Polymer Reaction Engineering
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Lecture - 48
Population Balance Modelling Other Techniques - II

Welcome to the second part of the population balanced modelling. In the previous lecture, we discussed about the concept of population balance modelling. We have discussed about the importance of this particular approach for the prediction of various properties of the polymeric system. We discussed about the drop coalescence process. We discussed about the different concepts and modelling procedure for the drop coalescence process.

In this particular lecture, we will discuss about the physical properties and phase equilibrium calculations attributed to the population balance modelling as well as we discussed about the emulsion polymerization. Now, let us have a look about the physical properties and the phase equilibrium calculations attributed to the polymeric system. There are various properties in questions 1 is the physical and transport property, this is one of the most relevant problem for modelling the suspension polymerization process.

Now, we can discuss couple of problems attributed to this one. One is that the estimation of the physical and transport properties of reacting system although the transport phenomena that deals with this kind of approach, but within the polymeric mass, it is extremely difficult to have a prediction or estimation of this one. So, the calculation of composition and partitioning of a different species that like polymer, initiator, catalyst, sometimes, inhibitors may be attached to this one.

So, you need to encounter the calculation approach of these compositions and partitioning in the various phases usually present in the polymeric system. So, this concept deals with the search kind of approaches. Now, especially when we talk about the suspension polymerization process, one can identify at least 3 phases. If you recall that during the suspension polymerization, we discussed this thing.
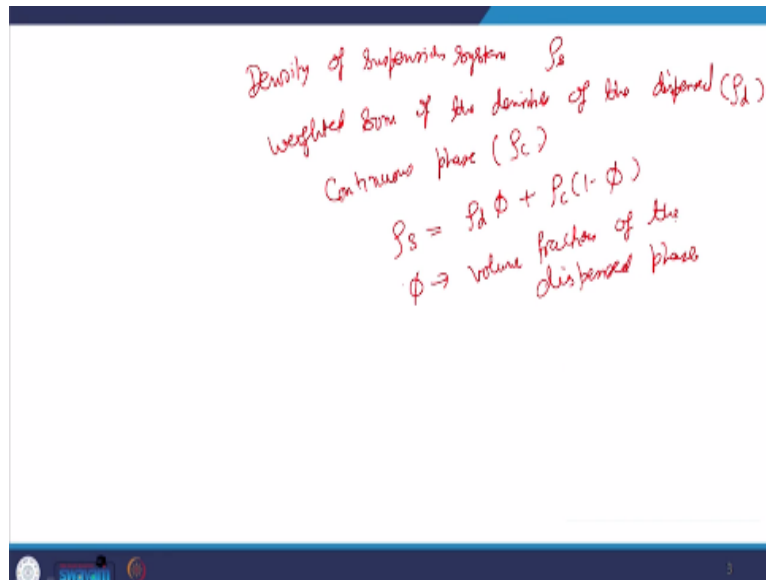
One is that the dispersed phase that is the polymerizing, monomer droplets etcetera. So, just try to correlate the things with the drop coalescence aspect, then the continuous aqueous phase

and third one is the gaseous phase. So, the dispersed phase can be either homogeneous if the polymer is soluble in monomer or sometimes it is heterogeneous. So, it can acquire any kind of phase depending upon the need of polymerization process.

In the powder suspension polymerization that dispersed phase usually consists of two different things or two different phases. One is, you may have the polymer rich phase; second is, maybe the monomer rich, you agree on that there are only two possibilities for these phases. So, in the continuous aqueous phase contains only small amount of monomer because rest other things they are participating in the polymerization process.

Now, the gas phase contains monomer and water vapours. So, when we talk about the modelling concept, then these things they play a very vital role and these assumptions and these concepts, they play a very vital role.

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So, let us have to start with the modelling approach the density, let us say

The **density of the suspension system**, ρ_s, can be calculated by the weighted sum of the densities of the dispersed (ρ_d) and continuous (ρ_c) phases:

$$\rho_s = \rho_d \phi + \rho_c(1 - \phi)$$

where ϕ is the volume fraction of the dispersed phase.

So, this density of dispersed phase will in turns be a function of corresponding density, so, of the polymer.

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The **density of the dispersed phase** will in turn be a function of the corresponding densities of the polymer (ρ_{pol}) and monomer (ρ_{mon}) and the extent of monomer conversion, x:

$$\rho_d = \left(\frac{x}{\rho_{pol}} + \frac{1-x}{\rho_{mon}} \right)^{-1}$$

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The **viscosity** of the dispersion system can be calculated by the following semi-empirical equation:

$$\eta_s = \frac{\eta_c}{1-\phi}\left(1 + \frac{1.5\eta_d\phi}{\eta_d + \eta_c}\right)$$

where η_d and η_c are the viscosities of the dispersed and continuous phases, respectively.

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For the suspension polymerization of VCM, the viscosity of the polymerizing monomer droplets, η_d, can be calculated from the Eilers equation:

$$\eta_d = \eta_{mon}\left(1 + \frac{0.5[\eta]_{pol}}{1 - \frac{\phi pol}{\phi cr}}\right)^2$$

where η_{mon} is the monomer viscosity, ϕ_{pol} is the volume fraction of the polymer in the dispersed phase, given by

$$\phi pol = x(\rho d/\rho pol)$$

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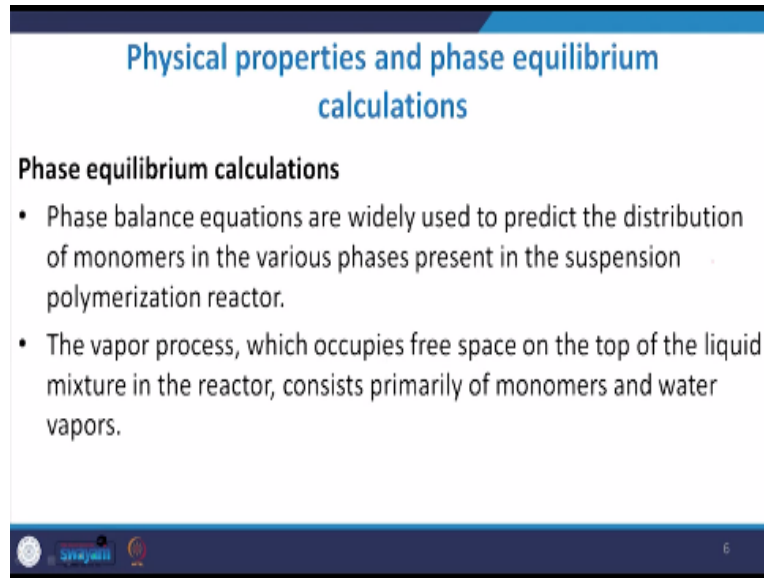ϕ_{cr} is the polymer volume fraction corresponding to the critical monomer conversion x_c.

When ϕ_{pol} approaches the ϕ_{cr} value, the dispersed-phase viscosity approaches a limiting constant value, corresponding to a rigid structure.

The value of ϕ_{cr} for the VCM suspension polymerization was taken equal to 0.3.

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So, this is the way through which one can predict the physical properties and the suspension under the head of suspension polymerization. Another is the phase equilibrium calculation. Now, this phase equilibrium concept is again a very important one while predicting the behaviour of polymer while predicting to have various kinds of modelling approaches in the polymeric system.

So, the phase balance equation, they are widely used to predict the distribution pattern of monomer in different phases present in the suspension polymerization reactor. So, sometimes, different type of phases present in suspension polymerization. So, you require a phase balance equation for the prediction of the behaviour, the vapour process which occupies the free space on the top of the liquid mixture in the reactor, it consists primarily of monomer and water droplets.

Now, during the entire duration of polymerization process, the 3 phases, 4 in the case of VCM polymerization, they are assumed to be in the thermodynamic equilibrium. So, the energy and other aspect or heat aspect, they are duly taken into account. So, as a result when we talk about the fugacity, because when we talk about the thermodynamic equilibrium, you cannot overrule the importance of fugacity.

As a result, the monomer fugacities in the three (four) phases will be equal:

$$f_{mon}^g = f_{mon}^w = f_{mon}^{pol}(= f_{mon}^{mon})$$

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So, like this fugacity of gaseous monomer should be equal to the dispersed phase, the fugacity of monomer in the dispersed phase, and then it should be equal to the fugacity of monomer under the polymeric phase and it should be equal to the fugacity of monomer within the monomer phase. So, you can see by this way, sometimes, people may surprised to see the four phases, but you see that the monomer in the gaseous phase, monomer in that water or which is used as a dispersed phase, then monomer in the polymer phase and then monomer itself in its phase.

The term in the brackets corresponds to the monomer fugacity in the monomer-rich phase in the case of the "powder" suspension polymerization (i.e., VCM polymerization).

For the EPS process, the fugacities of the n-pentane in the three phases should also be equal:

$$f_{pent}^g = f_{pent}^w = f_{pent}^{pol}$$

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Physical properties and phase equilibrium calculations

- The term in the brackets corresponds to the monomer fugacity in the monomer-rich phase in the case of the "powder" suspension polymerization (i.e., VCM polymerization).
- For the EPS process, the fugacities of the n-pentane in the three phases should also be equal: (Note)

$$f_{pent}^g = f_{pent}^w = f_{pent}^{pol}$$

So, in the EPS process, the fugacity of pentane, now, fugacity of pentane in the gaseous form should be equal to the fugacity of pentane in the water phase and then in the polymer phase, so, it should be equal.

Assuming that all the phases in the system are in thermodynamic equilibrium, the following pseudo-steady-state monomer mass balance:

$$W_{mono}(1 - x) = W_{mon}^{pol} + W_{mon}^w + W_{mon}^g(+W_{mon}^{mon})$$

where the symbols W_{mon0}, W^{pol}_{mon}, W^w_{mon} and W^g_{mon} denote the total monomer mass loaded in the reactor, the monomer mass in the polymer (pol), water (w) and gas (g) phases, respectively.

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So, we may write the pseudo steady state monomer mass balance equation. Now, this is represented as 1 minus x monomer under the head of the polymeric system, then monomer

under the either water or a dispersed phase, then monomer in the gaseous phase plus monomer within its phase. So, this denotes the total monomer mass loaded in the reactor, this represents the total monomer mass loaded in the reactor in various phases.

The mass of monomer in the aqueous phase can be considered at any time to be equal to its solubility in water:

$$W_{mon}^{w} = K \left(\frac{P}{P_{mon}^{sat}} \right) W_{water}^{w}$$

Where K is the monomer solubility in the aqueous phase

P^{sat}_{mon} is the saturated monomer vapor pressure at the polymerization temperature.

So, by this way, we can see the different approaches. Now, other is the effect of various operating conditions on particle size distribution. Now, particle size distribution is again the play a very vital role while deciding the fate of polymer produced. So, by increasing the input per unit mass, the turbulence amplitude and the presence of a velocity, variation increases.

Now, sometimes, the increased rate of liquid circulation results in the further drop coalescence and thereby increasing the drop coalescence rate that we discussed previously. Now, increased input power to the device sometimes, result in the increased drop breakage and thereby, the coalescence rate. So, these things are extremely important and they are attributed to the operating condition of a particle size distribution.

Now, let us have a discussion about the effect of viscosity of continuous and dispersed phase on the particle size distribution. So, usually an increase in the dispersed phase viscosity e sometimes, referred as eta d. This results in the reduction of both breakages and coalescence rate, sometimes, the increase in the holdup function fraction of the dispersed phase that is the phi, this decreases the turbulent intensity.

Now, in suspension polymerization of VCM more uniform polymer particles, they have been developed by increasing the viscosity of continuous process. So, this is again a very important concept related to the effect of viscosities. Now, at last let us have a look about the concept of emulsion polymerization. Although we cover certain parts of this emulsion polymerization in the previous lectures, but especially when we talk about the modelling of these things, then again let us have a brief look then we will start the modelling concept.

Now, emulsion polymerization is the technique leading to the colloidal polymer particle dispersion in continuous medium and water is most favourable media for this dispersion and this polymeric dispersion, they are called latex sometimes, latex and they are often spherical, but sometimes, they based on the morphological demand, they are greatly influenced by the application of various properties.

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So, you can see that here we are introducing the monomer droplets. There are certain free radical initiators if you recall that to initiate the polymerization process, you will require certain type of induced material. In this case, the induced material is free radical initiator and sometimes, because we are using the water as the continuous dispersion media, you may require some surfactant to alter the surface energy of water.

Then by this way, they may form the emulsion before the polymerization and you see here the polymerization start and you may experience certain the latex particle or emulsion polymerized particle being developed.
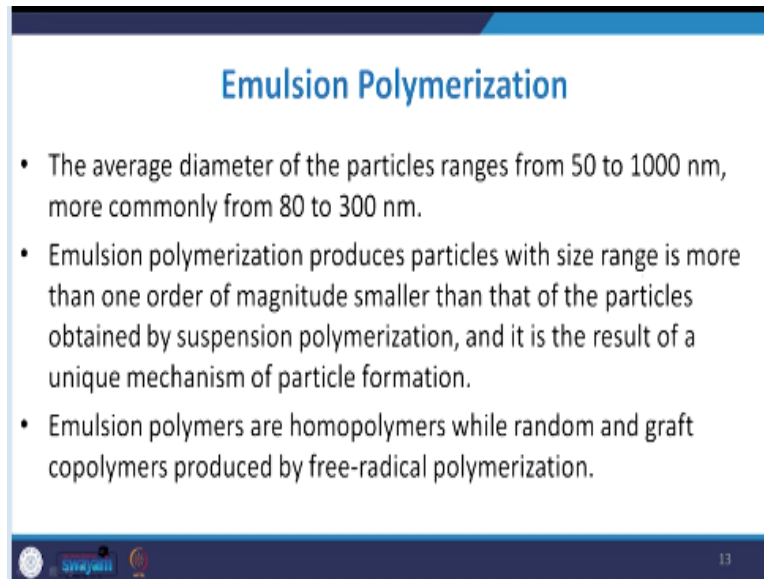
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This is a more, clearer picture. Here, you are having the various monomer droplets in the continuous phase there are certain more initiators, surfactants; they are roaming here and there

and they attach to form the micelle and this micelle in due course of time converted into the polymerized product.

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Emulsion Polymerization

- The average diameter of the particles ranges from 50 to 1000 nm, more commonly from 80 to 300 nm.
- Emulsion polymerization produces particles with size range is more than one order of magnitude smaller than that of the particles obtained by suspension polymerization, and it is the result of a unique mechanism of particle formation.
- Emulsion polymers are homopolymers while random and graft copolymers produced by free-radical polymerization.

So, the average diameter of the particle, this sometimes, ranges from 50 to 1000 nano-metres and more commonly, if you talk about the processability issue related to those polymer particles or polymers, polymer chains, they are ranging from 80 to 300 nano-meters. Now, this emulsion polymerization, this produces the particle with the size ranges sometimes, more than one order of magnitude is smaller than that of the particle obtain by the suspension polymerization.

So, that is why you can decide based on your suitability, you can decide the merits and demerits of various polymerization process whether you go for emulsion polymerization or suspension polymerization. Now, emulsion polymers, they are homo-polymers and random and graft copolymers sometimes, they produced by the free radical polymerization and sometimes, the synthetic polymer dispersions are also produced by the emulsion polymerization.

Now, let us briefly look about the main product and sometimes, different marketing this. Now, in a broad sense the polymer dispersion, this includes both natural rubber and synthetic polymer dispersion. Now, you see that always because of scarcity of the natural product, we are always looking for the substitute of those natural rubbers. So, these offer a very good approach for this substitution.

So, synthetic polymers sometimes, they include the waterborne dispersion, these are carboxylated styrene butadiene polymer, SBR, sometimes, referred as SBR rubber, vinyl acetate polymers, acrylic or styrene acrylic polymers, etcetera. So, you can see these are the

small structures of either carboxylated styrene butadiene and styrene acrylic polymers. Sometimes, the commercialised dry polymers are also play a very vital role.

And styrene butadiene rubber SBR is mean substitute for various speciality activities. They are produced through this way styrene butadiene rubber, nitrile rubbers and BR, HNBR, PVC. So, these are the various examples of these emulsion suspension polymerization process. Now, the yearly production of synthetic polymer dispersion is about 10% of the overall polymer consumption or production.

So, synthetic polymer dispersions, they are produced by the emulsion polymerization because the easy availability of dispersion media. You can see more than half of these polymers are commercialised as waterborne dispersion. And you see in day to day affair, there are various spectrum of polymeric products those who are the waterborne dispersion are available as on date. The main markets for these dispersions are paints and coatings (26%), paper coating (23%), adhesives (22%) and carpet backing (11%).

So, the figures, they are varying in nature based on the demand of those products. The polymer dispersions, they also found in the interesting market niche in biomedical applications like diagnosis, drug delivery. Drug delivery is again a very upcoming field for either the healthcare field aspect or in the polymer aspect. So, the polymer dispersion products, they offer a very good candidate see, for the drug delivery concept.

A substantial part of this synthetic polymer dispersion is commercialised as dry product. Let us have a brief look about that what are those commercialised product like SBR for various tires and they are the substitute of natural rubber, nitrile rubbers about 10% of the total PVC production, 75% of total acrylonitrile butadiene styrene or ABS usually an elastomer modified thermoplastic. This is used for the electrical and electronic equipment in house or office appliances. They can be used almost 75% in this category.

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Main products and markets

These include;

- styrene-butadiene rubber (SBR) for tires,
- nitrile rubbers, about 10% of the total poly(vinyl chloride) production,
- 75% of the total acrylonitrile-butadiene-styrene (ABS, an elastomer modified thermoplastic used in electrical and electronic equipment, house and office appliances and in the automotive industry) and redispersable powders for construction materials.
- Natural rubber accounted for 6.5 million tonnes per year, including about 1 million tonnes that is commercialized as a waterborne dispersion.

Natural rubber account for usually 6.5 million tonnes per year including about 1 million tonnes; that is commercialised as the waterborne dispersion. So, this brief statistical information related to this approach. Let us have discussed about the various products and especially the market like SBR. This is being used for the tires styrene butadiene rubber.

Nitrile rubber, they offer a very good substitute for different kinds of applications like 10% of total poly-vinyl chloride production. They offer the nitrile rubber. 75% of the total acrylonitrile butadiene styrene ABS usually, this is an elastomer modified thermoplastic and why having wide applicability in electrical and electronic equipment either the domestic way or in the office appliances and sometimes, in the automotive industry. This and the re-dispersible powder for the construction material.

Natural rubber offers almost 6.5 million tonnes per year. This includes about 1 million tonnes that is commercialised as waterborne dispersion.

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So, in this particular chapter, we discussed about different physical phenomena. We discussed about the emulsion polymerization. We took the help of various commercially available products and their market and what are the different substitutes, we discussed about the dispersion media with the help of waterborne systems, etcetera. Now, if you wish to have a more and more study in this area, we have enlisted couple of prominent references for your convenience.

You can have a look of all those references for future study and future research if you wish. Thank you very much.