properties of the polymer? Apart from this, there are certain other ingredients like stabilizers, and plasticizers, they also been added in those polymers. So, that is why this particular approach, the discussion between the affinity of the stabilizer, plasticizer, additive, fillers, and the polymer matrix is quite interesting. We need to address all those things. Now, these stabilizers are sometimes processing and sometimes lubricants, sometimes fillers, pigments to impart the flame retardancy, sometimes flame retardants, some impact modifiers and apart from this, the fibre reinforcements they are the best example of these kind of things. And ultimate aim of all these ingredients, apart from the polymer matrix is to improvise the properties of the polymer. The different categories of nanoparticles, nanoneedles, are somewhat more recent, and some of these have more significant rheological impact than others.

In addition to additives, fillers, stabilizers, the polymer frequently have morphology that results directly from the structure of the polymers. So, this makes them more and more complex in nature. The most prevalent illustration is the crystallinity, this is caused by the strict regularity. The occurrence of liquid crystal phases that last temperature above the crystalline melting point is one that is less frequent. The rheological behavior of liquid crystal polymers, LCPs is exceptionally unique.

The polymers frequently have morphology which is direct result of the polymer structure in addition to additives. The crystallinity, this is caused by the structural regularity, this is the most prevalent example. One that is less frequent is the existence of liquid crystal phases that last at temperatures higher than the crystalline melting point. A particularly unique type of rheological behavior is shown by the liquid crystal polymers or LCPs. So, let us talk about the polymers filled with the particulates because all these things like additive fillers, they are the contributing part of this particular concept.



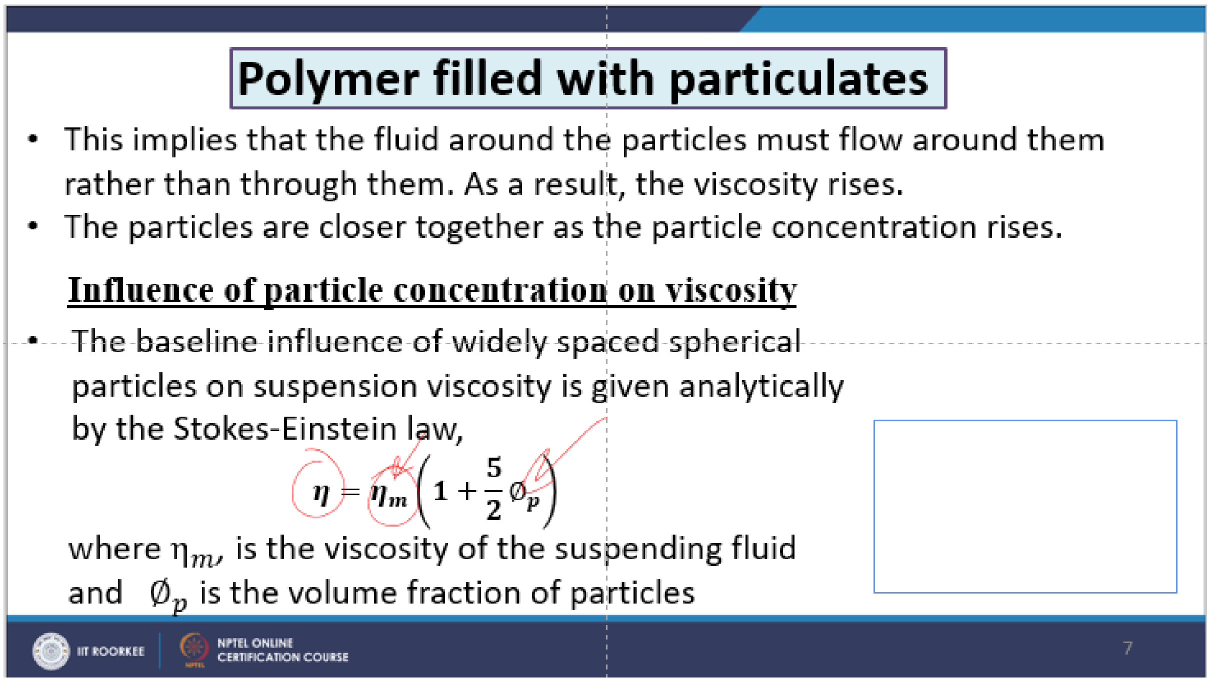
Polymer filled with particulates

- Solid fillers can be added to polymers to modify their properties at a cheap cost.
- In addition to coloring, solid fillers are frequently added to polymers to raise their heat-distortion temperature and modulus.
- As might be predicted, the fillers also make the resin's melt viscosity higher. Is this a significant issue, or does it have little impact? Below, we'll go over this query.
- Fillers occur in a variety of shapes and sizes, and both have an impact on rheology. However, they all share the quality of being solid.

The solid fillers, these can be added to the polymers to modify their properties at a cheap cost. So, in addition of coloring, the solid fillers are frequently added to polymers to raise their heat distortion temperature and modulus and sometimes the mechanical thermal or chemical stability. As might be predicted, the fillers also make the raisins melt viscosity higher. Is this a significant issue or does it have the little impact? We know we are going to over this particular query. The fillers occur in a variety of shapes and sizes and both they have an impact on rheology.

However, they will all share the quality of being solid. This implies that the fluid around the particle must flow around them rather than through them. As a result, the viscosity rises. Now, the particles, they are closer together as the particle concentration rises. Now influence of particle concentration on viscosity, the baseline influence of the widely spaced spherical particles on suspension viscosity is given analytically by Stokes Einstein law, that is, Nita is equal to the m into 1 plus 5 over 2 phi p, where this Nita m is the viscosity of the suspending fluid and phi p is the volume fraction of particles.

$$\eta = \eta_m\left(1+\frac{5}{2}\emptyset_p\right)$$



Polymer filled with particulates

- This implies that the fluid around the particles must flow around them rather than through them. As a result, the viscosity rises.
- The particles are closer together as the particle concentration rises.

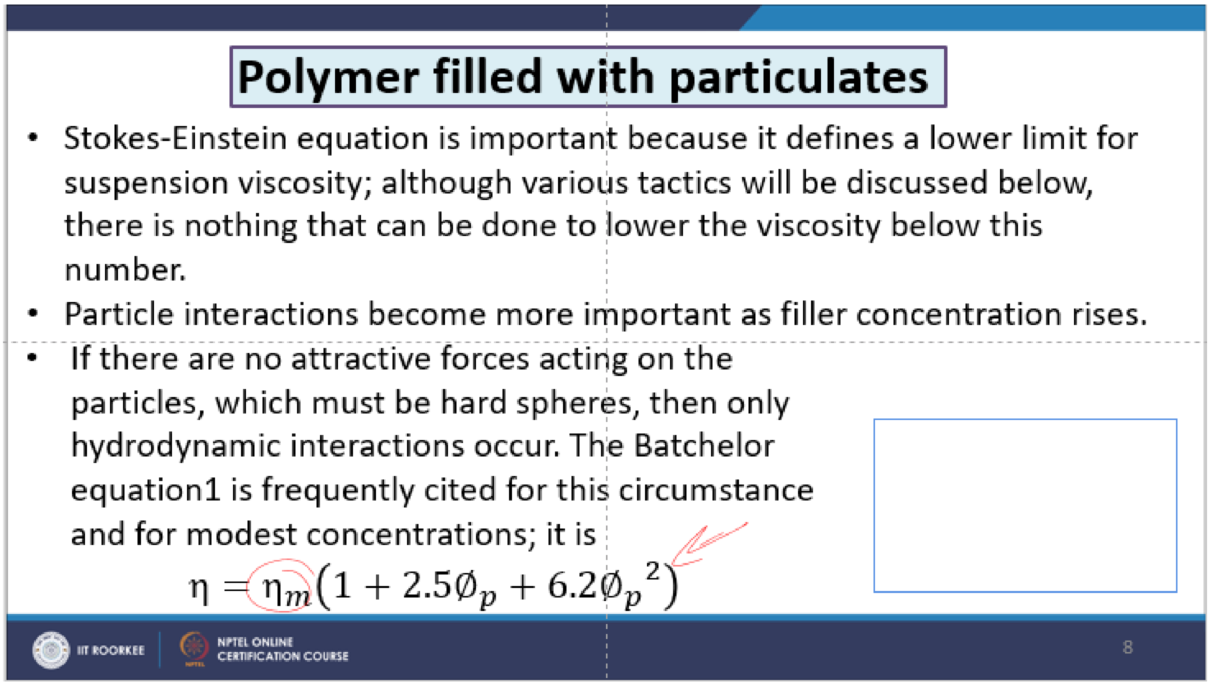
Influence of particle concentration on viscosity

- The baseline influence of widely spaced spherical particles on suspension viscosity is given analytically by the Stokes-Einstein law,

$$\eta = \eta_m\left(1 + \frac{5}{2}\emptyset_p\right)$$

where η_m, is the viscosity of the suspending fluid and $\emptyset_p$ is the volume fraction of particles

Now, Stokes Einstein equation is important because it defines a lower limit for suspension viscosity although various tactics, this can be discussed, there is nothing that can be done to lower the viscosity below this particular number. The particles interaction become more important as the filler concentration rises. Now, if there are no attractive force acting on the particles which must be hard spheres, then only hydrodynamic interaction occurs. The Batchelor equation is frequently cited for this circumstances and modest concentration, it is Nita is equal to Nita m into 1 plus 2.5 phi p plus 6.



Polymer filled with particulates

- Stokes-Einstein equation is important because it defines a lower limit for suspension viscosity; although various tactics will be discussed below, there is nothing that can be done to lower the viscosity below this number.
- Particle interactions become more important as filler concentration rises.
- If there are no attractive forces acting on the particles, which must be hard spheres, then only hydrodynamic interactions occur. The Batchelor equation1 is frequently cited for this circumstance and for modest concentrations; it is

$$\eta = \eta_m\left(1 + 2.5\emptyset_p + 6.2\emptyset_p{}^2\right)$$

2.5 phi p square. Now, as it is mentioned, the coefficient of for this particular factor is only applicable to the spherical non-agglomerating particles. However, this equation introduces a quadratic term that implies hydrodynamic interaction between the particles. Empirical and semi-theoretical relationship covering much of the concentration range. Now, there are couple of examples we have enlisted for the some as a summary of a popular equation for suspension viscosity like a Stokes Einstein equation, the Nita is equal to Nita m into 1 plus 2.

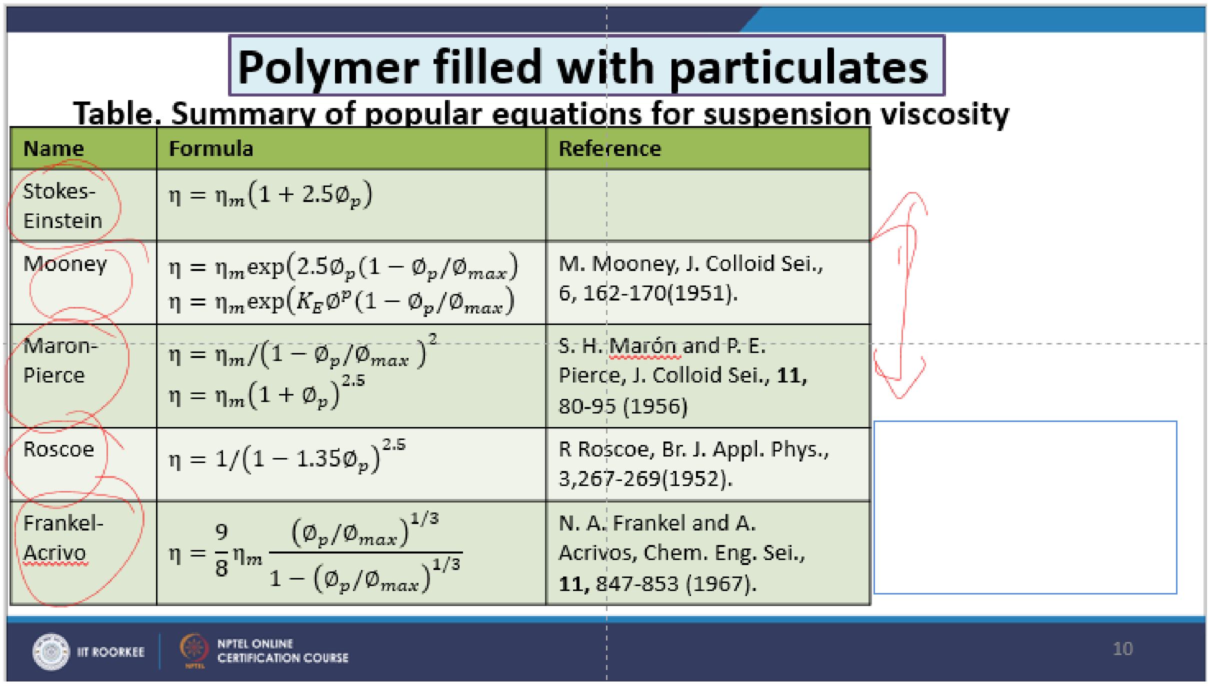


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Table. Summary of popular equations for suspension viscosity

Name	Formula	Reference
Stokes-Einstein	$\eta = \eta_m(1 + 2.5\varnothing_p)$	
Mooney	$\eta = \eta_m \exp\left(2.5\varnothing_p(1 - \varnothing_p/\varnothing_{max}\right)$ $\eta = \eta_m \exp\left(K_E\varnothing^p(1 - \varnothing_p/\varnothing_{max}\right)$	M. Mooney, J. Colloid Sei., 6, 162-170(1951).
Maron-Pierce	$\eta = \eta_m/(1 - \varnothing_p/\varnothing_{max})^2$ $\eta = \eta_m(1 + \varnothing_p)^{2.5}$	S. H. Marón and P. E. Pierce, J. Colloid Sei., **11**, 80-95 (1956)
Roscoe	$\eta = 1/(1 - 1.35\varnothing_p)^{2.5}$	R Roscoe, Br. J. Appl. Phys., 3,267-269(1952).
Frankel-Acrivo	$\eta = \frac{9}{8}\eta_m \frac{(\varnothing_p/\varnothing_{max})^{1/3}}{1 - (\varnothing_p/\varnothing_{max})^{1/3}}$	N. A. Frankel and A. Acrivos, Chem. Eng. Sei., **11,** 847-853 (1967).

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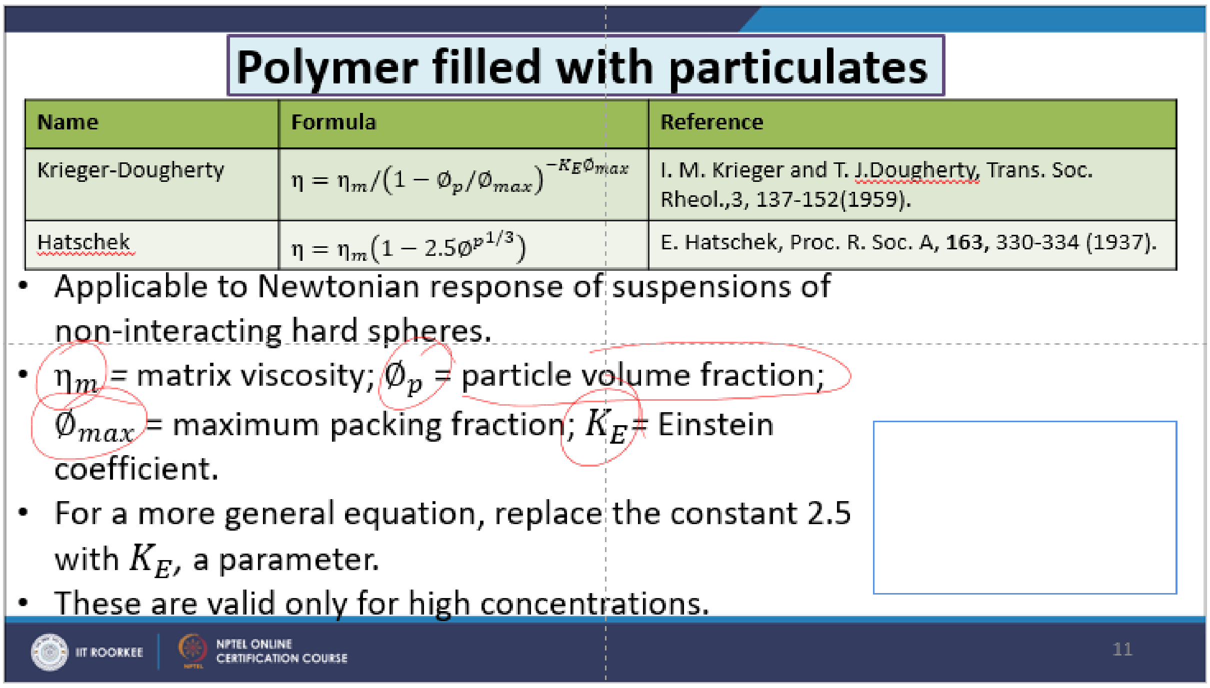
5 phi p. Now, Mooney, this is the Nita is equal to Nita m exponential 2.5 phi p into 1 plus phi p over phi max or Nita is equal to Nita m exponential k e phi p into one minus phi p over phi max. Similarly, the Maron-Pierce equation, Roscoe equation, and Frenkel RQ equation, all these equations are enlisted for the advanced study or references. Similarly, The Krieger-Dougherty equation and the Hatschek equation So, all these equations we have enlisted as a reference and as per the case, this can be utilized. Now, these applicable to the Newtonian response of the suspension of non-interacting hard spheres.



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Name	Formula	Reference
Krieger-Dougherty	$\eta = \eta_m/(1 - \varnothing_p/\varnothing_{max})^{-K_E\varnothing_{max}}$	I. M. Krieger and T. J.Dougherty, Trans. Soc. Rheol.,3, 137-152(1959).
Hatschek	$\eta = \eta_m(1 - 2.5\varnothing^{p^{1/3}})$	E. Hatschek, Proc. R. Soc. A, **163**, 330-334 (1937).

- Applicable to Newtonian response of suspensions of non-interacting hard spheres.
- η_m = matrix viscosity; $\varnothing_p$ = particle volume fraction; $\varnothing_{max}$ = maximum packing fraction; K_E = Einstein coefficient.
- For a more general equation, replace the constant 2.5 with K_E, a parameter.
- These are valid only for high concentrations.

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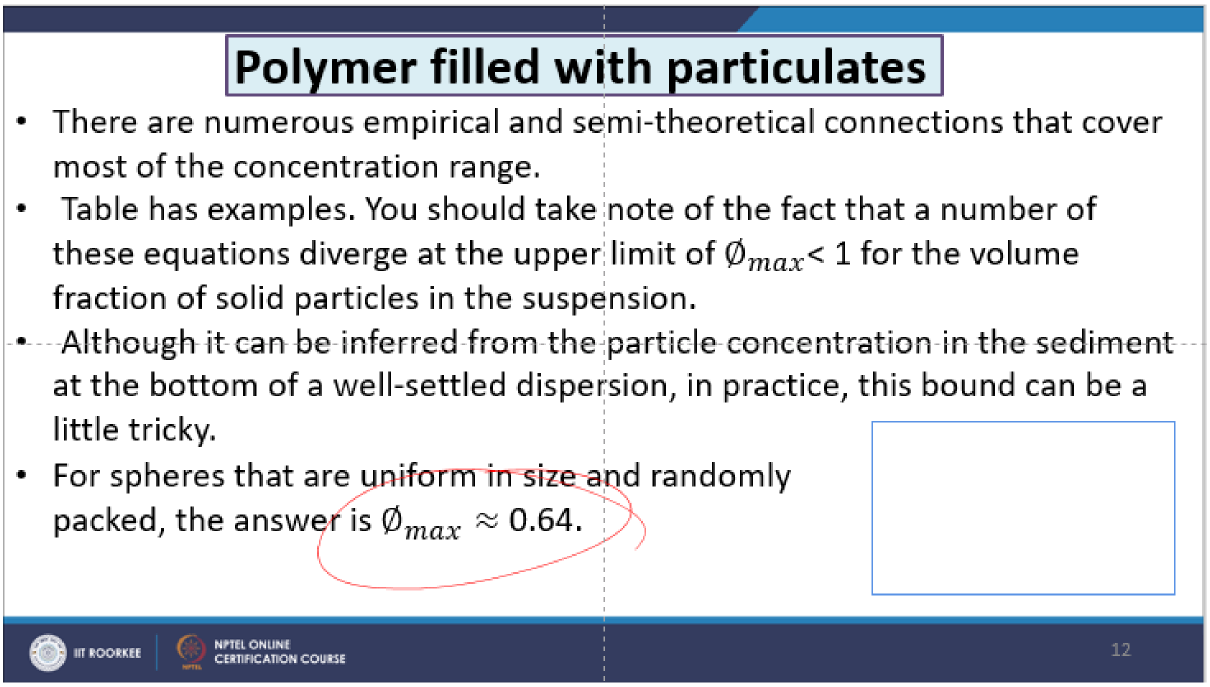
Here, the Nita m is the matrix viscosity, where phi p is the particle volume fraction in every equation and phi maximum is the maximum packing fraction and k e is the Einstein coefficient. For more general equation, this can be replaced to the constants 2.5 with k e a parameter and these are valid only for high concentration. Now, there are numerous empirical or semi-theoretical connections that cover most of the concentration range. Now, this table has an example, you should take note of fact that a number of these equation diverge at upper limit to of phi maximum is less than 1 for the volume fraction of a solid particle in the suspension.



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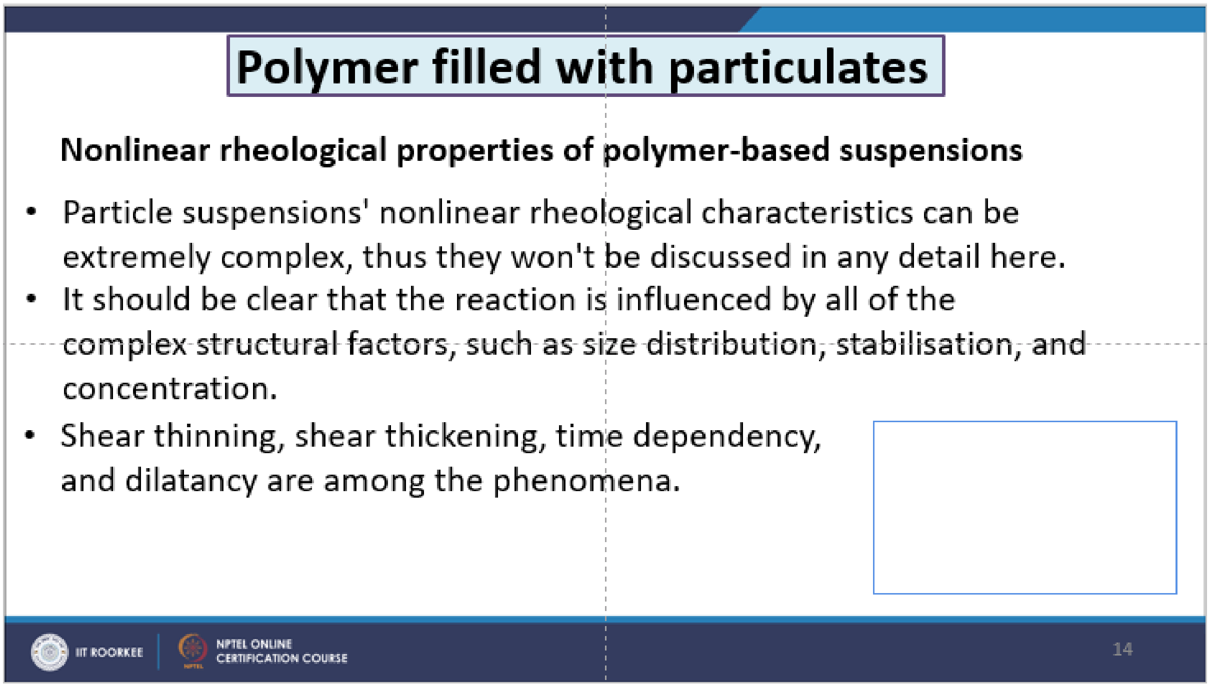
- There are numerous empirical and semi-theoretical connections that cover most of the concentration range.
- Table has examples. You should take note of the fact that a number of these equations diverge at the upper limit of $\emptyset_{max} < 1$ for the volume fraction of solid particles in the suspension.
- Although it can be inferred from the particle concentration in the sediment at the bottom of a well-settled dispersion, in practice, this bound can be a little tricky.
- For spheres that are uniform in size and randomly packed, the answer is $\emptyset_{max} \approx 0.64$.

although it can be inferred from the particle concentration in the sediment at the bottom of a well settled person. In practice, this bound can be a little tricky. For spheres that are uniform in size and randomly packed, the answer is phi maximum is almost equal to 0.64. By fitting the viscosity data at intermediate concentration, both k e and phi max are often extracted from these equations application.

The equation can be applied in this way to describe the viscosity of suspensions of slightly symmetrical particles. The issue of how to pack more particles into polymer is crucial or a particular concentration viscosity or to decrease it. Changing the particle size distribution so that small particles are distributed into voids is the simplest method left behind by the big ones. Let us talk about the non-rheological properties of the polymer-based suspension. The particle suspensions non-linear rheological characteristics can be extremely complex.



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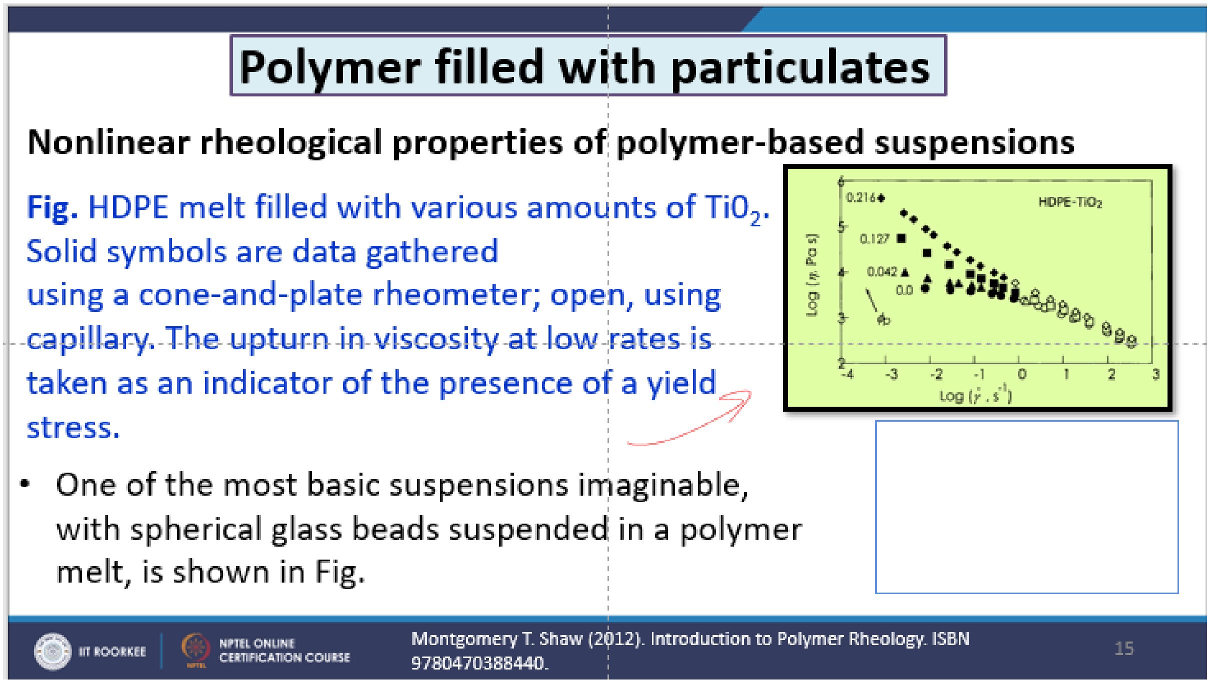
Nonlinear rheological properties of polymer-based suspensions

- Particle suspensions' nonlinear rheological characteristics can be extremely complex, thus they won't be discussed in any detail here.
- It should be clear that the reaction is influenced by all of the complex structural factors, such as size distribution, stabilisation, and concentration.
- Shear thinning, shear thickening, time dependency, and dilatancy are among the phenomena.

Thus, they do they will not be discussed in any detail. Now, it should be very clear in mind that the reaction and influenced by all of the complex structural factors like size distribution, stabilization and concentration. The shear thinning, shear thickening, time dependency and the dilatancy are among those phenomena. Now, in this particular figure, the HDPE melt filled with various amounts of titanium dioxide solids, most of the data are gathered. Now, using a cone and a plate rheometer open using capillary, the upturn in the viscosity at lower rate is taken as an indicator of the presence of the yield stress.



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Nonlinear rheological properties of polymer-based suspensions

Fig. HDPE melt filled with various amounts of TiO_2. Solid symbols are data gathered using a cone-and-plate rheometer; open, using capillary. The upturn in viscosity at low rates is taken as an indicator of the presence of a yield stress.

- One of the most basic suspensions imaginable, with spherical glass beads suspended in a polymer melt, is shown in Fig.

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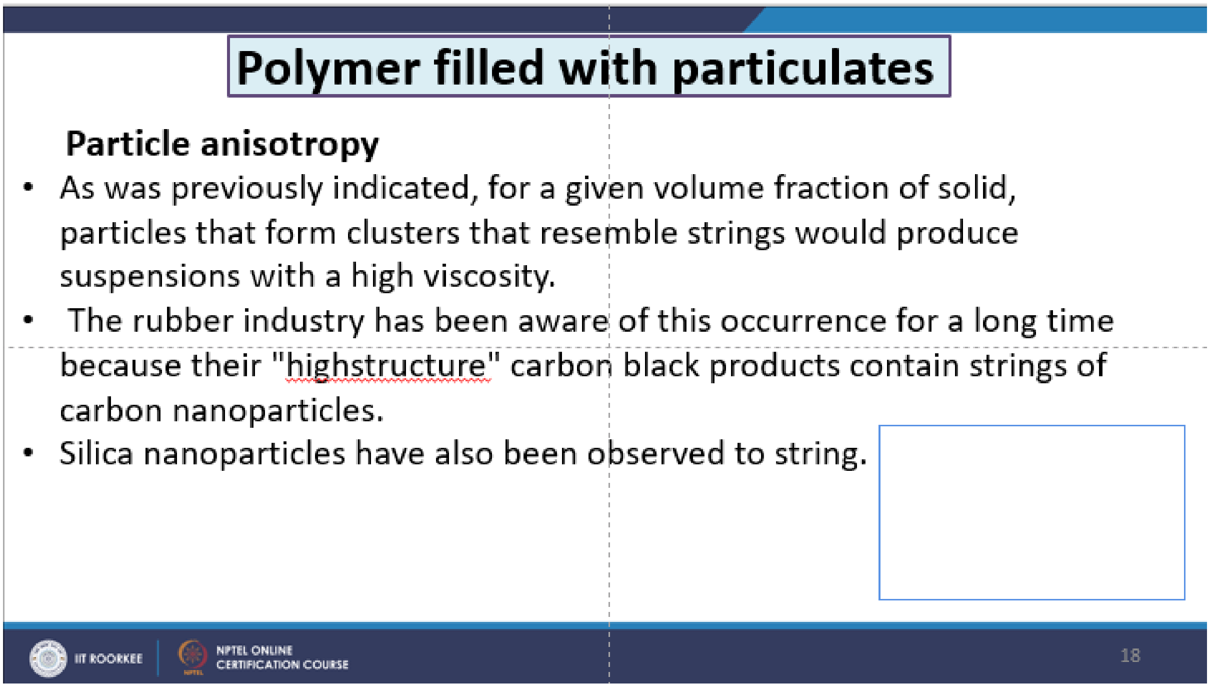
Now, one of the basic suspension imaginable with this spherical glass beads suspended in a polymer melt as per this particular figure. If one can recall that the power law exponent ranges from 1 for a Newtonian fluid to 0 for a material that is extremely thin under shear. The data in this particular figure does imply that adding particles make the suspension more pseudo plastic. The presence of higher than average shear rate between the particles and the particle propensity to the organize into the layer under the study shearing, they are the two-potential explanation for this particular aspect. But one need to exercise very cautiously.

The development of the yield at a relatively low volume fraction or filler is a frequent finding a particle-filled polymer solution and melts. As per this figure, where the sample is melting of high density polyethylene containing titanium dioxide. Let us talk about the particle anisotropy. Now, for a given volume fraction of solid particles that form cluster that resemble strings would produce suspension with a high viscosity. The rubber industry has been aware about this particular occurrence for a long time because of their high structure carbon black products contain string of carbon nanoparticles.



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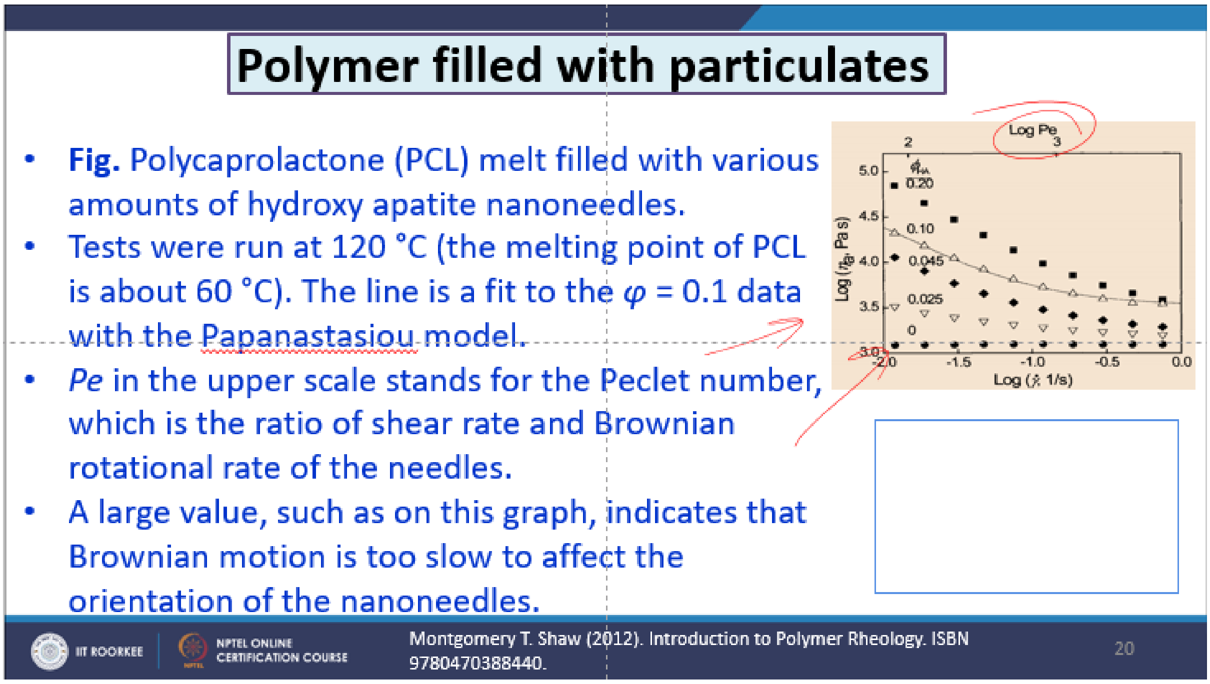
Particle anisotropy

- As was previously indicated, for a given volume fraction of solid, particles that form clusters that resemble strings would produce suspensions with a high viscosity.
- The rubber industry has been aware of this occurrence for a long time because their "highstructure" carbon black products contain strings of carbon nanoparticles.
- Silica nanoparticles have also been observed to string.

Silica nanoparticles have also been observed to string. Why is it so? First of all, in the absence of a strong long-range repulsive force, the high specific values of interfacial energy of small particle suspension particularly guarantee that the particle will aggregate. The reason a string form instead of a clump is related to the end particles extremely potent localized axially directed attraction to unattached particles. Now, let us take the example like polycaprolactone melt filled with the various amount of hydroxyapatite nanoneedles. Now, these tests were conducted at 120 degree Celsius at melting point of PCL is about 60 degree Celsius and the line is to fit the meshai of is equal to 0.



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- **Fig.** Polycaprolactone (PCL) melt filled with various amounts of hydroxy apatite nanoneedles.
- Tests were run at 120 °C (the melting point of PCL is about 60 °C). The line is a fit to the $\varphi = 0.1$ data with the Papanastasiou model.
- *Pe* in the upper scale stands for the Peclet number, which is the ratio of shear rate and Brownian rotational rate of the needles.
- A large value, such as on this graph, indicates that Brownian motion is too slow to affect the orientation of the nanoneedles.

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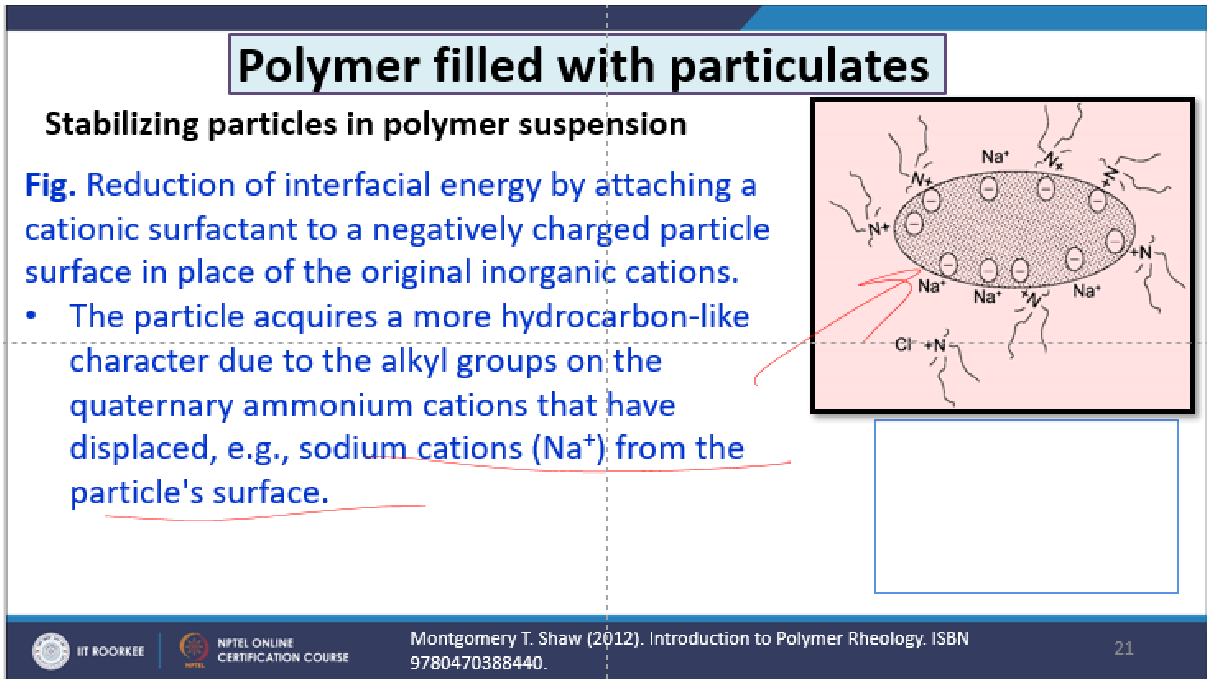
1 data with the PEP and STU model. Now, PE, the PE is the upper scale stand for the Peclet number which is the ratio of the shear rate and Brownian rotation rate of the needles. A large value such as on this particular graph indicates that Brownian motion is too slow to affect the orientation of nanoneedles. Now, if we talk about the stabilizing particles in the polymer suspension, the reduction of interfacial energy by attaching a cationic surfactant to a negatively charged particle surface in place of original inorganic cations. The particle acquires a more hydrocarbon like character due to the alkyl group on the quaternary ammonium cation that have displaced the sodium cation from the particle surface.



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Stabilizing particles in polymer suspension

Fig. Reduction of interfacial energy by attaching a cationic surfactant to a negatively charged particle surface in place of the original inorganic cations.

- The particle acquires a more hydrocarbon-like character due to the alkyl groups on the quaternary ammonium cations that have displaced, e.g., sodium cations (Na^+) from the particle's surface.

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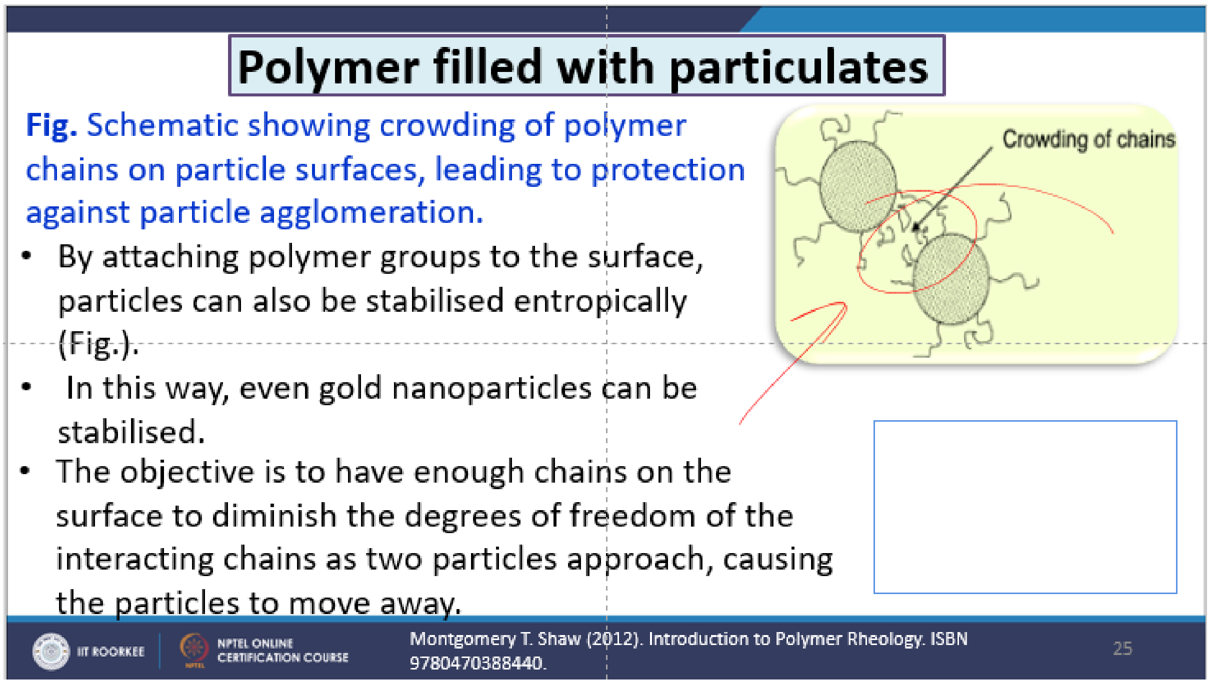
Now, agglomeration this can be avoided, not really, at least not without also changing the matrix of the property. And that is why the particle surface is significant as in the interfacial energies to start the typical method to add the surfactant which results in creation of inverse emulsion of a polar particle in a continuous organic matrix the particle. The surfactant can be useful, but they must have a low solubility in organic matrix and hydrophilic had with the low charge, otherwise it is likely that they will interact electrostatically negatively. In the matrix non, ionic surfactant is probably excessively soluble, a quaternary ammonium cationic surfactant replaces the cation on a negatively charged particle surface as a suitable compromise. Two of the four alkyl groups they are typically shorter and two are bulkier.

Grafting alkyl substitute silanes onto the neutral particle surface is replacement of for ion substitution. Now, this works well with some particles like glass or silica, but not so well with others. A water-resistant interface is a significant advantage of silane treatment and if not the composites mechanical quantities or qualities in the damp application may dramatically decrease and that is undesirable. This is the schematic diagram showing the crowding of polymer chain on particle surface leading to protection against particle agglomeration. So, if you attach a polymer group to the surface particles, this can also be stabilised entropically.



Polymer filled with particulates

Fig. Schematic showing crowding of polymer chains on particle surfaces, leading to protection against particle agglomeration.

- By attaching polymer groups to the surface, particles can also be stabilised entropically (Fig.).
- In this way, even gold nanoparticles can be stabilised.
- The objective is to have enough chains on the surface to diminish the degrees of freedom of the interacting chains as two particles approach, causing the particles to move away.

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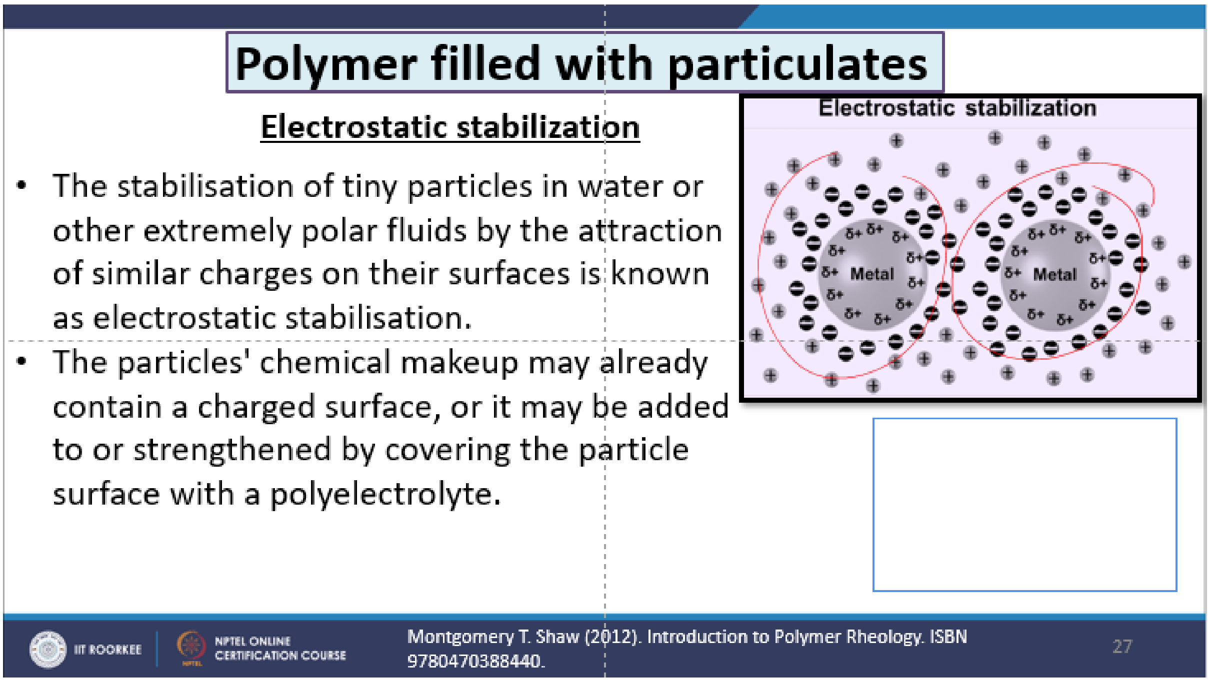
In this way even, gold nanoparticles can be stabilised. The objective is to have enough chains on the surface to diminish the degree of freedom of the interacting chain as two particles approach causing the particle to move away. Now, if the chains are lengthened as the particle they are separated, this works well. Now, this suggests that the chains on the surface are miscible with the matrix which may be a challenging criterion to satisfy. Otherwise, the particles will bunch together and the suspension would behave as an incompatible polymer blend.



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Electrostatic stabilization

- The stabilisation of tiny particles in water or other extremely polar fluids by the attraction of similar charges on their surfaces is known as electrostatic stabilisation.
- The particles' chemical makeup may already contain a charged surface, or it may be added to or strengthened by covering the particle surface with a polyelectrolyte.

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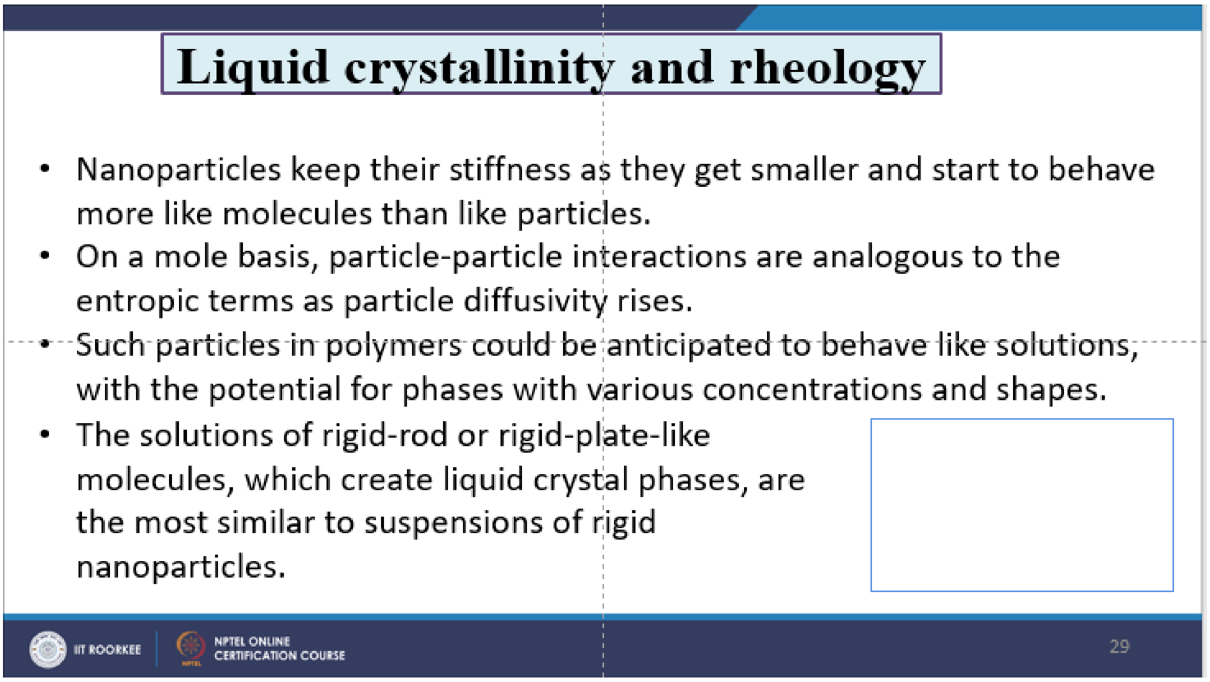
Let us talk about the electrostatic stabilisation. The stabilisation of a tiny particles in water or other extremely polar fluids by attraction of a similar charges on their surfaces is known as electrostatic stabilisation is can be represented by this particular figure. Now, the particles chemical makeup may already contain a charged surface or it may be added to be strengthened by covering the particle surface with a polyelectrolyte. The favourite neutralised poly acrylic, this may be causing a surface to become extremely anionic if they adhere to the particle surface and they are subjected to high pH solution. Of course, there are an equal number of cations to on contract to the negative charges on the carboxylate group but in water these cations will have a floating around and interacting with the water's anion.

A net negative particle charge is the outcome in the essence of the particle is a big and highly charged anion. Let us talk about the liquid crystallinity and rheology. Nanoparticles keep their stiffness as they get smaller and start to behave more like molecules than like particles. On a more basis particle-particle interactions are analogous to the entropic terms as particle diffusivity rises. Such particles in polymers could be anticipated to behave like solution with potential for phases with various concentration and shapes.



Liquid crystallinity and rheology

- Nanoparticles keep their stiffness as they get smaller and start to behave more like molecules than like particles.
- On a mole basis, particle-particle interactions are analogous to the entropic terms as particle diffusivity rises.
- Such particles in polymers could be anticipated to behave like solutions, with the potential for phases with various concentrations and shapes.
- The solutions of rigid-rod or rigid-plate-like molecules, which create liquid crystal phases, are the most similar to suspensions of rigid nanoparticles.

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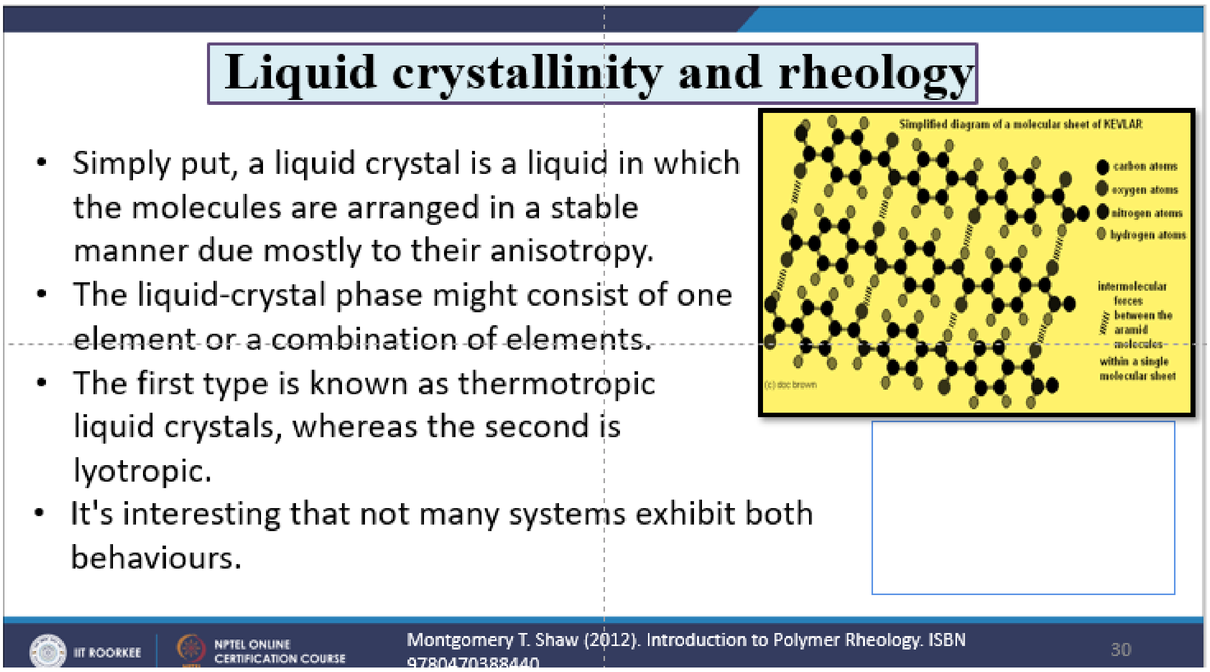
The solution of rigid rod or rigid plate like molecules which create liquid crystal phases are most similar to suspension of rigid nanoparticles. Simply put a liquid crystal is a liquid in which the molecules are arranged in a stable manner due mostly to their anisotropic. The liquid crystal phase might consist of one element or combination of elements. The first type is known as thermotropic liquid crystal whereas the second is lyotropic. It is interesting that not many systems exhibit both behaviours.



Liquid crystallinity and rheology

- Simply put, a liquid crystal is a liquid in which the molecules are arranged in a stable manner due mostly to their anisotropy.
- The liquid-crystal phase might consist of one element or a combination of elements.
- The first type is known as thermotropic liquid crystals, whereas the second is lyotropic.
- It's interesting that not many systems exhibit both behaviours.

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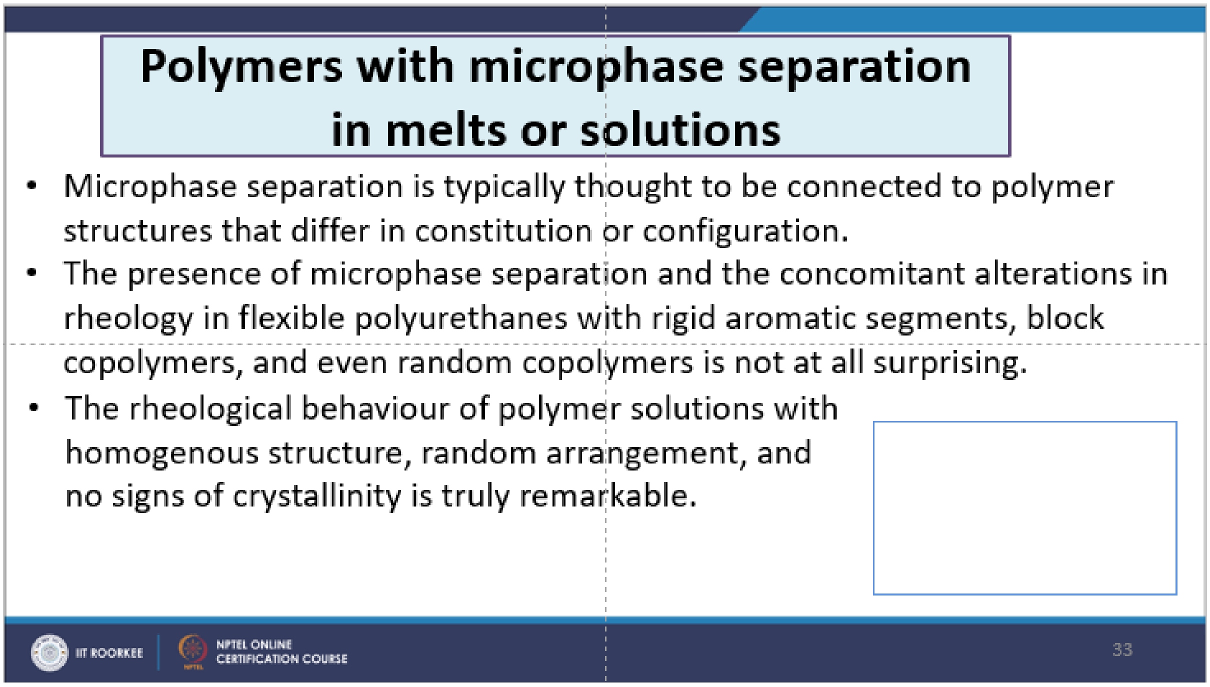
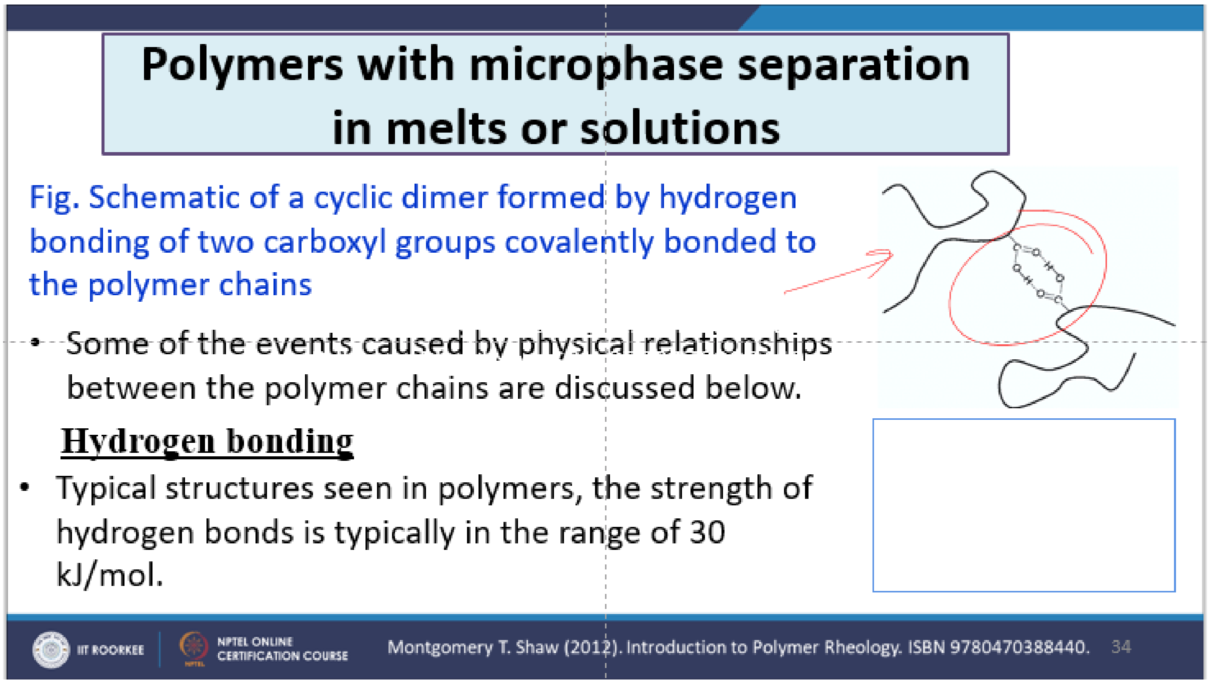
Additionally, the rod-shaped polymers molecule this can generate liquid crystal solution with extremely intricate rheological characteristics. Despite its hard-helical shape poly benzyl glutamate is commonly studied system when it is dissolved in one of many appropriate solvents. The larger benzyl group contributes to good solubility in a variety of a typical polymer solvents. But Kevlar an aromatic polyamide derived from the terephthalic acid really the acid chloride and 1,4-phenylene diamine may be the most commonly used lyotropic liquid crystal LCP and to break up the normal intermolecular hydrogen bond between adjacent chains, the Kevlar needs a strongly protic solvent such as sulphuric acid. Now, polymers with the micro phase separation in melts or solution the micro phase separation is typically thought to be connected to polymer structures that differ in constitution or configuration.



Polymers with microphase separation in melts or solutions

- Microphase separation is typically thought to be connected to polymer structures that differ in constitution or configuration.
- The presence of microphase separation and the concomitant alterations in rheology in flexible polyurethanes with rigid aromatic segments, block copolymers, and even random copolymers is not at all surprising.
- The rheological behaviour of polymer solutions with homogenous structure, random arrangement, and no signs of crystallinity is truly remarkable.

The presence of micro phase separation and alteration in the rheology is flexible polyurethanes with the rigid aromatic segment block copolymer and even random copolymer is not at all surprising. The rheological behaviour of polymer solution with homogeneous structure random arrangements and no sign of crystallinity is truly remarkable. Now, this particular figure represents a schematic of the cyclic dimer by hydrogen bonding of 2 carboxylic group covalently bonded to polymer chains. Some of the events caused by the physical relationship between the polymer chains they are we are going to discuss that particular thing one is the hydrogen bonding the typical structure seen in the polymer the strength of hydrogen bond is typically in the range of 30 kilojoule per mole. Usually, RT is approximately 4 kilojoule per mole at 200 degree Celsius as a result we can see the hydrogen bond can easily survive in the melt of many polymer while being weaker than a covalent bond.



Polymers with microphase separation in melts or solutions

Fig. Schematic of a cyclic dimer formed by hydrogen bonding of two carboxyl groups covalently bonded to the polymer chains

- Some of the events caused by physical relationships between the polymer chains are discussed below.

Hydrogen bonding

- Typical structures seen in polymers, the strength of hydrogen bonds is typically in the range of 30 kJ/mol.

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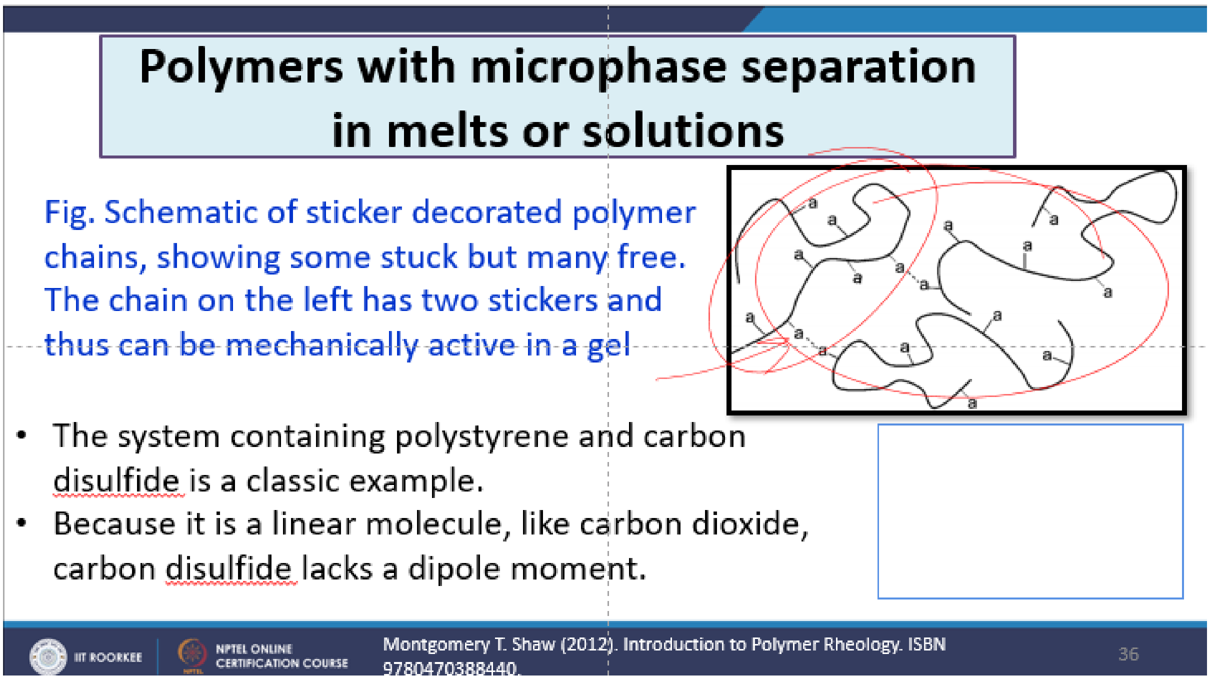
Now, the physical cross-linking, there are several rheological phenomena that involve even lesser secondary forces. The gelation of polymer solution containing low polarity linear polymer is most striking. Now, this particular figure represents the schematic representation of a sticker decorated polymer chain showing some mistake, but may free the chain on the left this one has 2 stickers and thus can be mechanically active in a gel. The system containing polystyrene and a carbon disulphide is a classic example because it is a linear molecule like carbon dioxide the carbon disulphide lacks a dipole moment while the phenyl group and the modest segmental dipole moment of the polystyrene may interact. It seems unlikely that these weak interactions will result in a sudden shift in rheology.



Polymers with microphase separation in melts or solutions

Fig. Schematic of sticker decorated polymer chains, showing some stuck but many free. The chain on the left has two stickers and thus can be mechanically active in a gel

- The system containing polystyrene and carbon disulfide is a classic example.
- Because it is a linear molecule, like carbon dioxide, carbon disulfide lacks a dipole moment.

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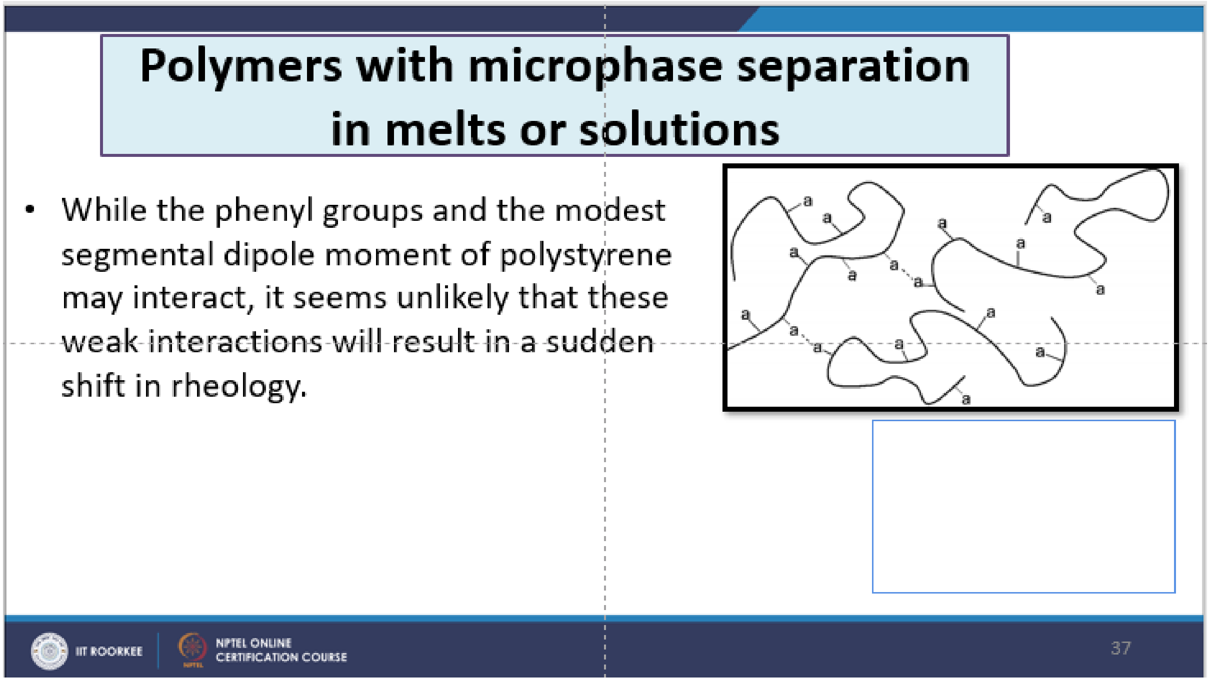
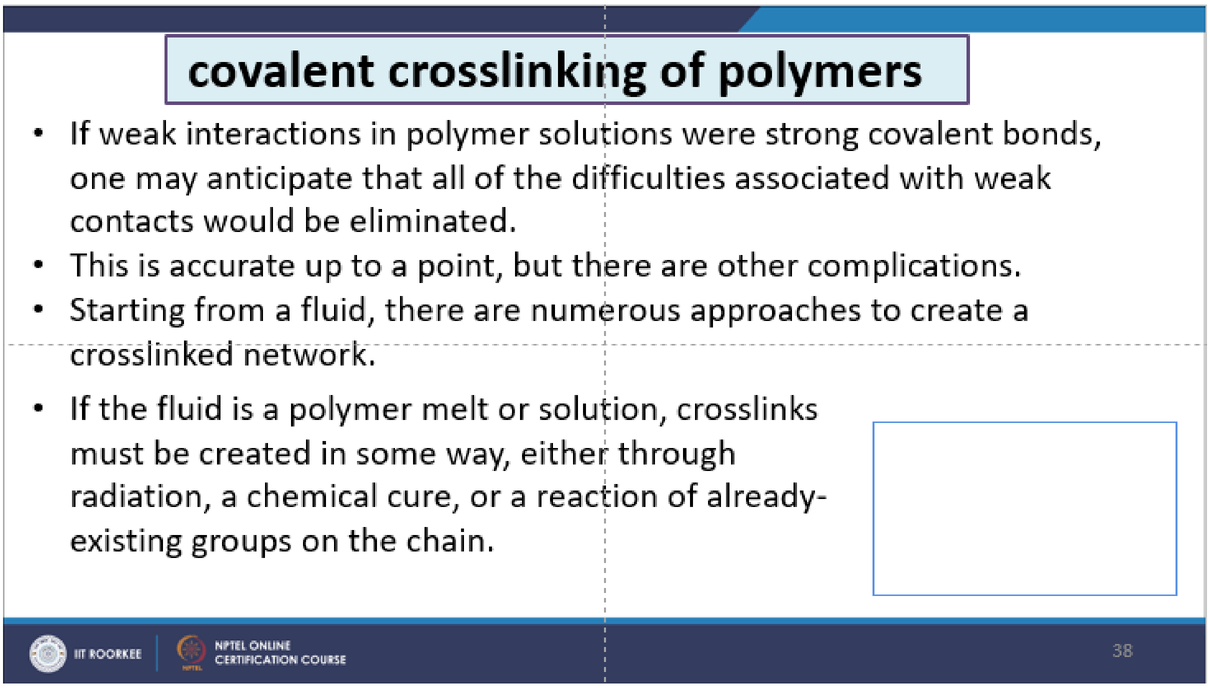
Let us talk about the covalent cross-linking of polymer. If weak interactions in polymer solution there were strong covalent bonds one may anticipate that all of the difficulties associated with weak contacts would be eliminated. Now, this is accurate up to a point, but there are other complications starting from fluid There are numerous approaches to create a cross-linked network. So, if the fluid is a polymer melt or a solution cross-links must be created in some way either through radiation or a chemical curing or with the help of a reaction of already existing group over the chain. Now, there are numerous examples when a polymer begins as an oligomer or a monomer, it is polymerized and simultaneously cross-linked to create a gel.



Polymers with microphase separation in melts or solutions

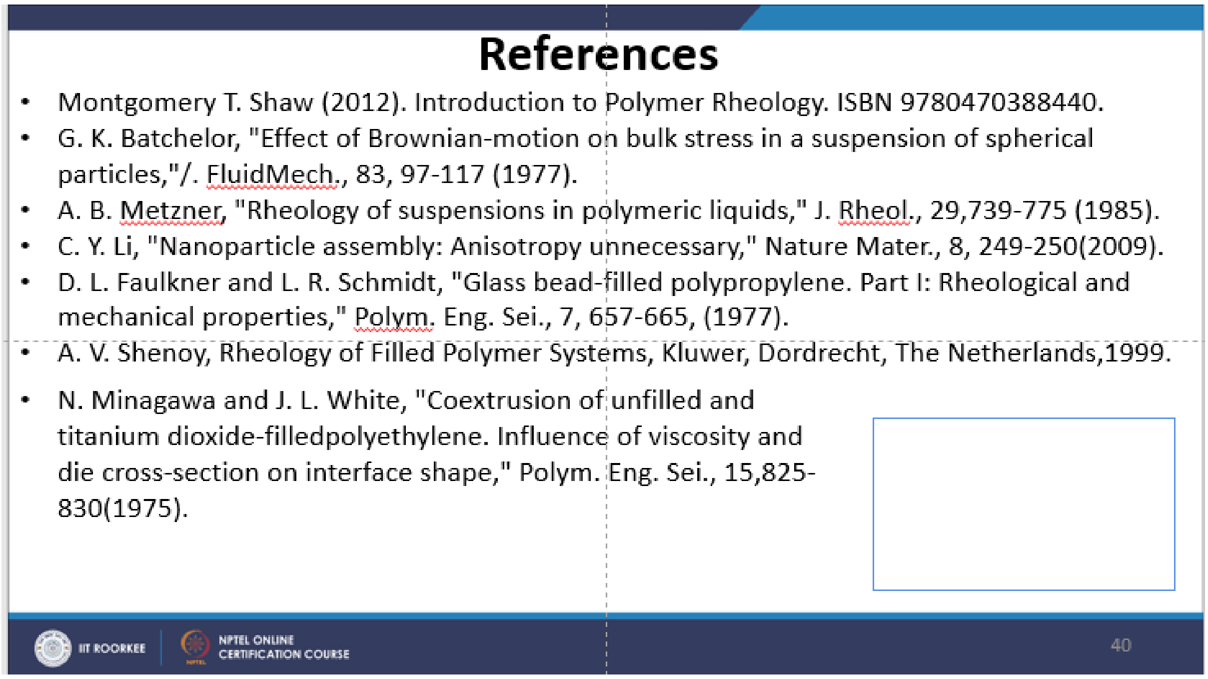
- While the phenyl groups and the modest segmental dipole moment of polystyrene may interact, it seems unlikely that these weak interactions will result in a sudden shift in rheology.



covalent crosslinking of polymers

- If weak interactions in polymer solutions were strong covalent bonds, one may anticipate that all of the difficulties associated with weak contacts would be eliminated.
- This is accurate up to a point, but there are other complications.
- Starting from a fluid, there are numerous approaches to create a crosslinked network.
- If the fluid is a polymer melt or solution, crosslinks must be created in some way, either through radiation, a chemical cure, or a reaction of already-existing groups on the chain.

Polyurethane, silicones, epoxies, thermoset polymers, bismaleimides, polyimides they are the couple of examples who can represent like this. So, dear friends in this particular segment we discussed about the rheological behaviour, we discussed about various kind of the bonding among the polymeric system and especially of this particular affinity. So, we discussed all those things and what is the impact of this one, how this can be covalently bonded or hydrogen bonded play a role all these things we have discussed in this particular segment.



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And for your convenience we have enlisted these 7 references which you can utilize if you need further studies. Thank you very much.