Polymer Reaction Engineering
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Lecture - 46
Heterogeneous Polymerization Introduction - II

Welcome to the second phase of the introductory part of heterogeneous polymerization. Now, in the previous lecture, we discussed about the basic concept of heterogeneous polymerization.

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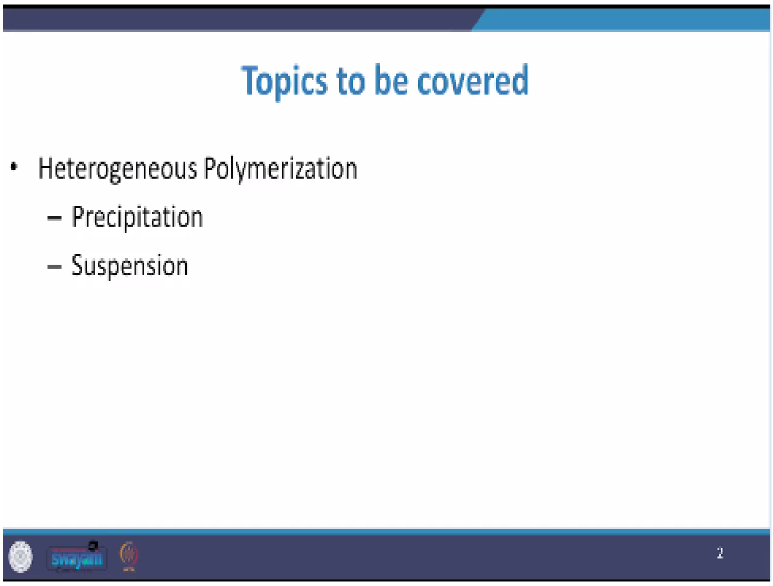

Topics to be covered

- Heterogeneous Polymerization
  - Precipitation
  - Suspension

We discussed about the precipitation polymerization. Then we started the suspension polymerization and we discussed the various aspects attributed to the suspension polymerization.

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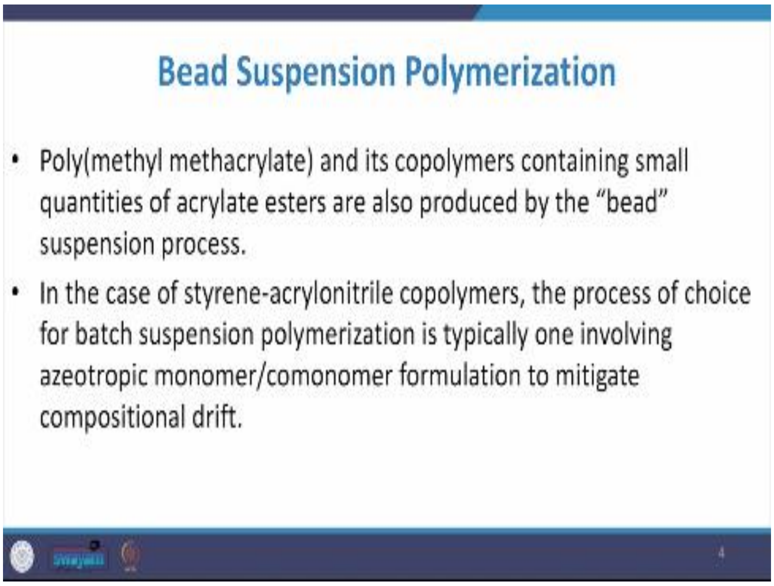

Bead Suspension Polymerization

- Poly(methyl methacrylate) and its copolymers containing small quantities of acrylate esters are also produced by the "bead" suspension process.
- In the case of styrene-acrylonitrile copolymers, the process of choice for batch suspension polymerization is typically one involving azeotropic monomer/comonomer formulation to mitigate compositional drift.

Now, let us have a look about the bead suspension polymerization, the bead suspension polymerization process, this, the bead form of suspension polymerization and the the polymer is soluble in its monomer. Therefore, the monomer polymer mixture is usually termed as homogeneous one. So, in that case, the suspension system may be viewed as an aqueous dispersion of time varying viscoelastic fluid.

So, this offers a usefulness of this particular polymerization process. So, poly styrene which is used in the injection moulding is manufactured by the suspension bead process, poly-methyl methacrylate and its copolymer usually containing small quantity of acrylate esters, they are also produced by the bead suspension process. So, in the case of styrene acrylonitrile copolymer, the process of choice of batch suspension polymerization is typically one involving say, sometimes as azeotropic monomer, sometimes co-monomer formulation to mitigate the compositional drift.

So, this is again the important factor which need to be addressed while we are discussing this bead suspension polymerization. Now, the problem also occur because in continuous aqueous process significantly more acrylonitrile then styrene being dissolved in due course of time. So, as the conversion proceeds the acrylonitrile diffuses into the polymer particles and the ratio of monomer in the bead varies this by creating a difference in the structure of a copolymer.

So, sometimes, it is feasible and sometimes, it is highly you can say the undesirable one. Now, the high impact polystyrene and acrylonitrile butadiene styrene copolymer, they are often prepared in combined bulk suspension process. So, this usually begins with a solution of poly-butadiene in the styrene or styrene acrylonitrile. Now, subsequently, the polymerization of styrene or styrene acrylonitrile is initiated and continues under the stirring until the phase inversion occurs.

So, that is the turning point for this polymerization process. Now, in the final stage water and dispersant are added to the system with the quite obvious reason and the polymerization is completed in suspension. Sometimes, this can be utilised in expendable polystyrene production. Now, this EPS or expendable polymer styrene is manufactured by the suspension polymerization in the presence of a blowing agent.

One of the foremost blowing agent is painting. So, it is also possible to inject the blowing agent to the polymer after the polymerization and allowing it to diffuse into the beads. So, sometimes, you may have a previous one and sometimes, you may inject afterward. So, this depends on the suitability of the process. The appropriate volume of de-ionized water is usually initially charged to the reactor at ambient temperature and thereby, you can begin the agitation.

So, this is the initial protocol of bead suspension polymerization. And you may add the styrene and initiator blend consisting of 4 main initiator with, which may have a low activation energy and the final one which may have the highest activation energy. So, then if you may introduce this thing as well as the stabiliser, just to prevent the coalescence of those polymer particles, they are injected into the reactor and the droplet size variation may occur throughout the heating period.

So, you may experience that the variation in the droplet size. So, when you achieve the specified de-polymerization temperature, the polymerization begins. So, usable polymerization temperature is around 75 to 95 degrees Celsius. So, the polymerization monomer droplet, they travel together in 3 different steps during which the rate of drop breakage or coalescence varies continuously.

So, this is the quite obvious phenomena. So, finally, clear spherical particles with a smooth surface and zero porosity are formed. You can introduce the porosity also. So, in that case, you require to add some porogen agent at the appropriate quantity. Now, auto-acceleration of a polymerization rate due to the jelly factor is appreciable at comparatively low monomer conversion that is sometimes about 30% and persists until a monomer conversion of about say 95% occurs, where the glassy state transformation occurs and the bead become more and more strong. So, this because suspension polymerization if you see that at start-up, the beads are having very low mechanical strength. So, whenever you use it, those beads into other further processing, sometimes these beads may not offer the desired properties. So, therefore, the mechanical strength of those beads are extremely important.

So, once the beads are hard or they possess the required mechanical strength, the reaction mixture is heated to the temperature above the glass transition temperature of the PS i.e. $T_g \sim 100\ ^{\circ}C$ or around 95 to 100 degrees Celsius. So, if you are the polystyrene system, then it is around 95 to 100 degrees Celsius. Subsequently may pressurise the reactor with the nitrogen say at around 7-9 bars and that is so called the impregnation stage, it starts.

Now, during this stage, you may diffuse the normal painting into the beads. At the same time, the free volume increases with the finishing initiator rapidly decompose to produce free radicals and resulting the relative increase in the monomer conversion to about say 99% that is quite significant in nature. Now, let us have a discuss about the effect of unpainted non-free radical suspension polymerization of styrene.

Now, it is observed that the presence of a painting, it reduces the polymerization rate due to increase of the free volume of the system and that delayed the appearance of gel effect. So, painting reduces the hydrogen abstraction rate from the styrene and a critical kinetic step for the transition of the chain to the monomer. So, that is the important thing. Now, let us have a look about the powder suspension polymerization.

You see that when we started this suspension polymerization concept, we said that there are 2 type of things can be observed in the suspension polymerization, one is the bead suspension polymerization and other one is the powder suspension polymerization. So, the powder suspension polymerization is the most important polymerization process which is being used in the production of poly-vinyl chloride.

Now, the key benefit of this method is that the large porous polymer particles can be produced say, in the range of 300 to 500 micrometre with a quick residual monomer removal rate and a large plasticizer absorption capability. So, the development of polymer particles with the desired PST and the porosity, this can be accomplished by adjusting the quantity and the form of stabiliser as well as the speed of the agitator without influencing the molecule properties of the product.

So, polymerization is usually dime or isothermal basis temperature ranges between 45 to 70 degrees Celsius depending upon the target molecular weight. Again, the importance of molecular weight comes into the picture. In free radical VCM polymerization, the first polymer chain, this is we are producing one example, the first polymer chain formed within the monomer droplet are precipitated to form the unstable polymer micro domains with a diameter between 10 to 20 nano-meter.

Now, these micro domains demonstrate the minimal stability and aggregates to form the nucleus of the primarily particle, they are also known as a domain. So, the monomer conversion, this start-up is in the range of say 0.01 to 10%. The initially stage or initial size of these domain this lies in the range between 80 to 100 nano-meters and the growth of these domain via the polymerization of the absorbed monomer or by the a aggregation of other domain results in the primarily particle with the diameter in the range of say, 100 to 200 metre.

Sometimes, the critical monomer conversion is again very important. So, at critical monomer conversion, say in the range of say 10 to 30%, massive aggregation of primarily particle, this lead to the formation of 3 dimensional polymer skeleton. So, by this stage, you can start observing the things to be happening. Now, the primary particle, they continue to grow until the disappearance of the free monomer phase that is the fractional monomer conversion sometimes referred as XF.

So, the presence of secondary stabilisers at low agitation speed, the aggregation and subsequent fusion of primary particle, this can be limited with the individual primary particle may continue to grow up to the say of 1 to 1.5 micrometre in diameter. So, in that case, the primarily particle can be bundled tightly together without any noticeable aggregation; you cannot, the clear cut aggregation cannot be observed in this case. So, this results the close packed structure having a low porosity particle.

The porosity of PVC grain increases as sometimes the agitation rate is increased. So, strong agitation can also favour the aggregation of the individual polymerization particle, this leads to the formation of irregular PVC grains with the size range of 50 to 250 micrometre in diameter. So, you may experience the irregularity in the sizes structure. So, sometimes if you wish to have a specific use of these PVC grains, then you need to go for meshing or sewing of those particles being generated.

The main difference between the bulk and suspension process is that agitation which is used to control not only the aggregation of the primary particle, but also the size distribution of the final grains. So, sometimes if you are having the more and more agitation, in that case, your final grain size may become more and more finer. So, as a result of this above mechanism, the polymerization of VCM droplets sometimes they loses its viscous character at a relatively low monomer conversion.

While at large monomer conversion ($x > 30\%$) it behaves like a rigid sphere due to the presence of continuous polymer skeleton and sometimes, you may not even be in a position to process that particular thing. So, the above critical conversion that is $x_c \sim 30\%$, the volume contraction of the polymer particle stops and which partially you can say they explain the appearance of internal particle porosity.

So, at this particular juncture, the agglomeration and the volume contraction ceases. So, that means, you can say that the generation of internal particle porosity, it starts at this juncture. In the VCM, the suspension polymerization, there are 2 types of stabilisers as we talk in the previous one that is the primary and secondary. The key function of primary surface active agent is to control the grain size but also influence the internal grain porosity because grain porosity is again very important in case of the processability.

The other hand if you talk about the secondary stabilisers, they are the surface active agent with the high lipophilic content that is sometimes poly-vinyl called stabilisers with a low degree of hydrolysis. The improved stabilisation of primarily particle, this due to the absorbed secondary stabilisers, this result in the decrease in the rate of aggregation of the primary particles with the containment decrease in the porosity of the PVC grains.

One of the most efficient way of removal of polymerization heat is to use the overhead reflects condenser. So, that you may have overhead reflects condenser. So, any kind of exothermicity, it can be removed in due course of time. Now, this VCM vapour, they are diluted and returned to the polymerization suspension, while an equivalent volume of VCM is vaporised to preserve that thermodynamic balance as we discussed in the previous point.

So, the reflects, sometimes the reflects affects, the morphological properties of polymer whatever you produced in due course of time, because the morphological properties again very crucial when we talk about other application of the polymer being produced under the head of a PSP. The particle size and the porosity of a PVC grains, this shows the direct proportion relation with the operation time of a condenser and reflects rate.

So, these two things are supplement to each other. It is also advisable to use the reflex condenser after a monomer conversion of about 5% is reached. So, you can say, this is the critical time to add the reflects condenser. Early utilisation sometimes can lead to the higher condenser fouling and sometimes of disturbed rates in concept. It just found that to be more safer and convenient to use the reflects when monomer conversion reaches about 20 to 30%.

Now, as its effect on PST becomes insignificant and a substantial effect on the grain porosity, you can easily observe. For the case of VCL suspension polymerization, reflects can introduces some operational problems. Let us take one example that non-condensable gases may be concentrated in the condenser which can reduce the heat removal capacity. So, this particular approach need to be required our attention.

Now, the value of non-condensable gases in vapour phase side, this depends on the quality of monomer. What kind of quality are you using? Then vacuum prior to polymerization and generation of various inert gases during the polymerization process. So, let us take the example like azo initiator, they can lead to the formation of N_2 as a by-product of the initiator decomposition. So, this creates significant effect within the reactor mass.

Now, sometimes if we use the carbonate buffer during the process, the CO_2 sometimes it will form and if the aqueous phase becomes more and more acidic in nature. So, in this particular lecture, we discussed about the various aspects of suspension polymerization, the special attention was attributed to the powder suspension polymerization.

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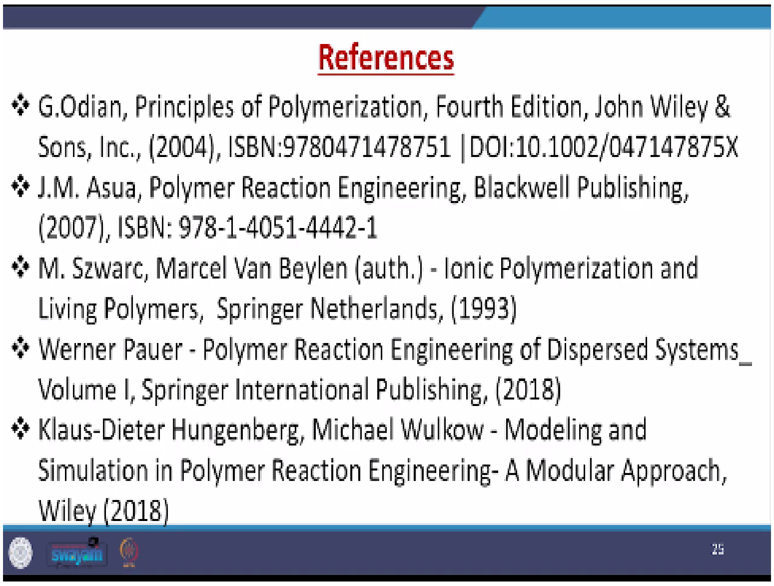

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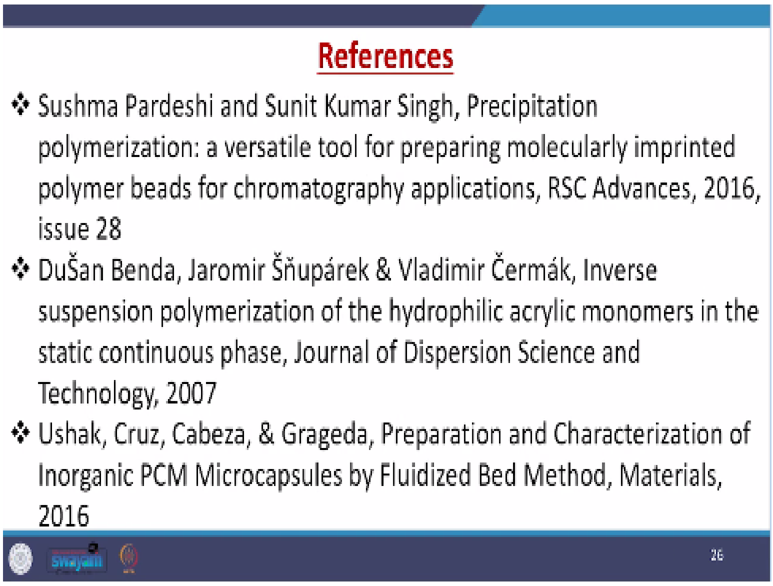

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And if you have anything in your mind, then you can refer to these references which are listed over here. Thank you very much for paying attention.