Polymer reaction Engineering
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Lecture – 54
PSD and Implementation of the Process - II

Welcome to the second part of particle size distribution and implementation of the process under the head of emulsion polymerization.

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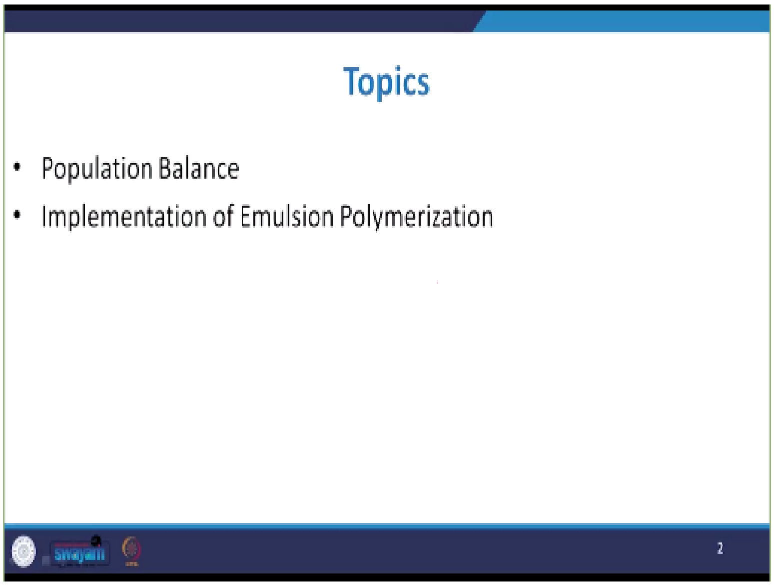

Topics

- Population Balance
- Implementation of Emulsion Polymerization

in the previous lecture we discussed about the various concepts and mathematical equation of population balance, and then we discussed in brief about the implementation of all these processes applicable for the emulsion polymerization especially, our emphasis was with respect to the various parameters associated emulsion polymerization with respect to the property of polymeric product.

So, if you recall that we discussed about the molecular distribution we discussed about the particle size distribution. So, in this aspect, the next approach is the particle morphology. the particle morphology is usually controlled by the interplay between the thermodynamics and kinetics. As you recall that thermodynamics a very vital role in all kind of chemical reactions and a polymerization process as the subset of those chemical reactions.

So, this thermodynamics and kinetics both play a very vital role in deciding the fate of polymerization process. The thermodynamically preferred morphology correspond to that of the minimum surface energy that is related to the Gibbs free energy. equilibrium favoured morphologies they are relatively simple to achieve since the particle morphology naturally evolves towards them.

In attempting to generate a given particle morphology, this morphology is one of one that the thermodynamically favoured that is the foremost requirement. this implies the modifying the interfacial tension. So, the polymer water interfacial tension it can be lowered maybe because of the increasing the emulsifier concentration by choosing the type of for consent initiator and the concentration of initiator in the synthesis.

So, ultimate aim is to alter the interfacial tension that is the ultimate objective to get these reactions thermodynamically favoured. initiator yielding the hydrophilic radicals, for example, like sulphate ions, radicals, they lower the polymer water interfacial tension. the use of a functional coco monomer may also substantially have modified the polymer water interface.

The use of block and graft copolymer they lower the polymer interfacial tension So, that they can enhance the polymerization process in a favourable direction by supplementing the thermodynamic approaches. in the case of in which the desired morphology cannot be made thermodynamically favoured, kinetic control sometimes be very feasible to achieve this desire, an example to this formation of hydrophobic shell over the hydrophilic core.

In this process the crosslinked hydrophilic polymer particles they are used as a seeds in a seeded semi continuous emulsion polymerization of the hydrophobic monomer. So, by this way hydrophobic shell and hydrophilic core, they play a vital role because sometimes, thermodynamic approach is not favour favoured and because of some other aspect maybe and this adversely affect the economics of the polymerization process.

And that is why we go for some other approaches to get the things in our favour. The hydrophobic polymer this cannot be accommodated within the polymer network of the seed and it is expelled to the surface where it forms a shell. Sometimes people may adopt another strategy to achieve the same morphology that is to carry out the process under very monomer starved conditions using initiators that form the hydrophilic radicals.

So, these conditions sometimes referred as surface anchoring of the entering radicals, they lead to the radical concentration profile with maximum values close to the particle surface. let us have another beautiful approach that is attributed to the residual monomer and VOC removal. Now there are 2 main ways to reduce the residual monomer content in the water board bond polymer, one is post polymerization another one is devolatilization.

De-volatilization is again a very important concept we will discuss brief in the subsequent slides. let us go to the post polymerization This consists of inserting fresh radical generated system to polymerize the remaining monomer at the completion of the main polymerization process. So, that is why this is just a pretermination is step so that any kind of a residual monomer which sometimes maybe because of some bad calculation, maybe because of some bad conditions, they may be may remain in the reaction mass.

So that particular post polymerization technique is adopted for this one. water soluble redox system they are favoured, because they can be applied as aqueous solution and produce a high radical flux under the moderate condition and this lead to a shorter post polymerization process. water soluble initiator that sometimes create the hydrophobic radicals like organic hydro peroxides, they are useful for the removal of monomer by post polymerization.

Monomer concentration in the aqueous phase is very low. So, it takes a longer time to proceed and that is why you require some some some additional process for triggering so that time fractor make may be given a due consideration. Consequently, a significant fraction of oligo radicals they may suffer because by mod molecular termination this might be leading to a low initiator efficiency.

The key benefit of post polymerization is that it can be carried out either in a polymerization reaction or in a storage tank and no external equipment is needed. See, either if you are carrying out this particular thing in the polymerization reactor, then obviously, there is no additional things are required and if you are putting all these content into a storage tank, then additionally there is no requirement of any furthermore equipment only thing is that you need to cater the warehouse requirement.

Sometimes it is evident that some initiator system may modify the polymer microstructure, which is both a problem and opportunity to extend the range of properties achievable by a given aqueous dispersion Polymer. another thing which we were discussing about that is devolatilization. although fresh devolatilization has been applied for high volatility monomer removal.

Vinyl chloride is the best example for this particular approach. So, when I will provide from PVC and filter time from the butadiene devolatilization of aqueous polymer dispersion is usually carried out using a stripping agent. devolatilization of aqueous phase dispersion is a mass transfer process, which involves the different steps as listed.

The diffusion of VOCs to the particle surface, volatile organic substances to the particle surface, then transfer of from the polymer surface to aqueous phase, diffusion through the aqueous phase and the transfer from the aqueous phase to the gas phase so that the cy entire cycle can be completed. In case of emulsion polymerization, the devolatilization rate of the monomer is always constrained by the mass transfer across the interface between the aqueous phase and the gas phase.

Therefore, all the process variable there those increase the interfacial arena area between the aqueous phase and the gas phase will boost the devolatilization process. There may be several equipment arrangements can be proposed to allow the faster devolatilization without affecting the stability of dispersion and avoid foaming. Foaming is again a very undesired effect during the polymerization process because it hinders or it creates a problem for the polymerization process to carry out.

For low glass transition temperature polymers that tank reactors they are more convenient. The undesirable foaming this can be suppressed by lowering the temperature, but sometimes this may reduce the recovery of low boiling substances. This is again an undesired effect during this process. Therefore, sometimes the chemical defoaming agents they are being used.

But sometimes they may accelerate the thermal degradation of the polymer because ultimately they are the chemical and sometimes they may favour them sometimes they may may may may act as a depressant of the polymerization process. So, they may sometimes accelerate the thermal degradation of the polymer when the polymer is processed at an elevated temperature.

sometimes it may occur with the PVC and it adds contaminants to the latex. So, a way to control the foam formation is by a sudden increase of pressure is again one of the most favourable tool to achieve this goal. this method is proven to be very efficient in the stripping of acrylic latex in a tank reactor. So, the combination of devolatilization and a post polymerization this has the proven to be the advantageous on various occasion.

The next step to watch in this category is the scale up. The purpose of the scale up is to manufacture on a commercial scale of the same nature as those produced in the laboratory. The production of industrial reactor is constrained by their heat removal capacity and there is a trend to use larger reactor sometimes up to 60 metre cube to increase the production. whenever we use the larger reactor again they are having some limitations related to the size, related to the concentration of initiator, related to the concentration of the monomer etcetera.

So, these thing need to be catered accordingly. sometimes geometrical consideration also plays a vital role. So, because of these geometrical concentration, the larger the volume of the reactor, the smaller the heat transfer area by volume ratio. So, therefore, larger require reactors they require the longer process times to carry out and the process under the good thermal control.

So, this approach is again need to be cater and optimise during the designing of these emulsion polymerization reactor. agitation sometime improves the heat transfer the workable range is usually limited, because vigorous agitation may cause the shear induced coagulation and sometimes the breakage of particles. So, whenever we go for this agitation parameter then we need to look very closely to the polymer reactor vitals that whether it is advantageous or disadvantageous that we that need to be addressed.

The reduction of latex viscosity by using the bimodal latex is not always a choice because this may modify the application properties. And therefore, it may create the further problem in the processability of those polymer. the heat removal capacity and the production rate sometimes it increases by increase in the polymerization temperature. Sometimes the use of non isothermal processes and then maybe starting the polymerization at a low temperature and using the polymerization enthalpy to heat the reactor.

Sometimes it may be a good tool for the advantages operation. The bottom line of that particular process is that for a given process temperature, the process time and the production rate for a given reactor is practically fixed, maybe it is the CSTR maybe it is the semi batch reactor maybe is a batch reactor. Therefore, the thermal performance of industrial scale reactor this should be scaled down to the laboratory reactor and the product must be developed taking into account of thermal limitations.

Because if you recall that we discussed that the thermal limitation or thermodynamic approach is a very crucial for any any kind of emulsion polymerization reactor efficiency. So, the challenge of scale of latex being developed accounting for these limitations are often related to the particle nucleation. So, again I am coming back to the nucleation aspect that nucleation is a fast highly nonlinear process therefore, a very sensitive to the local variation of the concentration of the reactants.

So, we discussed a lot of parameters during this course of study and you see that all these parameters they play a very vital role and usually triggered by this nucleation aspect. So, in a large scale reactor, it is very difficult to reproduce the nearly instantaneous mixing typical to small reactor and therefore, it is a common source of variability in particle nucleation therefore, the particle size distribution, so, all things are interrelated.

So, whenever you change the nucleation aspect ultimately it affects the particle size distribution and in situ molecular weight distribution. So, the particle size distribution this affects the radical distribution, which in turns influences the molecular weight distribution and a polymer architecture and consequently the latest property. So, ultimately whenever we talk about the final product, because ultimately as a consumer my intention is to get the useful product with my desired parameters.

So, in case if there is a slight variation in the either nucleation in case of any slight variation in the scale up, any slight variation in any kind of the concentration that ultimately affects the the particle size distribution and thereby molecular weight distribution and the polymer architecture and subsequently, sometimes you may experience that you may not be able to process the polymer as per your requirement.

So, the a usually you look for a way and the way of reducing this variability is to avoid the nucleation step by using a seed. Although this protocol is given, but sometimes you have to be very cautious about the use of these particular approaches. There are certain other things related to the inverse poly emulsion polymerization. Usually, sometimes it is favourable sometimes it is you can say the undesirable approach.

So, in this process an aqueous solution of a water soluble monomer like acrylamide is dispersed in an organic continuous base using an excess of surfactant. So, water in oil micelles are formed. The polymerization is usually initiated by oil soluble initiators and the mechanism involves involved in this particular process are similar to those occurring in emulsion polymerization.

The product is a dispersion of an aqueous solution of water soluble polymer in an organic liquid. Therefore, the separation you need to address this the problem of separation. So, polymer and co polymer of acrylamide for tertiary oil recovery and flocculants are reproduced by this technique. tertiary oil recovery is a very common phenomenon in crude oil reservoir.

When these polymers are injected to the to the reservoir for removal of us of our extraction of recovery of the remaining oil within the system. So, sometimes they are clubbed under the head of enhanced oil recovery and these polymers and copolymers they find it very useful in the recovery of the crude oil from the reservoir. So, they are having a very wide application this arena.

Then, we look into the mini emulsion polymerization. in mini emulsion polymerization, the size of a monomer droplet is substantially reduced. Sometimes the diameter is reduced to 50-1000 nm by combining a suitable emulsifier and efficient emulsification apparatus and stabilising the resulting monomer mini emulsion against the diffusional degradation.

Sometimes a co-stabiliser, which is hydrophobic low molecular weight compound is being used to achieve this particular mini emulsion polymerization. And although this mini emulsion polymerization is very widely applicable in different aspect of chemical industries. When we talk about the surface tension or surface properties. The available surface surfactant those adsorbed on the larger surface area of the droplets therefore, they inhibit the formation of micelles.

So, when the initiator is added to the system, the radical sometimes they enter into the monomer droplet and that become the polymer particles. So, that droplet of these nucleated or nucleated polymer particle they minimize the diffusional limitations they encountered in the conventional emulsion polymerization and allows the incorporation of water emulsion soluble compound.

So, it is just like that, they created a cordoning over the surface of nucleate and then they allow the regulated quantity of those surfactant or emulsions etcetera to become to form the polymer. So, they if they are they may act like a semi permeable system. The application they include the production of poly polymer and polymer inorganic material. They are sometimes referred as hybrid dispersion, the catalytic polymerization, controlled radical polymerization in the dispersed media in the production of high solid low viscosity latex.

So, sometimes these type of approaches are quite useful for very various kinds of speciality uses of those emulsion polymerization product. Let us talk about the micro emulsion polymerization. the micro emulsion polymerization this involves the polymerization of oil in water just reverse to the previous one and water in oil monomer micro emulsion So, the microemulsions they are thermodynamically stable.

So, whenever you talk about the thermodynamic calculation with respect to the Gibbs free energy it favours. Now isotropic dispersion and the durability again play a very vital role. Usually this is attributed to a very low interfacial tension obtained by the suitable emulsifier. particle nucleation sometimes occurs upon entry of a radical into the micro emulsion droplet.

micro emulsion polymerization allows the production of particles smaller than those obtained by the emulsion polymerization. So, sometimes it may lead to the higher number of polymer particles and they result in a more compartmentalised system. That means, you may form as different type of segments within the polymer mass so that you you may have some type of zonal approaches in those type of polymer products being developed.

So, under these conditions, the lifetime of polymer chain increases to ultra high molecular weights. one, one particular negative aspect is that, whenever you are intended to develop the high the high molecular weight polymer or high high range of molecular weight distribution, then you may use this particular approach. Otherwise, it is disadvantageous, because you won't be able to control the molecular weight.

inverse micro emulsion polymerization is sometimes used to produce high efficient flocculants. As I told you that, these flocculants are being frequently used in the enhanced oil recovery. Atlast, we will discuss the dispersion polymerization. dispersion polymerization is a very selective phenomenon under the head of emulsion polymerization. In this phenomena the monomer, the initiator and a stabiliser or sometimes referred as a stabiliser precursor they are dissolved in a solvent.

And that is not the solvent for the Polymer so that you may achieve the result. Otherwise, if you use that particular solvent for solvent which is favourable for the polymer, then you won't be able to carry out the the polymerization reaction. polymerization starts in a homogeneous phase and the polymer particles precipitates forming the unstable nuclei.

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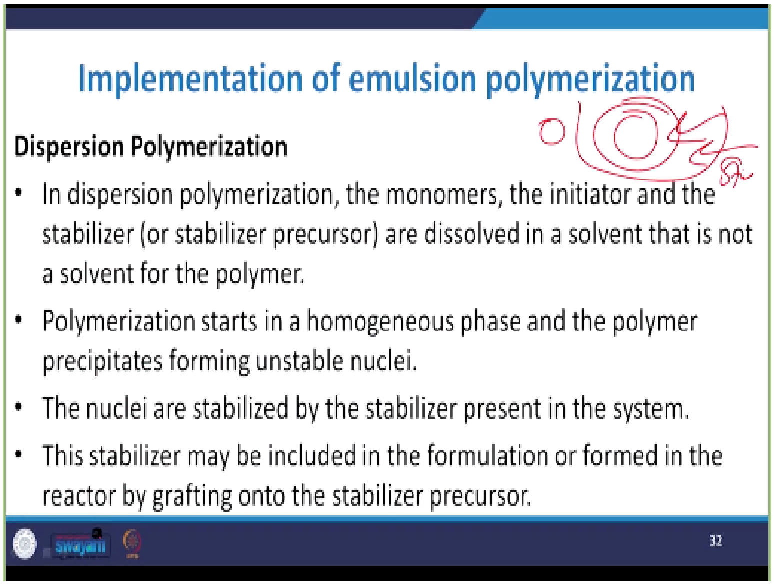

Implementation of emulsion polymerization

Dispersion Polymerization

- In dispersion polymerization, the monomers, the initiator and the stabilizer (or stabilizer precursor) are dissolved in a solvent that is not a solvent for the polymer.
- Polymerization starts in a homogeneous phase and the polymer precipitates forming unstable nuclei.
- The nuclei are stabilized by the stabilizer present in the system.
- This stabilizer may be included in the formulation or formed in the reactor by grafting onto the stabilizer precursor.

It is just like that, you start the things and thereafter, it agglomerates and formed the larger particles but that particle is unstable. these unstable nuclei they are stabilised by the stabiliser present in the system. So, you must have some stabilisers within the system which can stabilises and it provides the mechanical strength also to that particular polymer being developed.

these stabilisers may be included question arises that when it can be included? Sometimes it may be included in the formulation phase or formed in the reactor by grafting into the stabiliser precursor. So, sometimes you may add some other component to the the the system so that it can graft that is that chains and then easy to the facilitate these the stabilisation process of those unstable nuclei.

nucleation ends when the number of stable polymer particles increases to a point in which all new nuclei are captured by the existing stable particles. So, it is the self eating concept.

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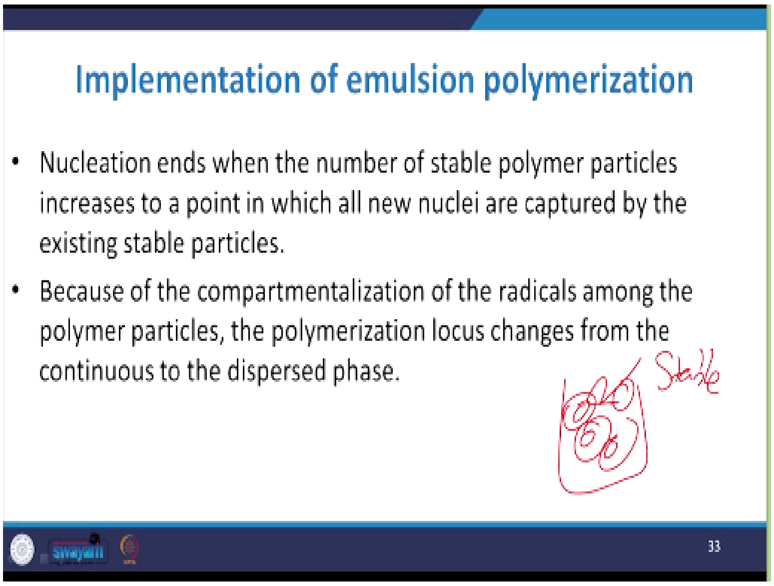

Implementation of emulsion polymerization

- Nucleation ends when the number of stable polymer particles increases to a point in which all new nuclei are captured by the existing stable particles.
- Because of the compartmentalization of the radicals among the polymer particles, the polymerization locus changes from the continuous to the dispersed phase.

Stable

when these particles they are being captured by the existing whatever is stable particles say you are looking into then this particular approach of nucleation ends because of the compartmentalization of the radicals among the polymer particles. here you see that there are the different polymer particles and compared compartmentalization is occurring.

The polymerization locus changes from continuous to the dispersed phase because the dispersion media is present adequately within the mass. So, that is why this process changes to the the the dispersed phase.

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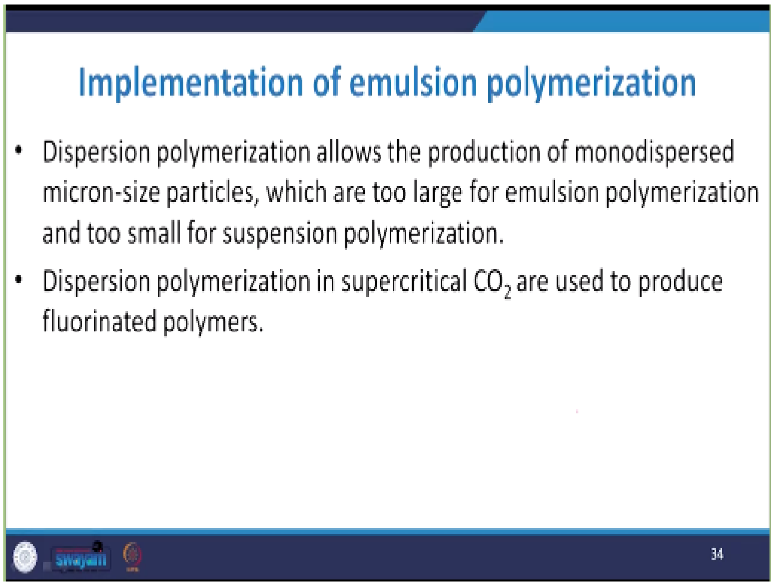

Implementation of emulsion polymerization

- Dispersion polymerization allows the production of monodispersed micron-size particles, which are too large for emulsion polymerization and too small for suspension polymerization.
- Dispersion polymerization in supercritical CO_2 are used to produce fluorinated polymers.

dispersion polymerization, this allows the production of mono dispersed micron size particles. They are too large for the emulsion polymerization and sometimes too small for the suspension polymerization. So, if you see the mass of those dispersion polymers, you will experience there is a haziness within the polymer polymer mass. So, the dispersion polymerization is supercritical carbon dioxide they are used to produce some type of fluorinated polymers.

And these fluorinated polymers are being used in various speciality approaches, some medical applications, some type of extractive oil recoveries etcetera. So, they are they find it very useful way in different type of aspect of industrial applications.

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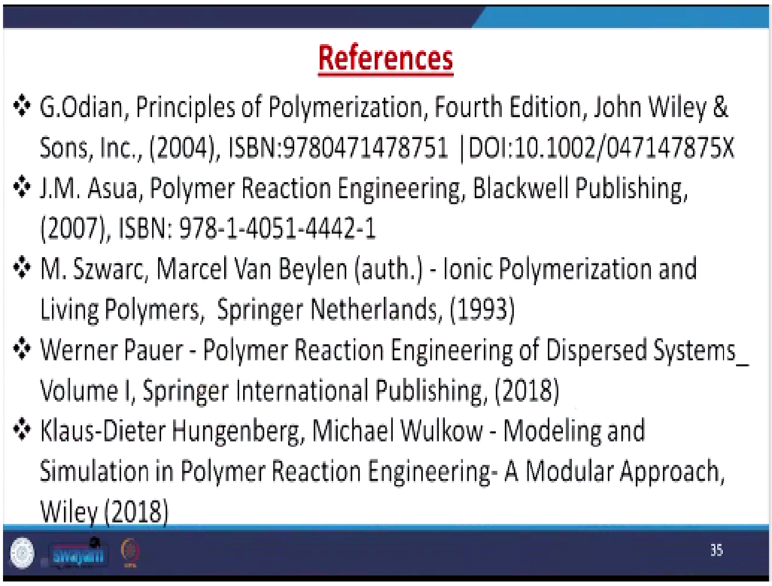

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So, by this way, we completed this emulsion polymerization process and implementation of various parameters, which we discussed in due course of time to the reactor designing as well as the reactor calculation. In due course of time we have discussed about the various mathematical equations, which are duly useful to carry out the reactor design. in case if you wish to have further study, we have enlisted various references for your convenience. You can go through all those references. Thank you very much.