Polymer Reaction Engineering
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Lecture - 09
Control on Polymer Synthesis-II

Welcome to the second lecture of control methodology on the polymer synthesis under the head of polymer reaction engineering. Now, in the last lecture, we studied about the importance of various controlled methodologies for the polymer synthesis, we discuss various parameters attached to those polymer syntheses. And we discussed about the importance of those parameters for the polymer synthesis like molecular weight distribution.

Last brief discussion about the glass transition temperature, different type of chemical, mechanical and thermal properties attributed to these polymeric systems and their importance towards the end properties of those polymer in question. We had a discussion about the bulk polymerization and different type of control parameters for the bulk polymerization or the mass polymerization. In this lecture, we will start with the solution polymerization.

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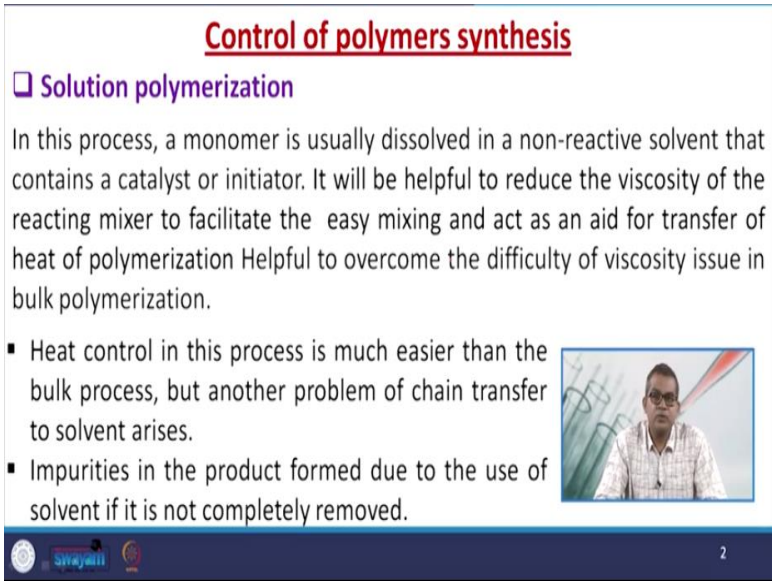

Now, in the solution polymerization, usually monomer dissolved in a non reactive solvent. Usually, that contains catalyst or initiator, if you again I am repeating that initiation, propagation and termination. So, it will be helpful to reduce the viscosity of reacting mass. Thereby, this facilitates the easy mixing and sometimes acting as an aid for the transfer of heat of polymerization.

Now, it is very helpful for to overcome the difficulty of viscosity issues as we faced in the bulk polymerization. Now, if you recall the bulk polymerization, discussed 2 things one is the problem of viscosity and second one was the problem of exothermicity. So, sometimes this solution polymerization tool it offers a small quantity of solution to that particular difficulties.

Usually, the heat control in this solution polymerization process is bit easier compared to the bulk polymerization. But another problem is attributed to this solution polymerization is that a chain transfer to the solvent. Now, this chain transfer to the solvent is again creating sometimes problem for the subsequent polymerization step. Now, second issue is that impurities in the product formed due to the use of solvent.

And if it is not completely removed, then it may create a problem for the further processing. So, it is because solvent sometimes it may unentangle the chains. And if you are looking for some kind of stiffness or toughness in the polymer, then it may create a problem, because sometimes it may offer the flexibility to the polymeric system. Another approach is the heterogeneous polymerization process.

Now, it is used to control the thermal and viscosity problem, which we saw in the bulk polymerization. Now, there are three different type of heterogeneous polymerization process, one is the suspension polymerization, second one is emulsion polymerization and third one is the precipitation polymerization. So, I am giving this the brief impetus towards the precipitation process, usually it is a homogeneous process.

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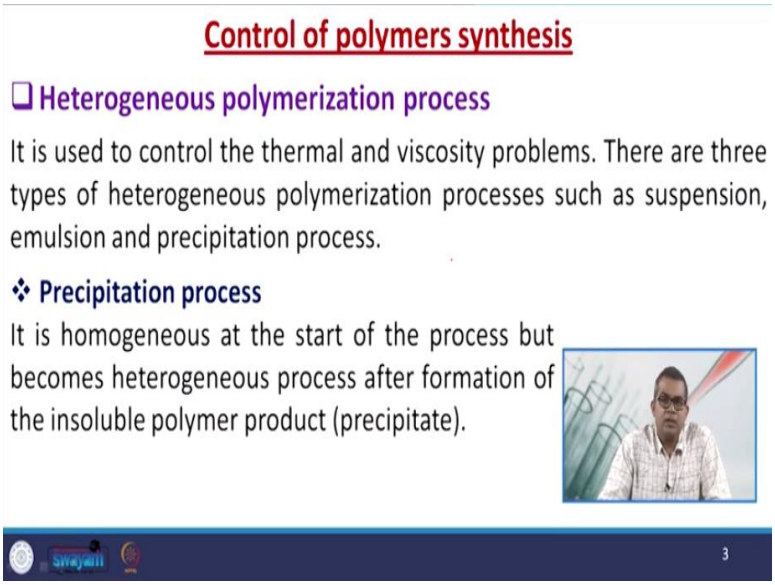

Now, at the start of the process, sometimes, later on it becomes the heterogeneous after the formation of insoluble polymer products precipitate. If you recall that the interfacial polymerization, we are sometimes reactants they hinder the further propagation of polymerization process. So, it may create some sort of same type of scenario in the polymerization process.

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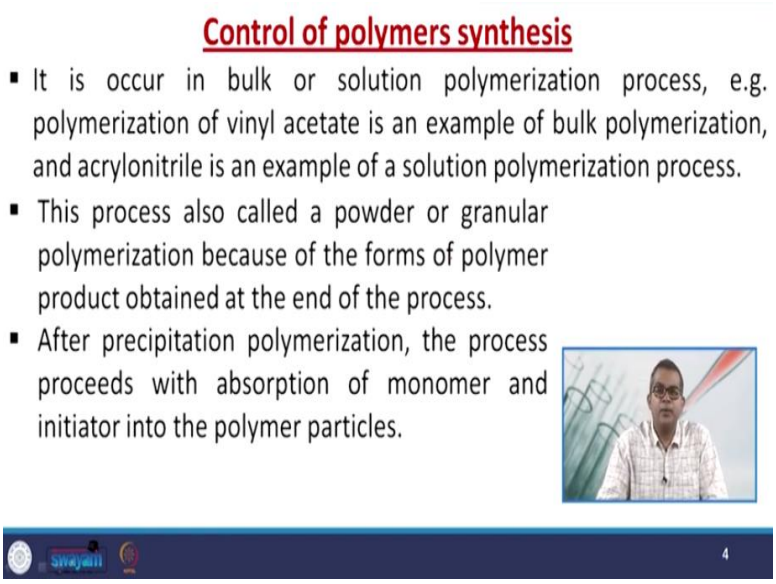

Now, it is occurred usually in bulk or solution polymerization process, that is, polymerization of sometimes you may take the example of polymerization of vinyl acetate for example. It is usually the bulk polymerization and acrylonitrile is used as a solvent on the solution polymerization process. Now, this process is also called a powder or a granular polymerization because of the formation of the polymer product obtained at the end of the process.

So, after precipitation polymerization the process proceeds with absorption of a monomer and initiated into the polymer particles. Another is that the suspension polymerization process usually it is carried out in the stirred batch reactor so that the viscosity and proper dissipation of heat or uniform distribution of the heat can be carried out.

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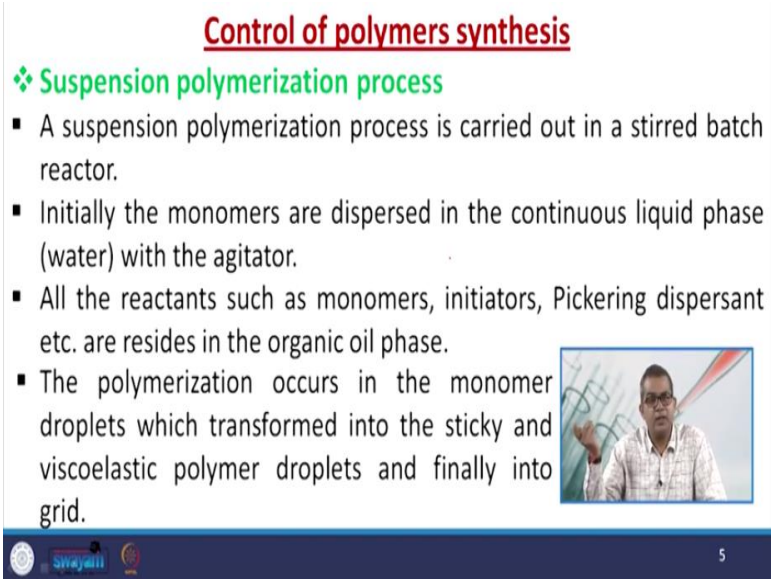

Initially the monomers are dispersed in the continuous liquid phase, sometimes it is water or sometimes it may be another solvent with an agitator. All the reactants such as monomer, initiator, sometimes Pickering dispersant etcetera, they are residing in the organic oil phase. The polymerization usually occurs in the monomer droplets which transformed into the sticky and viscoelastic polymer droplets and finally, formed a grid like a structure.

So, they just try some sort of the **(()) (06:16)** monomer this initiates the things and then all kind of monomer they try to stick in that particular monomer. Now, this is the suspension polymerization reactor you can see here.

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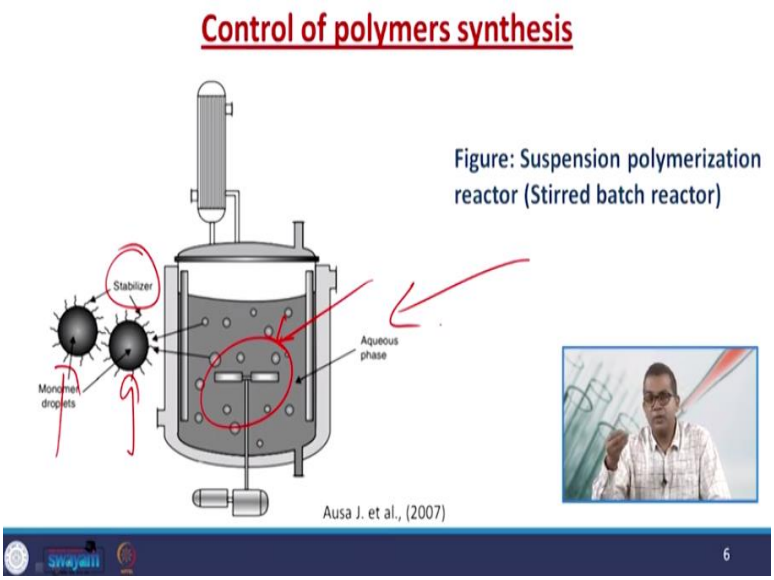

This is the aqueous phase and these are the monomer droplets and with the help of certain stabilizer and stirrer. So, this is the stereotype of a batch reactor and this type of approach is very common for the synthesis of polymeric beads. And these polymeric beads are usually the crosslink polystyrene beads. They are very good support for the catalytic or some they are used for the different type of supports for the ion exchangers.

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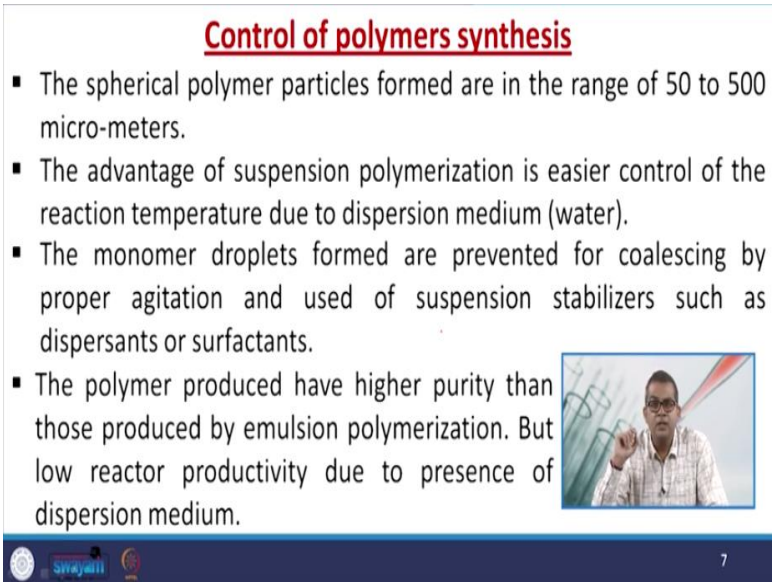

So, when you see this type of polymeric beads, they are spherical in nature and usually they are in the range of 50 to 500 micrometers. Now, usually it depends that how much surface area we require, how much porosity we require. Moreover, that in which system we are going to use it. Because the larger the particle size sometimes may adversely to the pressure system etcetera.

So, although it is having a very long range and there are various control methodologies are being used for synthesis of these kind of a spherical polymer particles, maybe the stirring speed, maybe the quantity of initiator, sometimes the particle formation, sometimes the porosity controllers. Now toluene sometimes is used as a porosity controller for this because ultimately when we are intended to use as an ion exchanger or support for ion exchanger or support for catalyst.

So, we are always looking for larger surface area, but sometimes if we use these kind of things excessively in that case, the polymer particles may become brittle and sometimes the regeneration or recyclability of these particular polymer particles are not at all feasible. So, they offer a very wide spectrum they offer a very good approach for the various kind of practical applications.

When we talk about the advantage of suspension polymerization, now, this particular polymerization process is easier to control with respect to the reaction temperature to the due to the dispersion medium that is water. So, water is universal you can say and particle size controller usually they dissolve in water. So, the monomer droplets formed, they are prevented by coalescing by proper agitation and use of suspension poly stabilizers such as sometime dispersant or surfactant.

See, if we do not use this agitation or if you do not use these kind of stabilizers, then there may be a chance that these polymer particles may form an agglomerate and they may form the lump. That particular lump may not be useful for any kind of a practical application. If you see the first line in this category that you are looking for specific type of polymer particles with the says 50 to 500 or more than this or less than this particular range.

So, the proper use of dispersant or surfactant that usually prevents the formation of lumping by this way, it creates a barrier in between these two droplets. So, the polymer produced they have a higher purity than those produced by any kind of emergent polymerization process. But lower reactor productivity due to the presence of any kind of dispersion media sometimes offer the disadvantage to this particular process.

Because of dispersion media again it carries significant volume within the reactor. So, this is some sort of deterrence in this particular approach. Now, sometimes the post treatment

because when you form the polymer particles so these post treatment usually includes the removal of all kinds of undesirable impurities such as suspending agents now before recycling.

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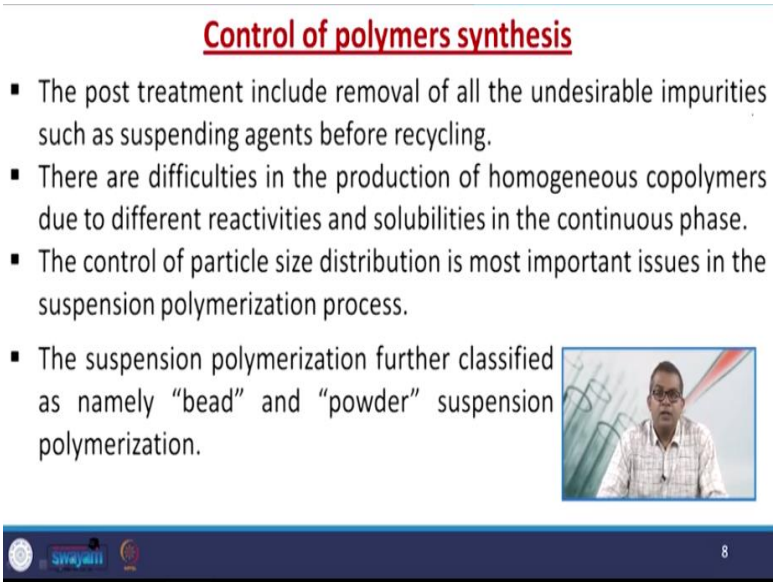

So, sometimes it is usually advisable to extract all kind of useful product from the post treatment methodology through post treatment methodology and then you recycle it. Now, the there are various difficulties in the production of some sort of homogeneous copolymers due to the different reactivities and solubilities in the continuous phase. Now, if you take the example of the suspension polymerization, water is the media.

In that case sometimes it creates a lot of problems with respect to the reactivities of different other reactive mass with respect to the water or some other solvent in question. The control of particle size distribution is very important as I discussed in the previous slide in this particular suspension polymerization process. Because, if you are having a very specific size requirement just take an example of your domestic RO system in which the different type of ion exchangers are being used.

They are having very specific size in nature, although they are having very larger surface area, so, that the reactive sides can be impregnated in the system. But, if you are having the larger size, sometimes it may create a problem with respect to the pressure, sometimes it may create a problem to the flow behavior. So, that is why there are certain components like polystyrene bead formation.

The gelatin is the particle size controller, and it is a very common particle size controller. So, small quantity in the concentration small quantity variation in the concentration of this deleting sometimes adversely affect the particle size distribution. So, that is why a critical particle size controller concentration is extremely essential in this kind of suspension polymerization process.

Now, the suspension polymerization they are further classified like beads or a powder suspension polymerization as per the requirement of your end product. Now, let us have a brief look about the bead or suspension polymerization.

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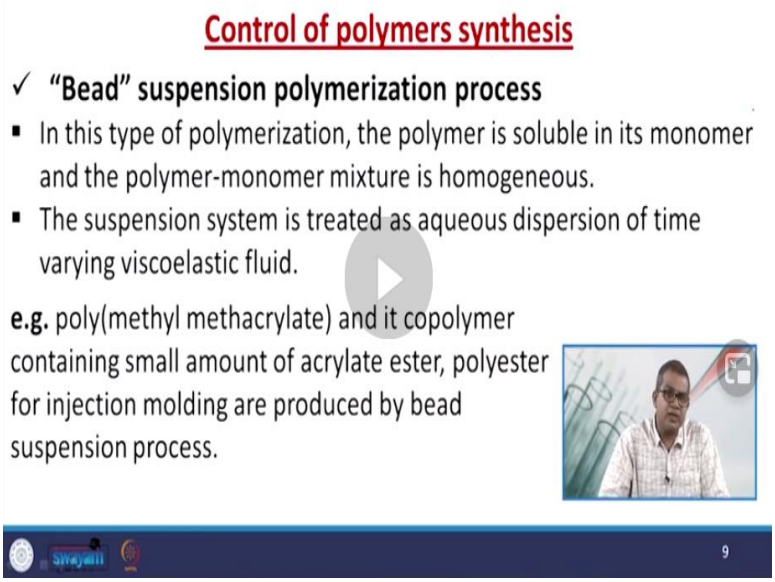

In this type of a polymerization process, usually the polymer is soluble in its monomer and the polymer monomer mixture is usually homogeneous. The suspension system is treated as aqueous dispersion of time varying viscoelastic fluid. One example is that poly methyl methacrylate and its copolymer they contain a small amount of acrylate ester, polyester for injection molding. They are produced by the bead suspension process.

Sometimes, if you go for any kind of injection molding or any kind of polymer process, you see that they are using the beads of either polyesters or different type of polymers. So, the these beads are usually they are with the help of suspension polymerization, you can have a look about these size of these beads.

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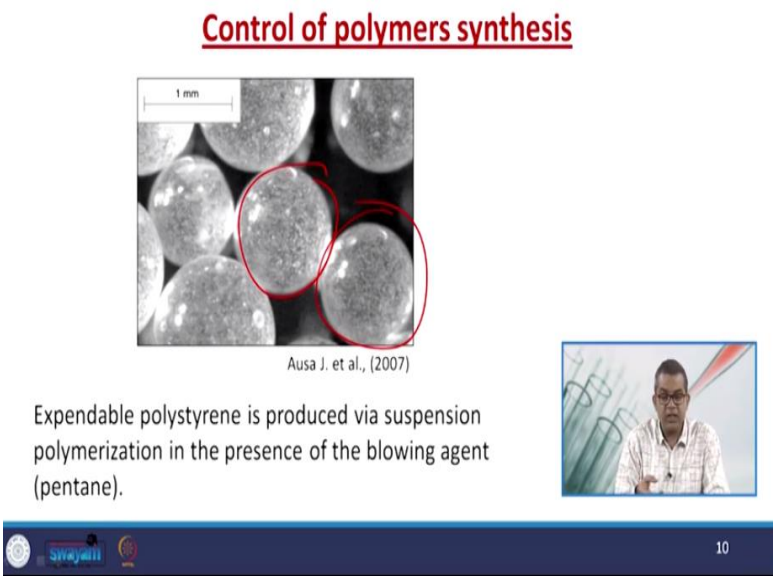

These are the expendable polystyrene beads being produced with the help of suspension polymerization in the presence of blowing agent. Now, here the blowing agent is being used as a painting. So, these beads are have offered a very good support for a different type of catalyst.

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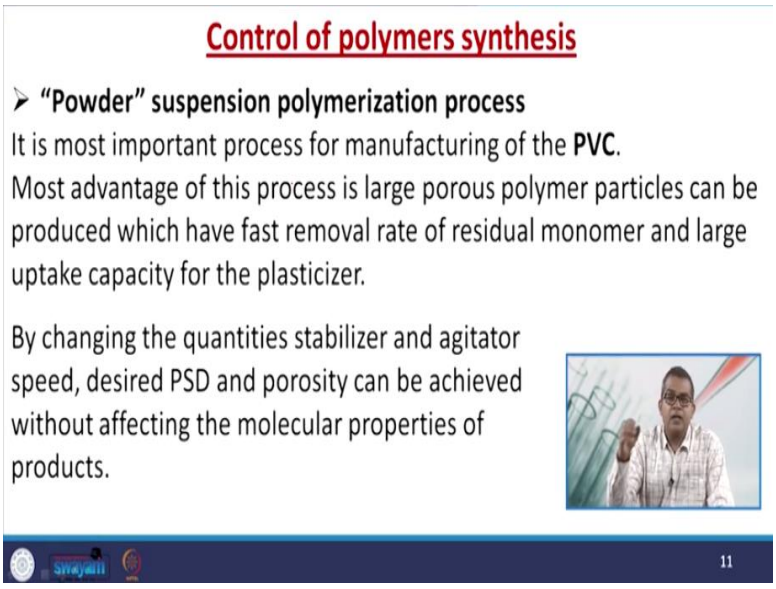

Another class is the powder suspension polymerization process. Now, it is one of the most important process for the manufacturing of polyvinyl chloride PVC. It is commonly available in the market. Now, the advantage of this process is the large porous polymer particles you can produced which have the faster removal rate of residual monomer and large uptake capacity for the plasticizer.

Now, sometimes by changing the quantities of stabilizers, you recall that stabilizer is again a very key factor of these polymerization process. So, if you change the quantity of a stablizer or you change the agitator speed, maybe on the higher side or maybe on the lower side. So, if you are having the higher side agitator speed, then you may get the fine particles. And if you are lower size, then the you can increase the particle size.

Ah then desired PSD the particle size distributors and the porosity you can be achieved without affecting the molecular properties of the product. So, you are having various variables for changing the size of the polymer particles without adversely affecting the **(()) (16:07)** molecular properties. So, one is that the chemical phenomena and other one is the physical phenomena.

Physical phenomena that means, in which shape you require your polymer, maybe in the bead form, maybe in the powder form, maybe in the some other form, but the molecular properties are similar. So, these parameters like the stabilizer, agitator speed, porosity controller, they are not changing the molecular properties, but simultaneously they may change the physical shape of your desired product.

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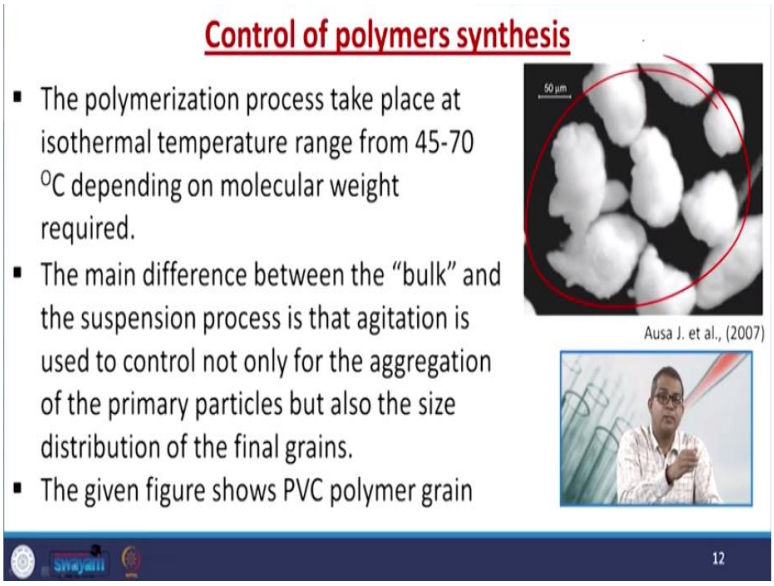

Now, polymerization process takes place usually in an isothermal temperature range of 45 to 70 degree Celsius depending upon how you are controlling the molecular weight and what is the specific requirement about your molecular weight required molecular weight. So, it all depends on these type of things. The main difference between the bulk and the suspension

process is that agitation is used to control not only for the aggregation of the primary particles, but also the size distribution of the final grains.

Now, here you can see this particular figure shows the PVC polymer grains. You can see the size if you compare with the polystyrene bead and this PVC polymer again you can see the difference in the size.

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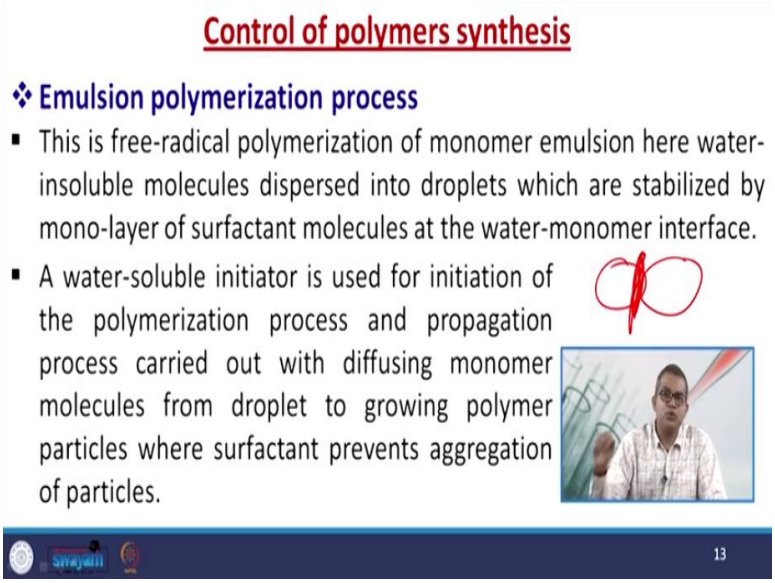

Another approach is the emulsion polymerization process. Now, this is referred as free radical polymerization of a monomer emulsion. Here, the water insoluble molecules are dispersed into the droplets, which are usually stabilized by mono layer of surfactant molecules at the water monomer interface. So, the interface the water and monomer interface play a very vital role.

So, usually a water-soluble initiator is used for initiation of the polymerization process and propagation process is carried out with diffusing monomer molecules from droplet to growing polymer particle where surfactant prevents the aggregation of the particle. So, surfactant usually offers the resistance of any kind of aggregation. So, it forms a thin film over the surface of the droplets.

So, that they can the they cannot accumulate each other so that you can control the particle size. So, this is again a very important aspect in addressing such kind of issue. Now, the particle formed they are mostly spherical in shape and having the morphology that affects the properties of the polymer.

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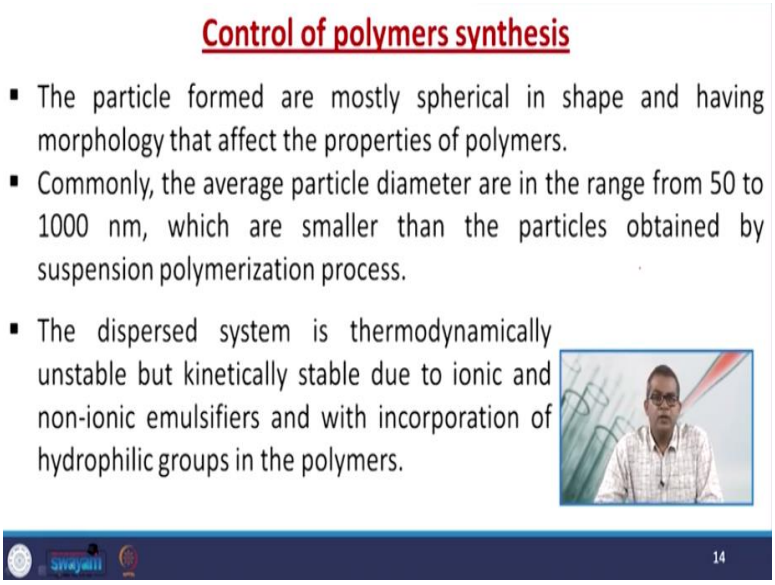

As I told you that the spherical size sometimes they of they are carrying significant property approach with respect to the end use of polymer. Now, commonly average particle diameter usually they are in the range from 50 to 1000 nanometer, which are smaller than the particle obtained by the suspension polymerization process. So, you are having a very good spectrum or you are having a very good choice through which you can adopt if you are looking for smaller particle size go for this one.

Now the dispersed system usable is thermodynamically unstable but kinetically stable due to the ionic and non-ionic emulsifiers those who are present in that particular system. Now sometimes of sometimes incorporation of hydrophilic groups in the polymer mass or a reaction mass plays a very vital role for deciding these properties.

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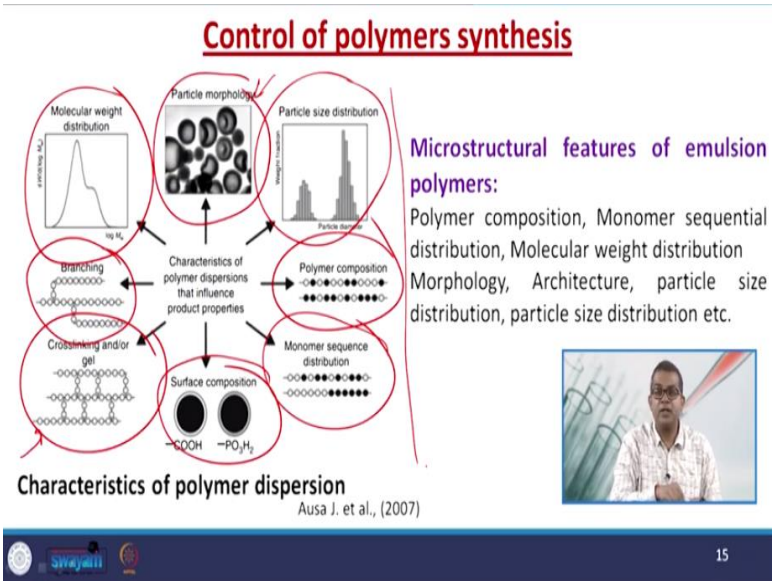

Now, here you can see the microstructure feature of various emulsion polymerization, now, the polymer composition monomers sequential distribution, molecular weight distribution, morphology, architecture of different polymeric chain size distribution, particle size distribution etcetera. Now, you see here different type of characteristics if you see that here, we discussed about the molecular weight distribution.

Here you see the particle morphology because not only the synthesis of polymer particle is crucial, but because the size and other things they play a very vital role for the further processability of those polymer particles. So, the polymer morphology is again a vital role and this again become more and more critical.

When you use these polymer particles for some specific use like catalytic support, like support for various kind of ion exchangers or development on any kind of a functional group over these over the surface of these polymer particles, particle or surface morphology plays a very vital role. Then the particle size distribution you see that in the previous slides, we discuss about the different type of a particle size.

Like suppose if you are using polystyrene diagonal benzene beads they may offer they may be required to have a particle size of say 16 to 25 mesh size. In that case, because they are having this specific use and if you are having the larger size, then definitely it may create a problem in the future use. Similarly, you are always looking for that branching maybe the cross linking or linear or a branch changed like polystyrene diagonal benzene.

I gave you the example they are cross linked polymer. So, diagonal benzene acts as a cross linking agent for that polymer beads. Then the surface composition now surface composition usually attributed to the functional group attached to those polymer particles. Now, if you are using it for ion exchanger definitely, we are using that particular ion exchanger to the waste stream wastewater stream then definitely you are looking for some specific functional group attached to that particular polymer particle.

Now, the role of this specific functional group is again twofold one is that it should offer the good exchange of those ions, and moreover, it should not get dissociated over the period of time from the surface of that particular polymer. So, it must have a proper bonding with the polymeric surface. So, there are various tools available as on date through which you can offer this type of thing.

Then you are always looking for the polymer composition that what kind of a polymer composition, polyester, polyethylene etcetera Then, you are always looking for the monomers sequencing that what kind of may be random may be regular etcetera. So, this these approaches are extremely important for determining the fate of any kind of emulsion polymerization.

Especially, when you talk about the branch, if you talk about the linear one, then the architecture of those chains also plays a very vital role. See, I gave you an example of this particular pen and you try to heat then this acquires the rubbery structure that depends on the architecture. So, that is why this particular approach is extremely useful, while deciding the fate of those polymers.

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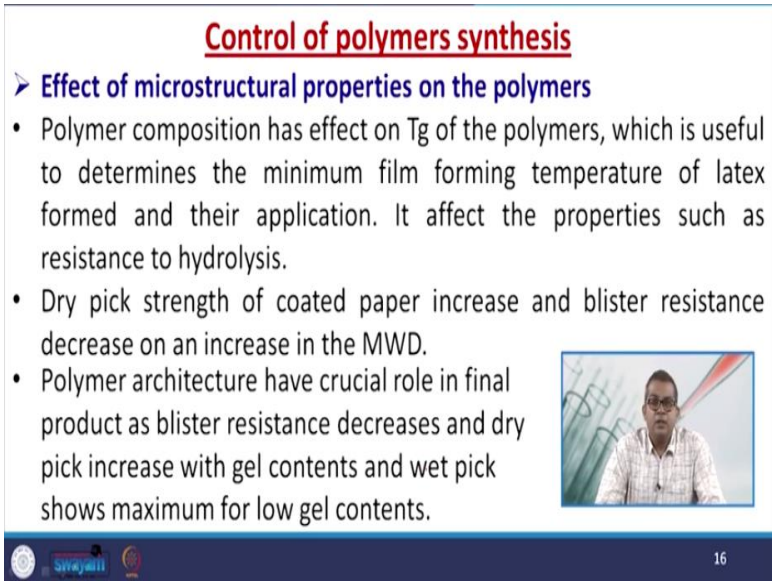

Now, there are certain effects you would like to address of this micro structural properties on the polymer. The polymer composition has effect on glass transition of polymers, which is useful to determine the minimum film forming temperature of say latex formation and their application. Now, it usually affects the properties sometimes the resistance to the hydrolysis etcetera. So, you are having very specific use of these type of polymers.

Now, sometimes the dry pick strength of coated paper is increased and the blister resistance of decrease on the increase of a molecular weight distribution. Again, this plays a very vital role. So, these are the some of the specific properties you need to address. Now, polymer architecture they have a very crucial role in the final product as sometimes the blister resistance decreases, the dry pick increases and the gel content and the wet pickoff sometimes they show the maximum for the low gel content etcetera.

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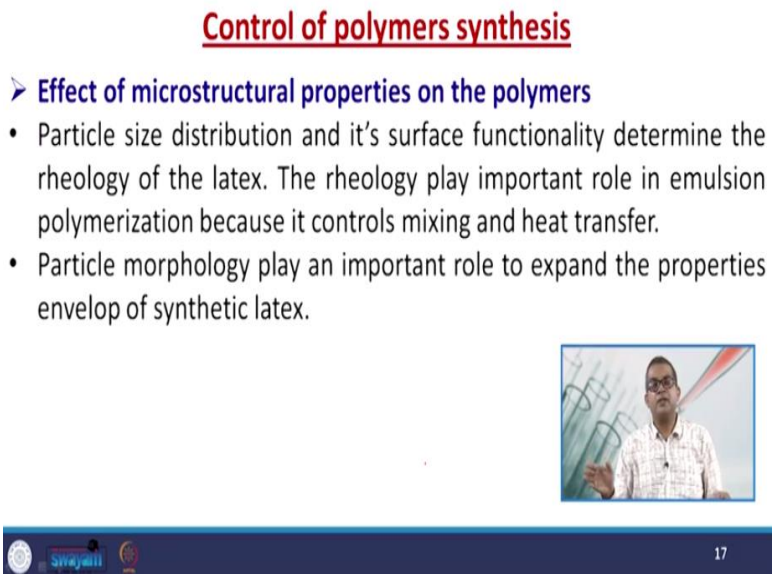

So, the objective of this particular thing is that you can further improvise the properties of those polymer you synthesize in due course of time sometimes the particle size distribution and its surface functionality, if you recall that we discussed about the surface functionality, because, if you are use with an example of ion exchanger. So, its surface functionality usually determines the rheology of any kind of a product.

Now, this rheology plays a very vital role in emulsion polymerization because it controls mixing and heat transfer. More and more viscous in nature then definitely it may create a problem with the mixing and when there is a problem in the mixture then there may be a chance that there the mixture will become so viscous then sometimes your mixer will fail, sometimes your impeller or agitator may fail over the period of time.

And if it fails then proper heat transfer will take place. So, this particular thing is very crucial. Now, particle morphology, they play a very vital role to expand the properties envelop of any kind of synthetic polymer or maybe like in the latex etcetera. Now, let us have about a brief discussion about the main product of the emulsion polymerization as a concluding remark.

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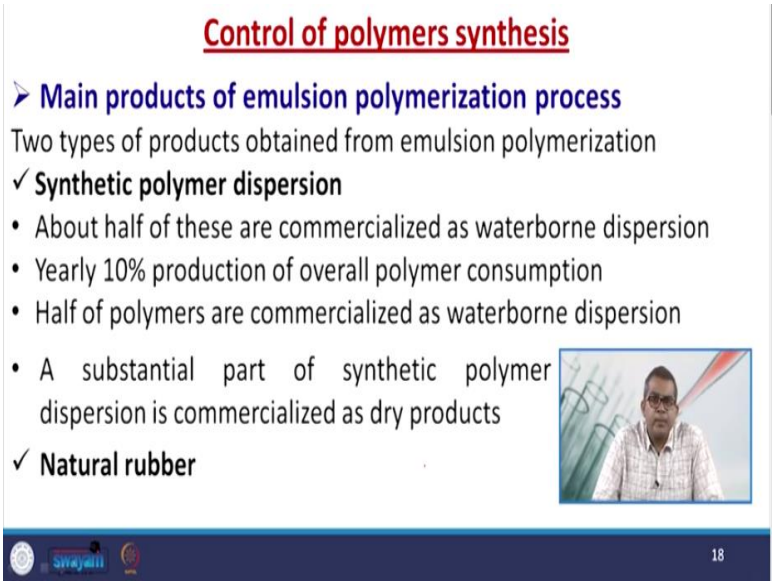

Now, there are two type of products you can obtain from the emulsion polymerization. One is that synthetic polymer dispersion so usually half of these are commercially available as a waterborne dispersant. Now, yearly 10% production of overall polymer consumption is attributed to this emulsion polymerization in situ to this the polymer dispersion.

Ah half of polymers they are commercialized as a waterborne dispersion usually a substantial part of synthetic polymer dispersion is commercialized as a dry product. And foremost is the natural rubber.

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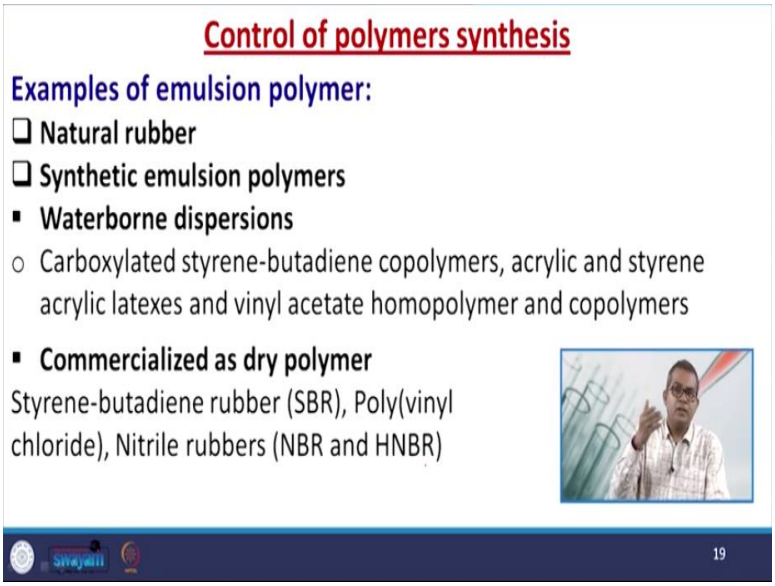

Then, there are certain other waterborne dispersions like carboxylated styrene butadiene copolymer, acrylic and styrene, sometimes acrylic latex, vinyl acetate homopolymer,

copolymer etcetera. Sometimes, the styrene butadiene rubber, poly vinyl chloride, nitrile rubbers, etcetera. So, these are some of the examples of these commercialized dry polymers.

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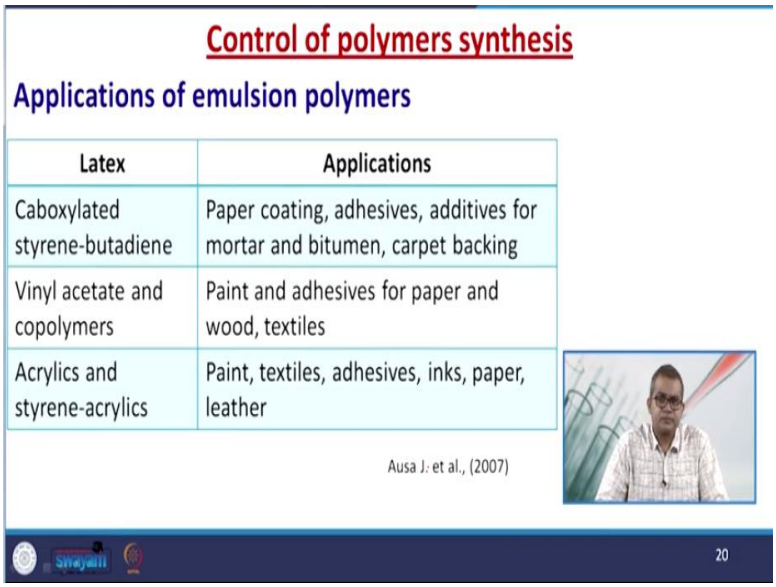

Now, here you can see the various applications of these emulsion polymerization like carboxylated styrene butadiene is useful for the paper coating, adhesives. It can be used as adhesives, additive for different type of a mortar or bitumen or sometimes carpet backing if you see the carpet there are certain layer for the protective layer that is attributed to this tiny butadiene.

Vinyl acetate and copolymer like paint adhesive very common application of this vinyl acetate copolymer in the paint and adhesive for the paper and wood textile. There are certain acrylics and styrene acrylics like paint, textile, adhesives, sometimes ink, paper, leather etcetera.

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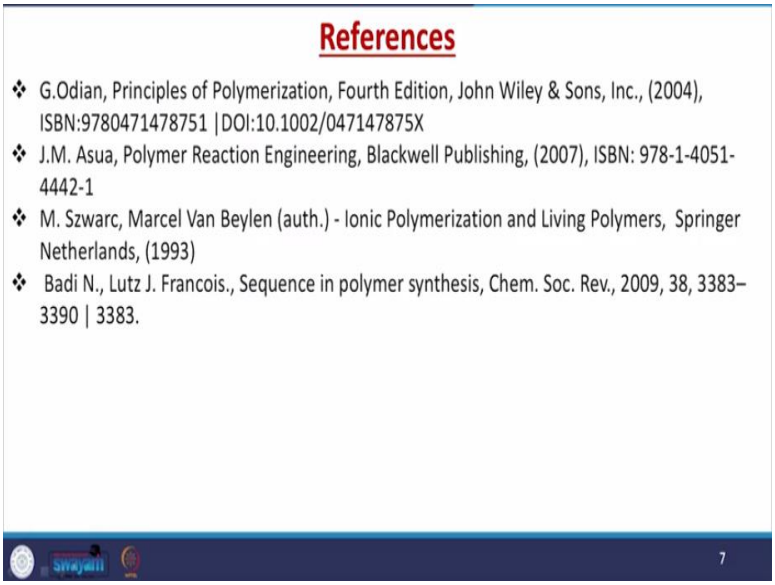

So, in this particular lecture, we discussed about the emulsion polymerizations then various applications of these emulsion polymerization, how the different ingredients may play a vital role in deciding the properties of emulsion polymerization. Thank you very much.