

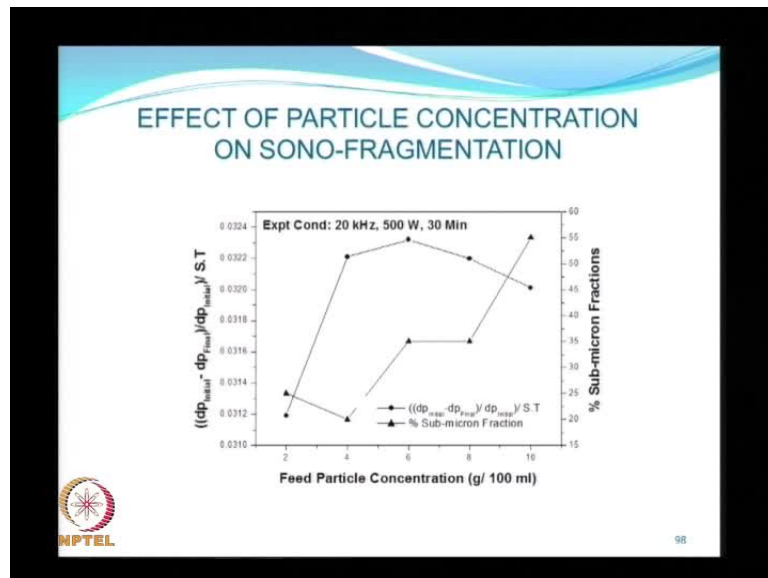
Particle Characterization
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Module No. # 11

Lecture No. # 31

Nano-particle Characterization:
Dispersion

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Welcome to the thirty first lecture in our Particle Characterization course. In the previous lecture, we have looked at various methods of synthesis of nano-particles. Initially, we discussed bottom-up approaches, and later, we started reviewing methods for making nano-particles by a top-down approach, where you start with particles that are larger in size and then fragment them to smaller dimensions.

In particular, we looked at high energy ball milling as a method that can be used for making fine particles. However, the mechanism involved in a ball mill is such that, as particle size gets smaller and smaller, it becomes increasingly more difficult and energy inefficient to produce additional surface area. So, we introduced the method of sono-fragmentation, which is the use of an acoustic field which is coupled to a liquid medium,

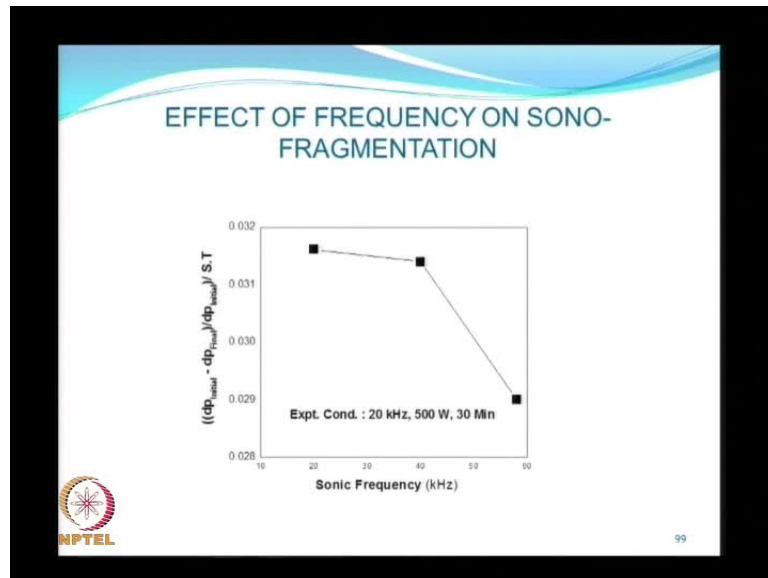
and the propagation of this acoustic field in the liquid produces standing waves, that are characterized by compression and rarefaction cycles. And essentially, in an acoustic field you form bubbles during the rarefaction phase, which are compressed and which implode during the compression phase, and as they do they release a large amount of energy in the form of a shock wave. And when this shock wave impacts on a particle, you can actually cause it to shatter, producing many fine particles.

The other mechanism is that, one particle can be accelerated and made to impact on another particle, and the combined effect on these two mechanisms is to produce smaller particles starting from a feed size that is considerably larger. So, we were reviewing some data from this process of top-down method of nano particles synthesis, and we will continue to do that in this lecture. So, one of the key parameters is particle concentration and its effect on sono-fragmentation efficiency.

If you plot the size reduction characteristics against the feed particle concentration, you see that there is an interesting behavior that happens, which is that, the mean size actually is reduced to the greatest extent at some intermediate value of particle concentration. If the concentration is lower or higher than this optimal value, then size reduction is reduced. And the reason for this is because there are two mechanisms involved in sono-fragmentation. Initially, as particle concentration increases, the particle to particle distance decreases, and therefore, the probability of one particle impacting on another increases. So, essentially an increase in particle concentration leads to an increase in fragmentation efficiency. However, above a certain threshold concentration, the particle mass loading in the liquid becomes so high that the cavitation field itself is dampened or suppressed, and you start seeing the reverse effect, whereas, particle concentration increases, the fragmentation efficiency decreases.

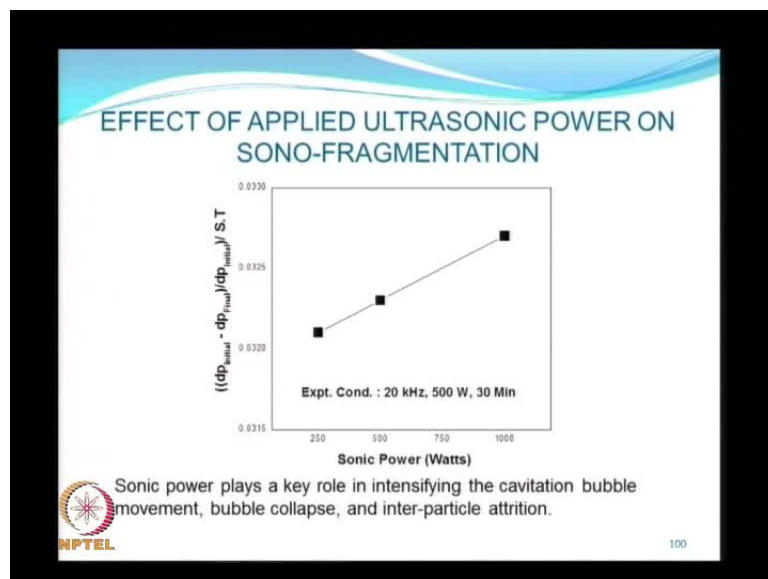
So, there is an optimum value of particle concentration at which the fragmentation efficiency is a maximum. However, if you look at the submicron fraction percentage, which is plotted on the right hand side vertical axis, you will see that this behavior is much more monotonic in nature, and that as particle concentration increases, we continued to see an increase in the percentage of particles that are reduced to a submicron size range.

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The effect of frequency on sono-fragmentation is fairly obvious as frequency increases, as we have discussed earlier, there is a drop in cavitation intensity, which scales as 1 over f cubed. So, as the frequency increases, there is a very rapid drop in cavitation intensity and there is accompanying reduction in the rate at which particles are fragmented, and this is shown in this particular case.

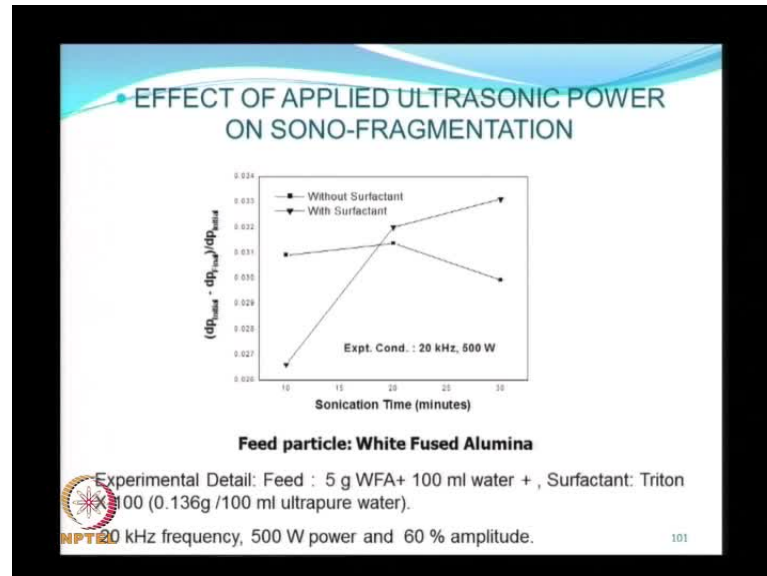
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Power also has a linear relationship to fragmentation. As you increase the power of the acoustic field, that is the input power or amplitude, there is a corresponding increase in

size reduction efficiency, and therefore, essentially by using higher power ultrasound, you can get additional break down of particles by the fragmentation mechanism.

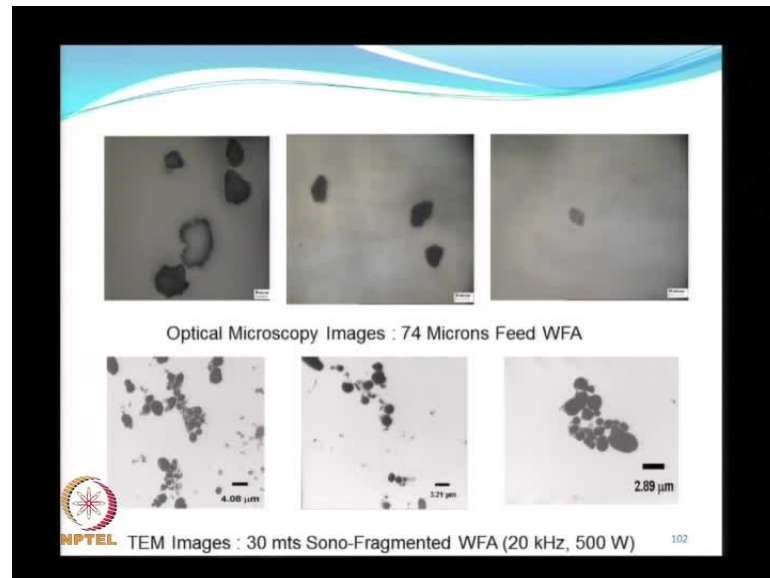
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And in this case, what we are plotting is time versus size reduction efficiency. And here you see that, as the time increases, the reduction in particle size keeps increasing, particularly, when you use a surfactant. Now, the use of a surfactant is very critical for two reasons. One is that, the surfactant can actually coat on the nano particles that are produced and keep them from agglomerating. As we have discussed in earlier lectures, particle cohesion is a major phenomenon in nano particle suspensions, and by coating the particle with a suitable substance, you can essentially make the particles repel each other in suspension, and keep them from agglomerating.

So, if you compare these two graphs; one with surfactant and other without the surfactant. **Without the surfactant**, the fragmentation rate is eventually equaled or exceeded by the rate of agglomeration. So, even though you may be fragmenting the particles by ultrasound, they will reattach or re-agglomerate, and therefore, there is no sustained particle reduction beyond a certain time. However, with the use of surfactant, as you increase the amount of sonication time, you will see that the size reduction keeps increasing, although the rate of size reduction does tend to reach a saturation point.

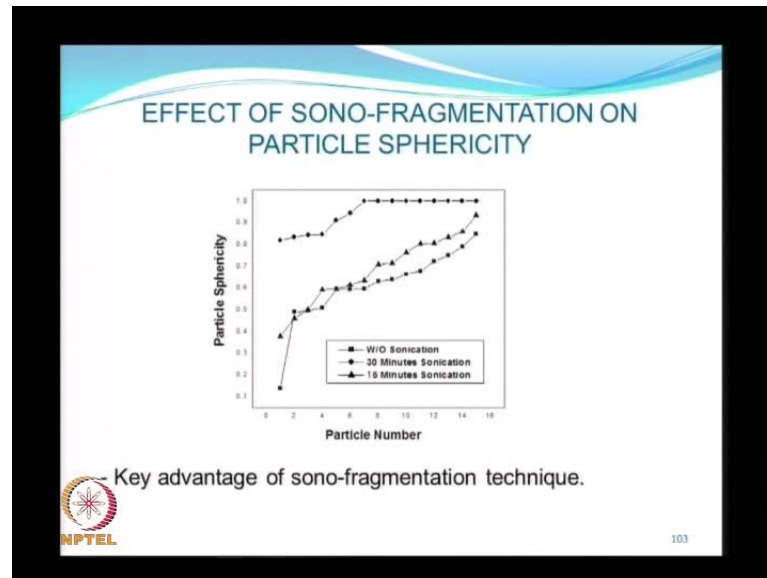
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Now, in terms of characterizing these particles that are produced by sono-fragmentation, microscopy is, obviously, very useful technique. Now, to look at the feed alumina particles, optical microscopy is sufficient, since these are in the micron size range. The feed particles size here is in the 74 micron range. However, after sono-fragmentation you really cannot see the particles any more using optical microscopy. As we have discussed earlier, optical microscopy is limited by its magnification, even the best optical microscopes that are available today can produce only about a 1000 x magnification, which is still not sufficient for us to be able to see and resolve nano dimensional particles, so then, you resort the techniques like SEM and TEM. And the pictures below show TEM images of white fused alumina particles that have been exposed to 30 minutes of sono-fragmentation at 20 kilohertz and 500 watt input power. And you can see that, there is a substantial size reduction, many of the particle that you see in the picture are in the micro to submicron range. And also the level of agglomeration is not very significant, although the picture on the right hand side shows increased agglomeration.

One of the advantages of the ultrasonic method of size reduction is that, unlike ball milling, which actually promotes agglomeration, the mechanism of sono-fragmentation provides for simultaneous dispersion. So, as you are reducing size, you are also dispersing the particles.

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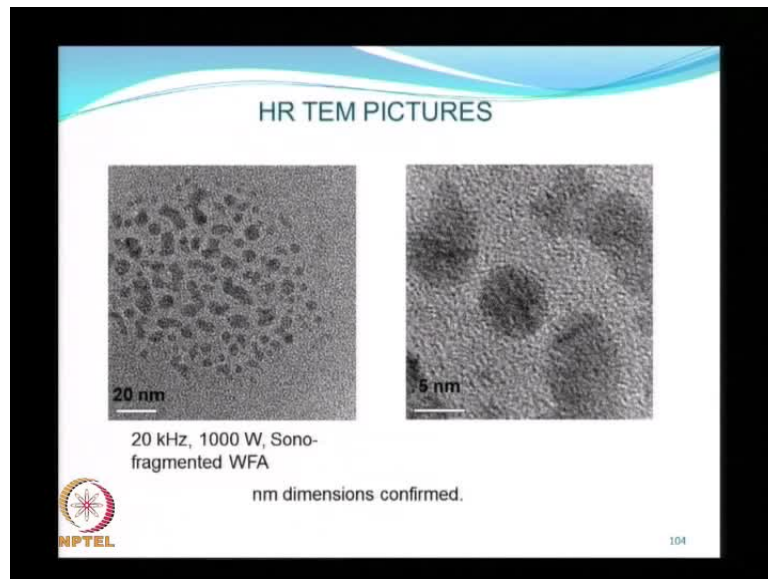
So, the extent of agglomeration that you see, is significantly less in sono-fragmentation method of top-down nano particle synthesis compared to various other methods, that are in use. Another interesting effect of sono-fragmentation has to do with shape, as we discussed in the first lecture, the two most significant characteristics of particle are size and shape, from a morphology view point.

And in the previous SEM pictures, we saw the effect of fragmentation on size; here we are looking at its effect on sphericity. It turns out that, when you expose particles that are crystalline in their structure to sono-fragmentation, they become increasingly rounded. So, sono-fragmentation actually has the effect of increasing the sphericity of the particles. So, here we are plotting particle sphericity in the three different conditions; before sonication, after thirty minutes sonication, and after fifteen minutes sonication. And you can see that the particles that before sonication, were very low in their sphericity index, eventually reach virtually 1.0 on their sphericity index, after 30 minutes of sonication. Here, the sphericity is being defined as, essentially, an l by d ratio, which is a reasonably simple and straight forward representation of particle shape. The biggest limitation of [here](#), of course, is that it essentially reduces the three-dimensional object, like a particle, to its two-dimensional representation, but conventionally l by d ratio have been accepted as measure of sphericity or elongation.

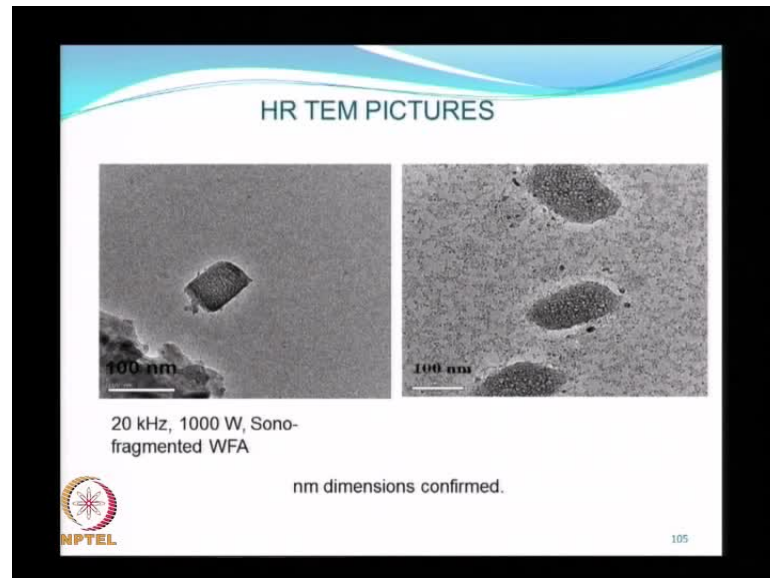
So, when we look at fifteen particles at random, and the data are plotted in this graph, you can see that out of the fifteen particles, about more than half of them are perfectly spherical after thirty minutes of sonication, even though before you began the sonication, virtually none of them were spherical in shape.

So, this rounding off effect could be an advantage of this technique depending on the application. There are certain nano applications, where rounded particles are preferred over elongated particles, and there are applications, where that is not a such good thing. So, you have to match the technique of synthesis to the application at hand, and in this case, shape analysis is an important aspect of determining what process to use.

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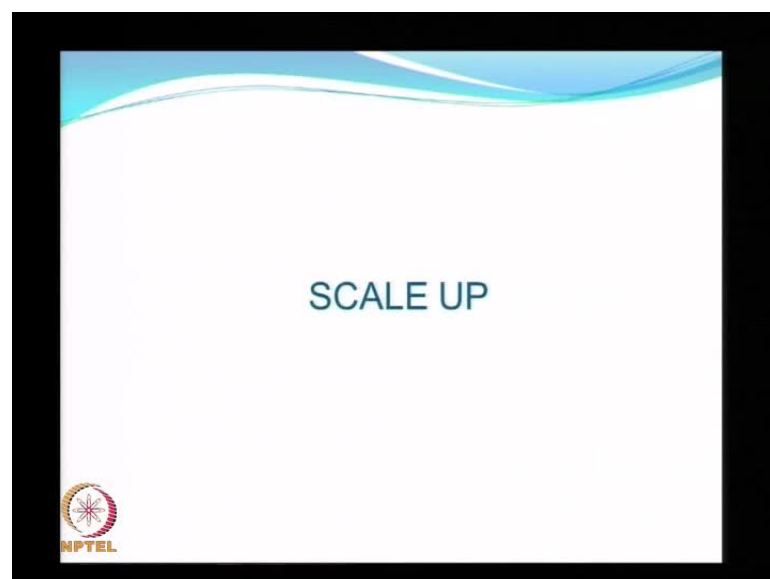


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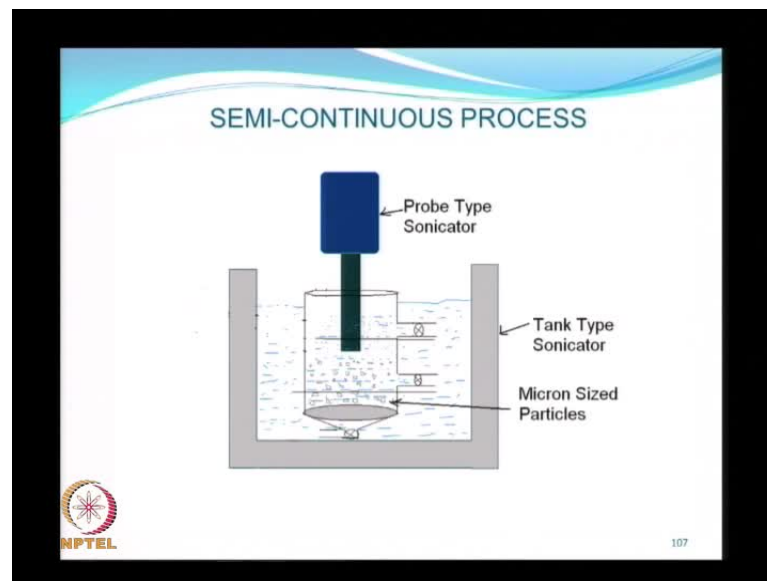
These are more high resolution TEM pictures of nano dimensional particles produced using sono-fragmentation. This was done with a probe type fragmented at 20 kilohertz frequency and 1 kilowatt input power. And essentially, by using these high resolution TEM pictures, we have been able to confirm that we are producing a large number of particles, that are in the nanometer dimensions. And here are some more pictures of the nano particles that are produced by the method of sono-fragmentation.

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Now, one of the important considerations for engineers, and again as I mentioned earlier, what differentiates nano science from nano technology is our ability to scale up to commercial volumes. It is not enough if we produce enough material to play with in the lab, it has to be something that can be produced and ship to the market in large enough quantities, that it actually makes a difference to a large numbers of consumers.

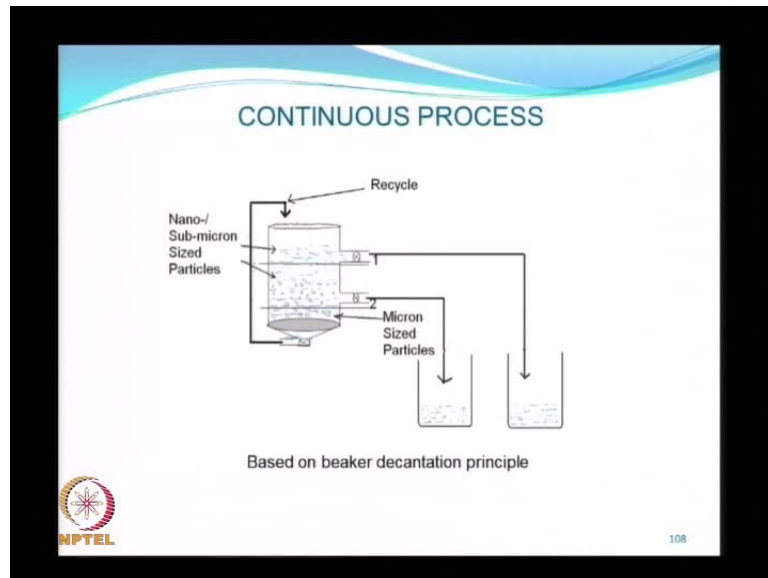
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For that, scale up is a very important consideration. Now when we look at this method of sono-fragmentation, it actually lends itself very well to scale up. The reason is that, when we do sonication, we are producing a variety of particle sizes, many of the particles are getting size reduced to submicron and nano dimensions, and many particles that are not **impacted** directly by the ultrasonic energy will remain as micron size particles.

So, if you can combine this sonicator setup with some kind of a beaker decantation type of a arrangement, which will continuously separate the size reduced nano dimensional and submicron particles from the micron sized feed particles, and setup a recirculation recycle loop, where the course particles are continuously fed back into the sonication bath. In concept, you can actually setup a continuous flow process or at least a semi-continuous process, to make nano particles and to separate them by size, using a combination of sono-fragmentation and beaker decantation.

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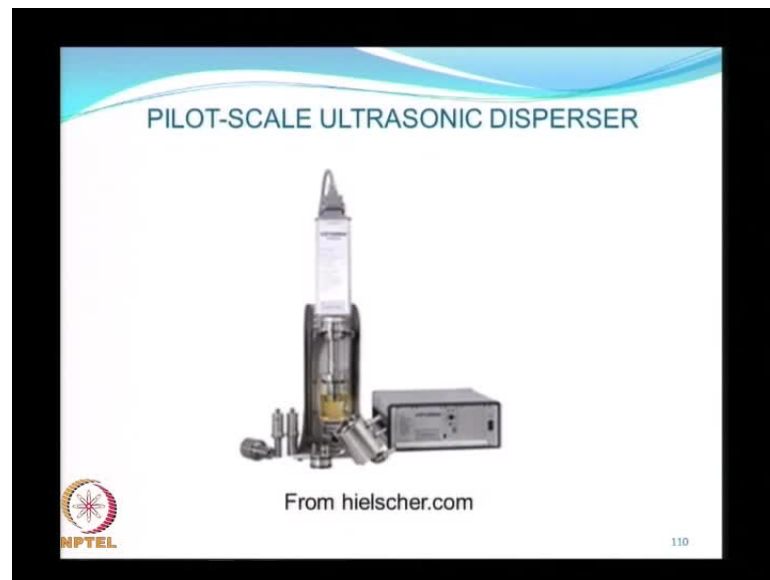
So, in the case of a continuous process, what we would do is, essentially have a solution that contains these feed particles, exposed them to ultrasonics, and convert a fraction of them to nano and submicron dimensions, and drain these off into a collector and capture them, for subsequent use. Whereas, the larger particles that are not yet size reduced, will sink to the bottom of this container just because of gravity and sedimentation, so they can be taken out from the bottom and recycled back into the sonication chamber and size reduced further.

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So, you can imagine that this type of a simple setup can be easily fabricated to produce a continuous stream of nano and submicron sized particles, which can be collected for subsequent use. And in fact, there are various commercial equipment that are available to do size reduction using acoustic technology. At lab-scale, ultrasonic homogenizers are widely used. These are essentially mixers, so they are more used for the purpose of dispersion. When you have a nano suspension, as we have repeatedly said, one of the biggest challenges is to keep the particles dispersed in suspension, as an ultrasonic homogenizer essentially works by imparting an acoustic a high frequency acoustic field to the suspension, which constantly keeps it mixed and keeps the particles well segregated.

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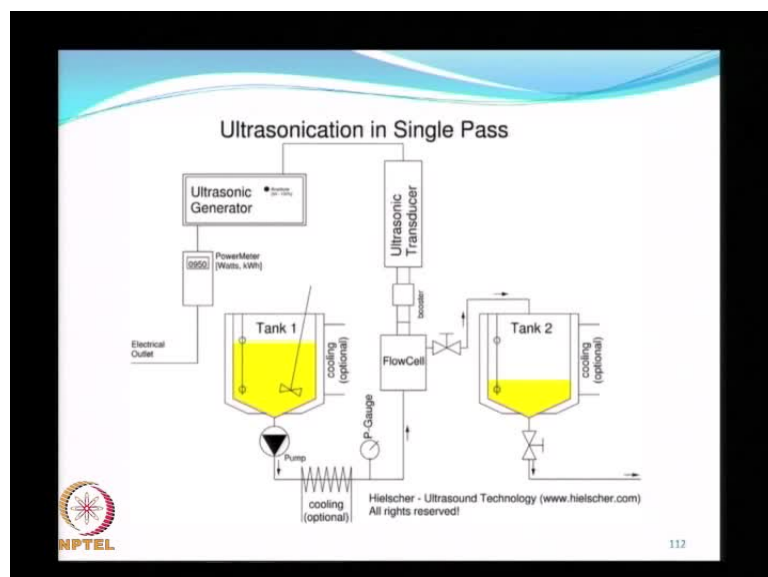


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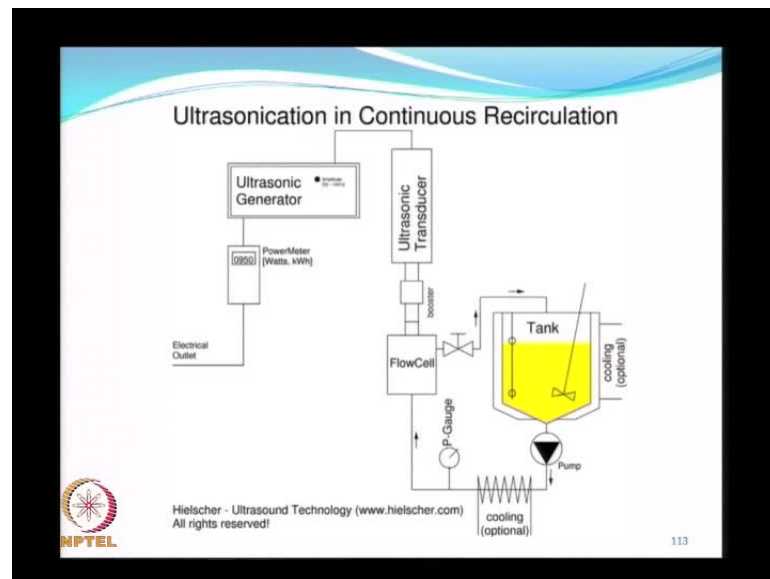
At pilot-scale, the same ultrasonic disperser can look like this. So, it uses pretty much the same principle, except that it is now at a slightly larger scale, that can be used to process liters per hour of suspension volume. And you can keep scaling this up to industrial scale, and there are industrial scale ultrasonic dispersers that are in the market today, and they have, what is known as a flow cell, so this is basically the continuous through put kind of a system that I had sketched in a couple of slides ago, where these suspension containing micron size particles **are** is constantly being pumped through a flow cell, where the suspension is exposed to an ultrasonic field and size reduction happens.

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So in this case, you can setup a process by which you are constantly pumping in micron size suspensions and drawing out submicron and nano dimensional suspensions. Now, ultrasonication can be done in two ways. One is the single pass mode, and again this is actually commercially available setup, that is marketed by a company called Hielscher in Germany. And you can see here that, essentially you have a flow cell, into which you are pumping liquid from tank 1, size reduction happens and the output from the flow cell is then collected in tank 2.

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So, this is essentially a single pass type of an arrangement, where material is taken from tank 1, exposed to ultrasound, and then the outlet goes into a collection tank, tank 2. In continuous recirculation mode, this arrangement can be modified, so that you also build in the ability to recycle material. So here, there is a single tank in which material is stored, which is pumped to the flow cell, and size reduction happens, and the solution is then pumped back into the tank.

The difference between this and the concept of beaker decantation, that I had sketched earlier is, in this arrangement, there is no active separation of the nano sized particles and the larger size particles. So, in some ways this is kind of an inefficient arrangement, because you are recycling everything from the flow cell. So, even particles that have already been size reduced will be exposed to further ultrasound, which kind of defeats the purpose. So, by combining this setup with a probaton for doing beaker decantation and

automatic separation of particles by size, you can improve the efficiency of this process by several degrees. So far what we have talking about is, essentially synthesis of nano particles and using bottom-up as well as top-down approaches. And we have briefly indicated some characterization techniques that are used to follow the efficiency of these processes. Because when we talk about nano synthesis, the primary morphological characteristics are size and shape, and we have seen some examples of how these can be characterized.

However, the challenge still remains once you have synthesis nano particles, how do you keep them in their nano form. So, dispersion is an important consideration in colloidal suspensions as well as composite materials. So, particles dispersion needs to happen in fluids as well as in solids. So, when we talk about particle dispersion in fluids, **we are** primarily talking about suspensions of nano particles, mostly in liquids, and how we can keep these nano particles separate and apart from each other during their storage.

Whereas, when we talk about nano particle dispersion in composites, we are talking about dispersing the nano particles uniformly in a solid surface, like for example, a polymer. And so these are two different, again, interesting challenges and techniques that work for keeping particles uniformly dispersed in solutions are also of some importance to keeping them dispersed in solid surfaces. However, there are some fine differences between the two as well as, we will see.

And the other thing that we would note is that, characterization techniques that were particularly useful for monitoring size reduction in nano particle synthesis are not always the same techniques, that are used to characterize dispersion of nano particles. We really use a different set of techniques to monitor dispersion compare to size reduction.

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The slide is titled "NANOPARTICLES IN SUSPENSION" and contains the following content:

- Cohesive tendency
 - Hydrophobic particles in water attract
 - Hydrophilic particles in water repel
 - Hence, surfactant coating of nanoparticles in suspensions helps keep them apart
- Dynamic behavior
 - Mean size increases with time
 - Total # decreases with time
 - Population balance modeling required

Dispersion just prior to processing is generally required

NPTEL 115

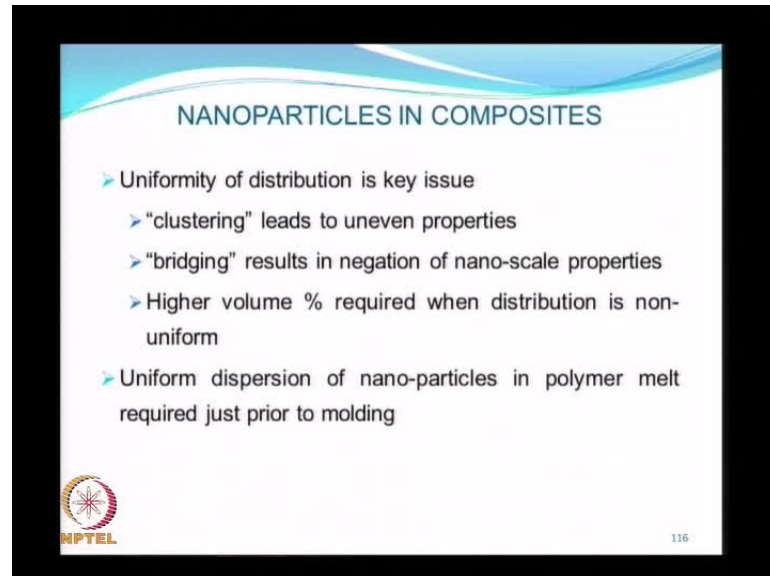
So, when we talk about nano particles in suspension, the cohesive tendency is something that we always have to deal with, and we have discussed this quite extensively in previous lectures. So, when you have hydrophobic particles in water, as we saw earlier, they will tend to attract. When you have hydrophilic particles in water, they will tend to ripple each other, because they have more affinity for water molecules. So, surfactant coating of nano particles in suspensions will help keep them apart.

Now, in terms of dynamic behavior of nano particles in suspension, because of the tendency to agglomerate, the mean size will always increase with time, and the total number will always decrease with time. And we have previously looked at equations that governed the kinetics of this process.

So, **the** to characterize the dynamic behavior of particles in suspension, requires population balance modeling, which will take into account formation of particle clusters by the mechanism of agglomeration as well as the breakup of clusters of molecules through the dispersion process. Now in general, because nano particles have a tendency to attach, you need to disperse them just before processing. So, for example, if you are trying to make nano fertilizers, and you want to add some nano particles into your fertilizer to make it more effective, it is better to disperse these nano particles into your fertilizer product just before you are ready to seal up the fertilizer in bags and shift them to customers. Dispersion is something that has to be done virtually just in time, if you do

dispersion very early in your process, by the time you get to the end of the process the particles would have reattached, so it does not really help much.

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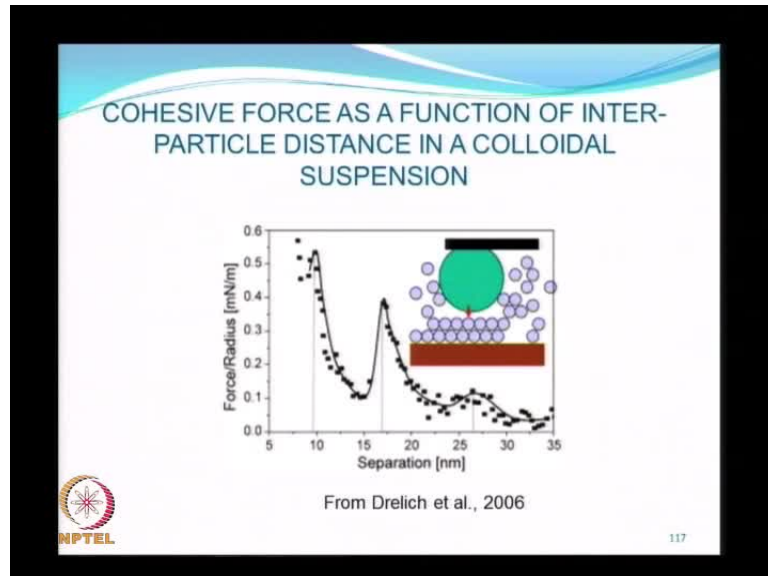
Nano particles in composites, again uniformity of distribution is the key issue. Nano composites, as we know, have some wonderful properties in terms of increased **wire** resistance, in terms of increased conductivities, in terms of increased strength and so on; however, they all rely on uniform distribution of the nano materials in the polymer matrix.

If the particles cluster, that can lead to uneven properties. So, you may have high strength in one area and low strength in other areas. Bridging can also result in negation of nano scale properties. You are relying on the nano particles to be present in isolated form, in order to achieve the property enhancements that you are looking for, if you allow particles to cluster or bridge it can defeat the purpose. Higher volume percent may be required when distribution is non-uniform.

One of the main attractions of using nano adhesives is that, for the same volume of material you can get a much greater enhancement when you use it in nano, because of the increase surface area per unit volume. However, if the distribution is not uniform, then you lose that advantage, and you have to increase the volume percent of material that you use, so the cost advantage is lost. So here, particularly when you are making

nano composite polymers, uniform dispersion of nano particles in the polymer melt is an absolute requirement, and it should be done just prior to molding the plastic material.

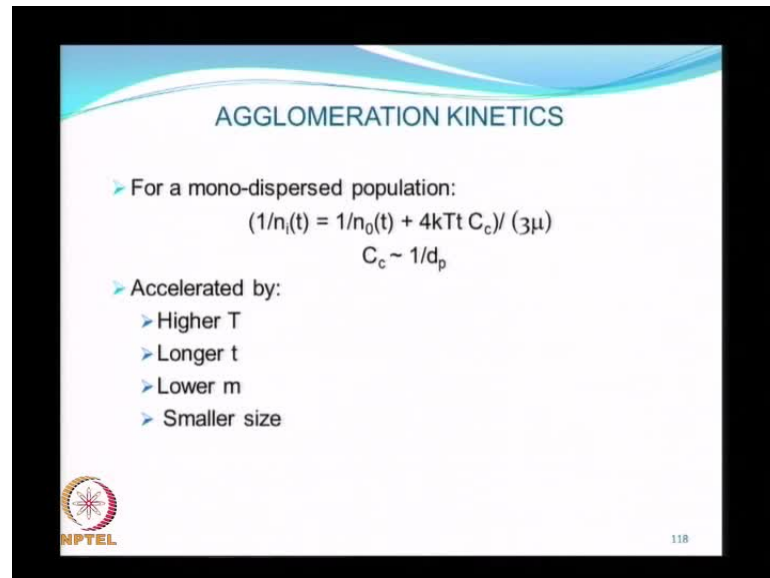
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Now, previously we have discussed how inter particles adhesion forces vary as a function of particle size, inter particle distance and so on. Here is a chart from Drelich et al, 2006, that shows the force per radius of the particle versus the distance of separation between the particles, and you can see that in general, there is a decrease in trend as particles move away from each other.

So, the implication of this for cohesion is that, if you have a more dilute suspension, your chances of avoiding cohesion are much better. But as the particles concentration in suspension increases and the inter particle distance decreases, the forces of adhesion between the particles becomes much larger.

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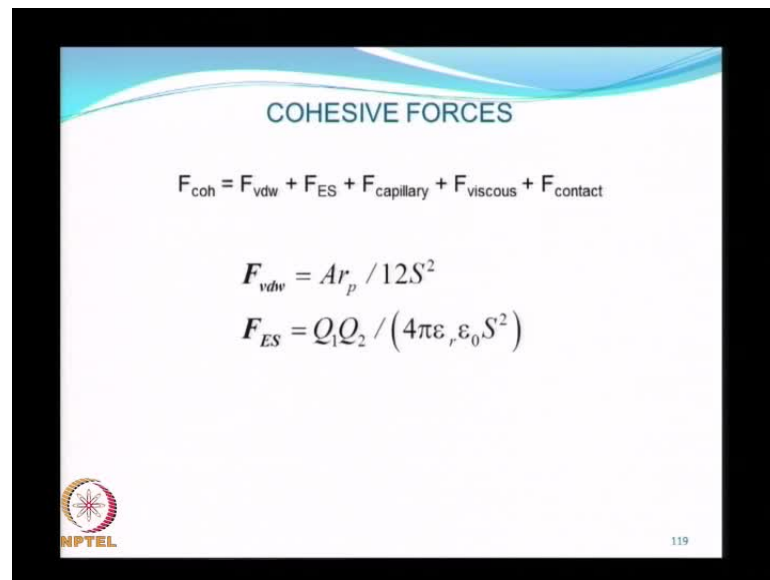
The slide is titled "AGGLOMERATION KINETICS" and contains the following content:

- For a mono-dispersed population:
$$\left(\frac{1}{n_i(t)}\right) = \frac{1}{n_0(t)} + \frac{4kTt C_c}{3\mu}$$
$$C_c \sim 1/d_p$$
- Accelerated by:
 - Higher T
 - Longer t
 - Lower μ
 - Smaller size

The slide also features the NPTEL logo in the bottom left corner and the number 118 in the bottom right corner.

Agglomeration kinetics, we have reviewed this in one of the earlier lectures, for a mono dispersed population, that is, populations containing particles of a single size, $1/n_i$ as a function of time equals $1/n_0$ as a function of time plus $4kTtC_c/3\mu$; where C_c is the stokes Cunningham correction factor, μ is viscosity, upper case t is temperature, lower case t is time, n_0 is the number of particles at time equal to 0 and n_i is the number of particles at time equals t . You can see from this equation that, agglomeration is accelerated at higher temperatures over longer time durations, and when the viscosity is lower, there is an increased agglomeration tendency, and of course, smaller sizes lead to higher cohesive behavior.

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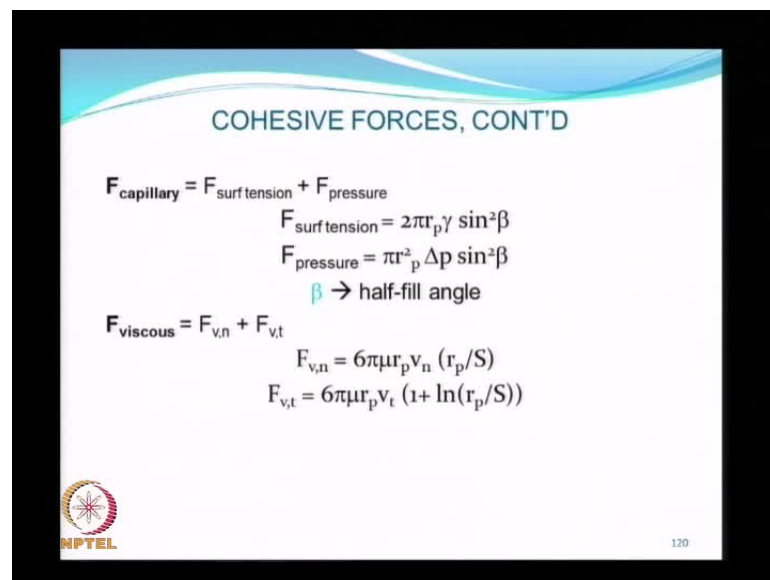
COHESIVE FORCES

$$F_{\text{coh}} = F_{\text{vdw}} + F_{\text{ES}} + F_{\text{capillary}} + F_{\text{viscous}} + F_{\text{contact}}$$
$$F_{\text{vdw}} = Ar_p / 12S^2$$
$$F_{\text{ES}} = Q_1Q_2 / (4\pi\epsilon_r\epsilon_0S^2)$$

NPTEL 119

And again, we have previously reviewed cohesive forces between particles, which can be looked at as a sum of Van der Waals forces, electro static forces, capillary forces, viscous forces and contact forces. And we have seen the expression for these forces.

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COHESIVE FORCES, CONT'D

$$F_{\text{capillary}} = F_{\text{surf tension}} + F_{\text{pressure}}$$
$$F_{\text{surf tension}} = 2\pi r_p \gamma \sin^2\beta$$
$$F_{\text{pressure}} = \pi r_p^2 \Delta p \sin^2\beta$$

$\beta \rightarrow$ half-fill angle

$$F_{\text{viscous}} = F_{\text{v,n}} + F_{\text{v,t}}$$
$$F_{\text{v,n}} = 6\pi\mu r_p v_n (r_p/S)$$
$$F_{\text{v,t}} = 6\pi\mu r_p v_t (1 + \ln(r_p/S))$$

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COHESIVE FORCES, CONT'D

$$F_{\text{contact}} = F_{\text{contact},n} + F_{\text{contact},t}$$

$$F_{\text{contact},n} = k_n \alpha^{3/2}$$


$$\alpha = r_{p,1} + r_{p,2} - S_{12}$$

$$k_n = 4/3 E^* (r_p^*)^{1/2}$$

$$1/E^* = [(1-\nu_1^2)/E_1 + (1-\nu_2^2)/E_2]$$

$$1/r_p^* = 1/r_{p,1} + 1/r_{p,2}$$

$$F_{\text{contact},t} = F_{\text{contact},t=0} - k_t (\Delta S)$$

$$\Delta S = v_t dt$$


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The van der Waals force goes as it is propositional to the radius of the particle and inversely propositional to the square of the distance of separation, the electrostatic forces are go as $Q_1 Q_2 / 4 \pi \epsilon_0 r^2$, and we have looked at the expressions for capillary forces which are a sum of surface tension and pressure forces, and viscous forces which are the sum of normal and tangential viscous forces, and contact forces which are the sum of normal contact forces and tangential contact forces.

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Distributive Mixing

		POOR	GOOD
Dispersive Mixing	POOR	(a) 	(b) 
	GOOD	(c) 	(d) 

From rti.edu



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These equations we have reviewed quite extensively in earlier lectures. Now, the net result of all these forces is mixing. Now, when we talk about particles in suspension, there are two aspects of particle distribution and dispersion that we need to look at.

When we talk about dispersion, that is only one part of it. If you look at these figures a, b c and d, here a represents both poor distribution as well as poor dispersion. What we mean by that is the particles are clustered, which implies poor dispersion, and also these clusters are not uniformly distributed in the suspension or the matrix. So, distribution is poor as well. So, the top left hand quadrant represents, kind of the worst case, poor dispersion and poor mixing.

Now, case b actually represents good distribution. The particles are clustered, but the clusters themselves are well distributed, uniformly distributed. So, this is the case where you have good distribution but poor dispersion. **Then** you have case c which is the inverse, you have actually good dispersion. The particles are not clustered, they are not agglomerated; however, they are not uniformly distributed.

So, these are examples of good dispersion, **but** poor distribution. So, ideally the scenario that we want to achieve is shown in d, which shows good distribution and good dispersion. The particles are all present as isolated discrete particles, so there is no dispersion, I mean there is no agglomeration or cohesion, and also, all the particles are well distributed in the matrix that we are looking at. So, this combination of good dispersion and good distribution is what we try to achieve, whether we are trying to make nano particles in suspension or nano composite materials.

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The slide is titled "Methods of Dispersion in Suspensions & Composites". It lists three methods: Stirring, Orbital shaking, and Sonication. A photograph shows a magnetic stirrer with a beaker containing a white substance. The NPTEL logo is in the bottom left, and the number 123 is in the bottom right.

Methods of Dispersion in
Suspensions & Composites

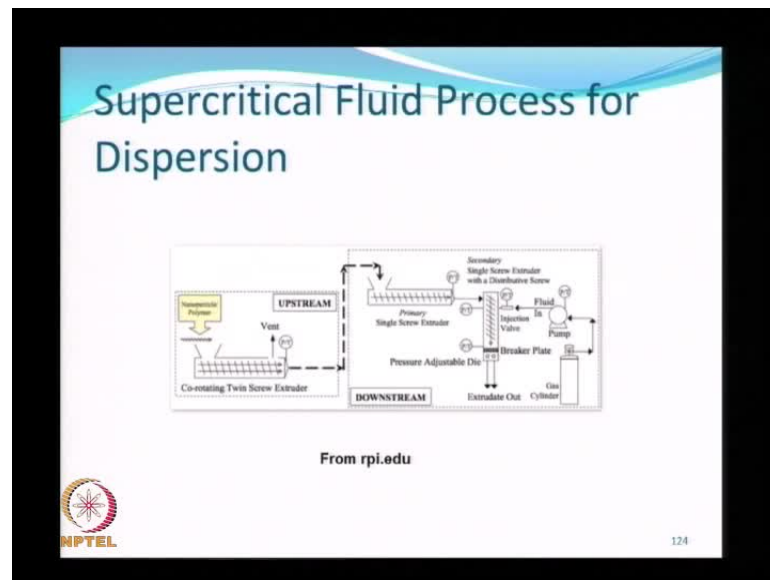
- Stirring
- Orbital shaking
- Sonication

Preparation of a polymer gel on a magnetic stirrer

NPTEL 123

So, what are the methods of dispersion of nano particles in suspensions and composites? Well, the most common methods are Stirring, Orbital shaking and Sonication. As you can imagine, in the Stirring process you essentially use a stirrer, whether it is a magnetic stirrer or an electrical stirrer or otherwise, to keep the suspension well stirred, so that the particles are uniformly distributed and dispersed. An Orbital shaker essentially provides a centrifugal force, which can again prevent particles from becoming dispersed. And finally Sonication, as we have seen earlier, in addition to providing high cavitation intensity for fragmenting particles, the fields associated with sonication can also keep the particles well dispersed in solution.

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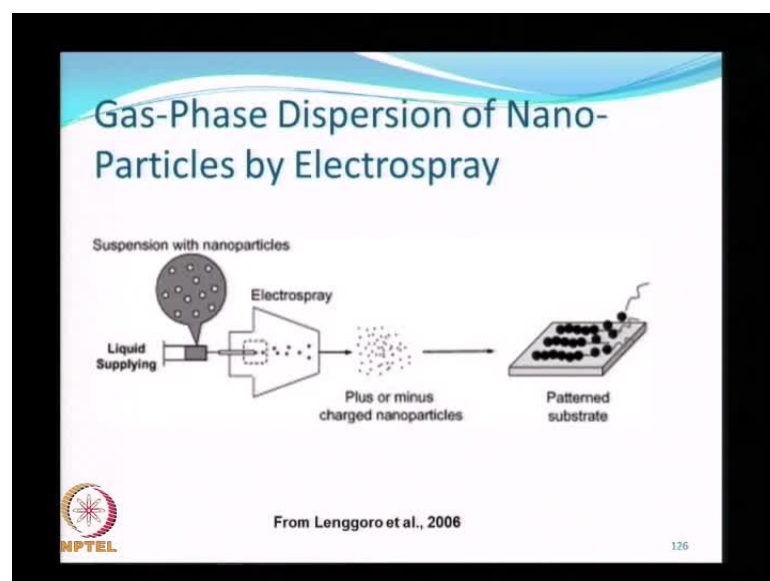


Another interesting process for dispersion is to use supercritical fluids, for this purpose. Essentially, a supercritical fluid is one that combines some of the properties of a gas with some other properties of a liquid. So, it has the high viscosity that characterizes a liquid, but it has the high diffusivity that characterizes a gas. So here, you can take advantage of the high diffusivities in order to make the nano particles dispersed very well in solution, and you can make use of the high viscosities to keep the particles in place once **they are** dispersed. So here, essentially you achieve your **distribute** dispersion and distribution in a two step process, and use the high density and viscosity of the supercritical fluid to keep the particles in place, once you have dispersed them.

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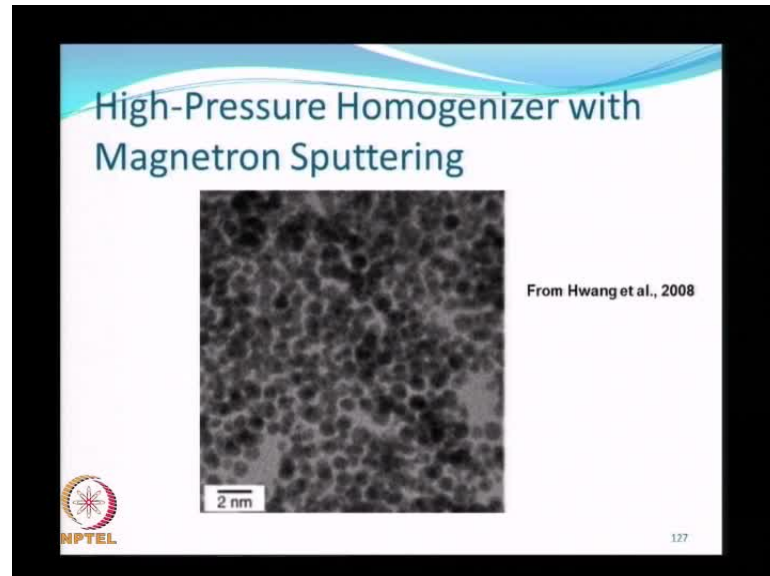
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Magnetic dispersion will work for particles that are magnetizable. So, if you are trying to make a composite material that has magnetic nano particles, or you have a solution of magnetic particles in suspension, you can keep them segregated dispersed by them by appropriately applying a magnetic field. Another technique that can be used for dispersion of nano particles, which is particularly effective in the gas phase, is Electro spray. So, here you intentionally induce a charge on the particles. And since a particle charges that is been induced is the same, whether it is a plus or a minus, all the

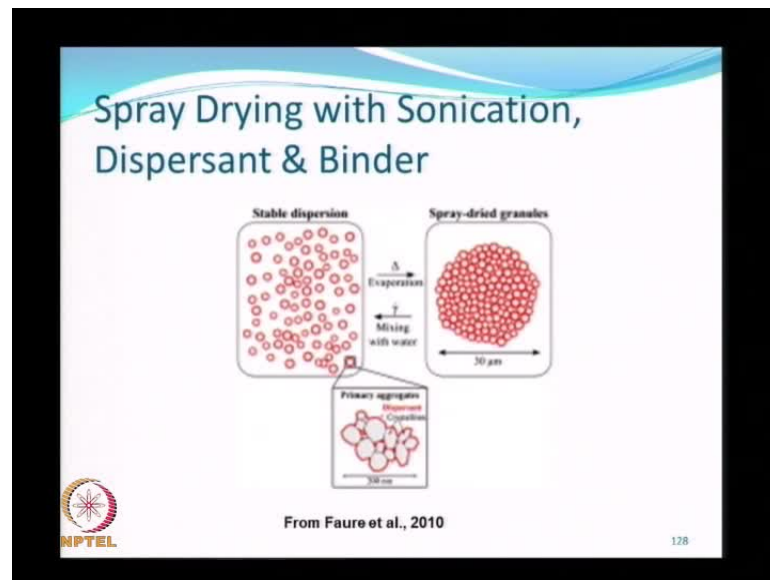
particles will have the same charge and therefore, there will be automatically repulsive field setup between the particles.

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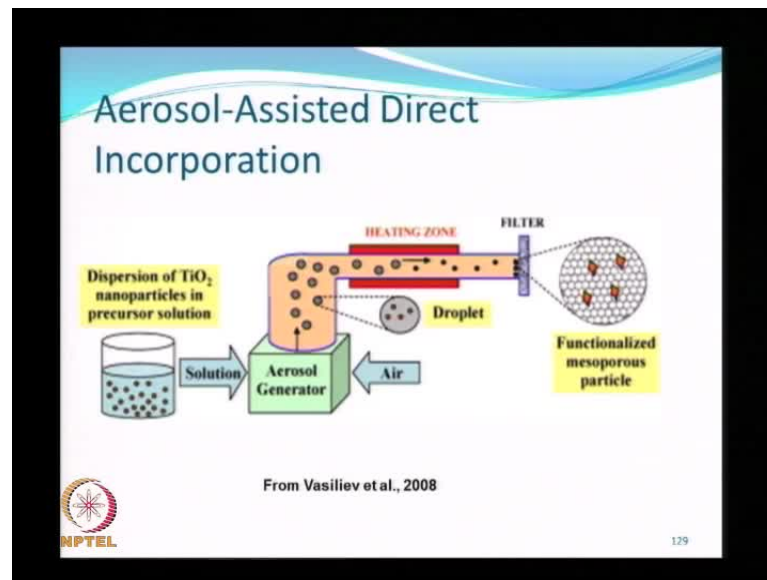
So, by inducing light charges on nano particles in gas phase, you can essentially combat the tendency to agglomerate and keep the particles well separated. A High- Pressure Homogenizer with Magnetron Sputtering is another example of achieving a high level of dispersion. So here, essentially what you are doing is, providing energy to the particles. When you energize the particles, they have a tendency to reach an equilibrium state, and this equilibrium state essentially will require that they establish positions, that are separated from each other. And so, by combining High- Pressure Homogenization with a Magnetron Sputtering Process, you can energize the particles and make them reach an equilibrium position, that is well dispersed in the suspension.

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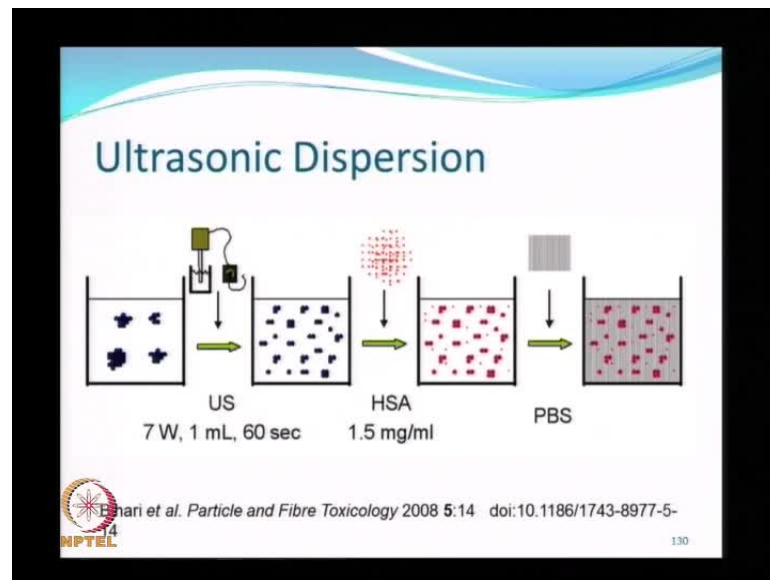
Spray Drying is another example of particle dispersion. In a spray drier, essentially you take a liquid suspension and accelerate it through a nozzle, and you expose it to the co-current or counter current flow of a hot gas. Now, as you do that, the excess water will evaporate, and you will get a structure that looks like, what on the right hand side. So, the spray dried granules themselves tend to be very uniform in size; however, in the conventional spray drying process, unless you add a dispersant they will tend to agglomerate into clusters. So, when you combine Spray Drying, either with Sonication to do downstream dispersion, or with the addition of a dispersant which will essentially coat on these particles and keep them dispersed, you can obtain well dispersed nanoparticles, by using spray drying as the methods of obtaining these particles.

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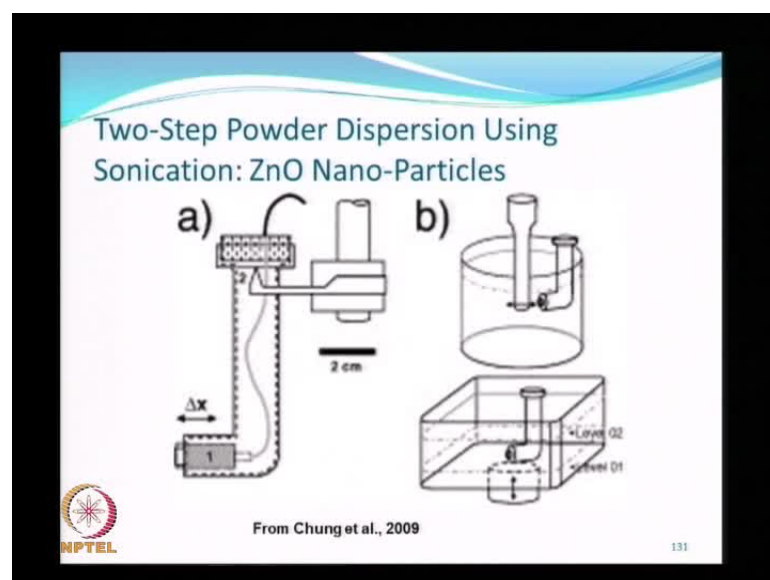
Another process that is used to get well dispersed nano particles is called Aerosol-Assisted Direct Incorporation. So here, you first prepare a dispersion of the nano-particles in a precursor solution, and then convert it into an aerosol, because an aerosol is essentially a suspension of droplets in air. So, by introducing air into the solution, containing the nano particles, you can make a droplet aerosol. And then, you heat it to evaporate the solvent, and then you take it through a filter to produce nano-particles that are of a well contained size range. And then you directly impact the surface, on which you are trying to deposit these nano-particles, for example, this may be a porous surface, into which you are trying to install these nano-particles. So in this case, you will take the aerosols that are coming out of this chamber, and directly impact the surface with these materials and obtain a functionalized mesoporous particle substance. The primary consideration here is that, you want the aerosol to impact the surface as a line of sight phenomenon, so that individual particles get captured in individual pores. So here, the porosity of the substrate is used to keep the particles segregated. Once the particles get incorporated in these pores, they really cannot move around anymore and fine each other.

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And finally, Ultrasonic Dispersion is something that many have looked at. In Ultrasonic Dispersion, you combine ultrasonics with a liquid phase in order to achieve both size reduction as well as dispersion. And as you can see in this schematic, you can achieve both the size reduction as well uniform dispersion and distribution, by utilizing an ultrasonic technology.

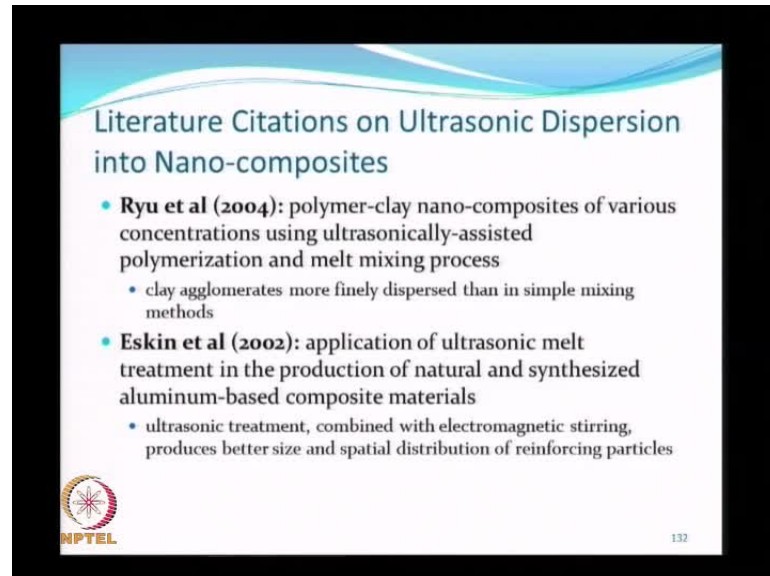
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This is a schematic of a Two-Step Powder Dispersion using Sonication. Again this is for zinc oxide nano-particles, where essentially in step 1, you are using the ultrasound to


produce nano sized zinc oxide particles, and then in step 2 or b, you are using higher frequency ultrasonics to disperse the zinc oxide nano particles uniformly in suspension.

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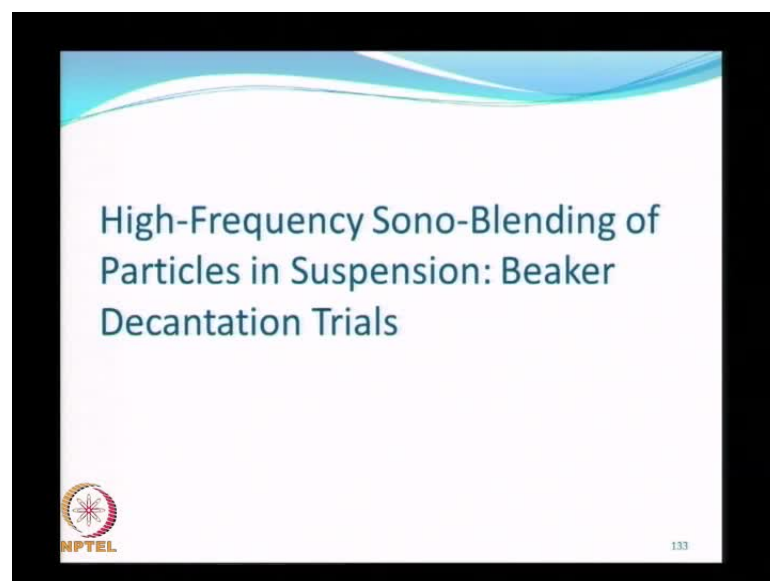
Literature Citations on Ultrasonic Dispersion into Nano-composites

- **Ryu et al (2004):** polymer-clay nano-composites of various concentrations using ultrasonically-assisted polymerization and melt mixing process
 - clay agglomerates more finely dispersed than in simple mixing methods
- **Eskin et al (2002):** application of ultrasonic melt treatment in the production of natural and synthesized aluminum-based composite materials
 - ultrasonic treatment, combined with electromagnetic stirring, produces better size and spatial distribution of reinforcing particles


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There are many literature citations on ultrasonic dispersion, particularly in nano composites, and these are a couple of examples; polymer clay nano composites, and also natural and synthesized aluminum based composite materials, which are very effectively produced by using Sono Technology.

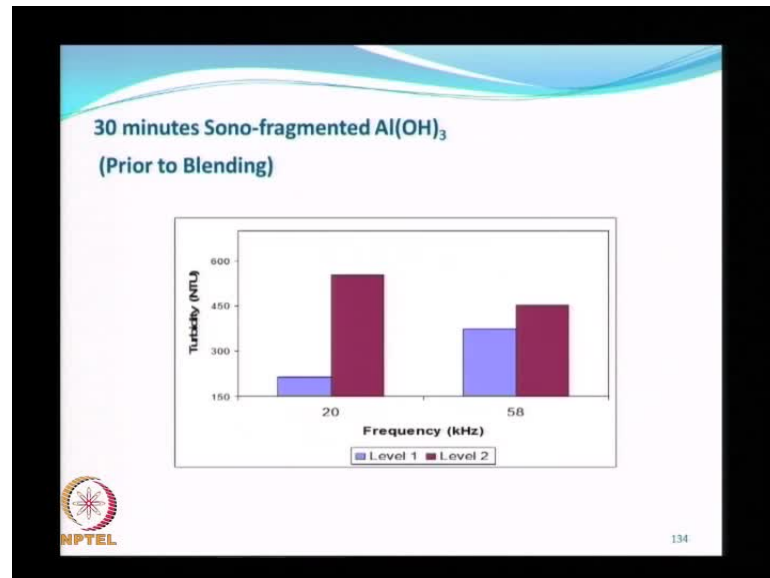
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High-Frequency Sono-Blending of Particles in Suspension: Beaker Decantation Trials

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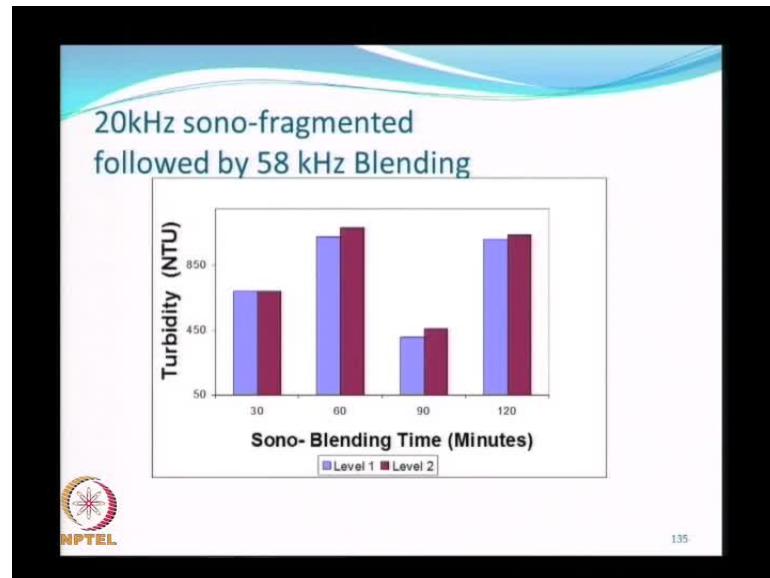


When we look at this Sono- Blending process, how do you characterize dispersion efficiency? Again coming back to the main theme of this course, characterization, unless you can quantify the degree of dispersion, you cannot really measure it or control it or optimize it. So, we are constantly looking for ways to characterize dispersion efficiency. So, we will look at some methods of doing this quantitative characterization

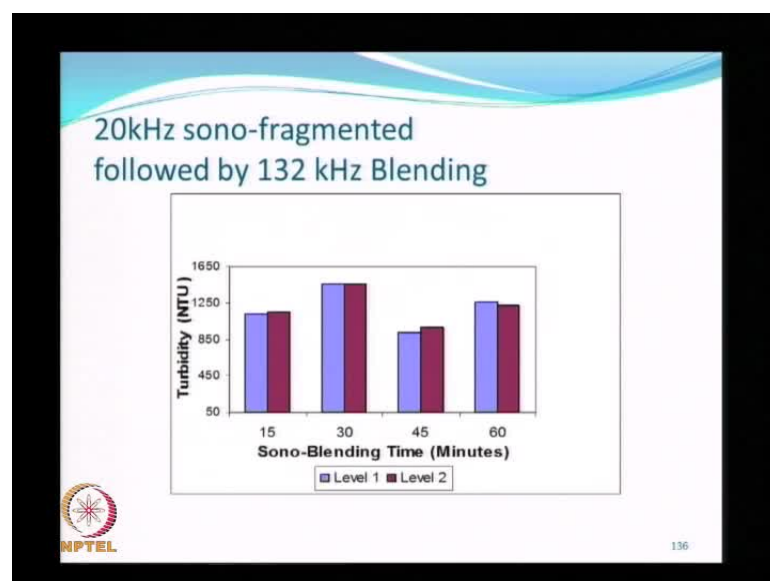
One method simply utilizes turbidity measurements. As we have seen before, turbidity is a measure of particle scattering cross section in a liquid. So, suppose you take a liquid in which particles are suspended, divide it into two layers and measure the turbidity of each layer separately. The more uniformly the particles are dispersed, the closer should be these turbidity values.

So, that is a very simple concept that is used here, where we take a suspension of nano particles, and these are as they are manufactured, so there has been no effort to blend them very well, for example, using high frequency ultrasonics. And you measure the turbidity of level 1 and level 2 of the suspension. And you can see that the turbidity values are very different in these two cases, between the two levels, which is indicative of the fact that the particles are not well dispersed in solution.

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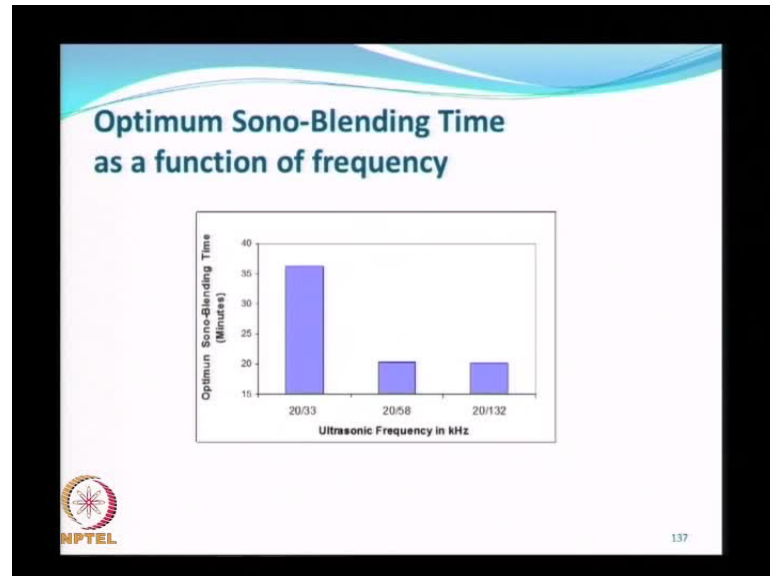
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Now, suppose we take this same suspension and apply 58 kilohertz ultrasonics, to blend the particles, to mix them, to disperse them, and then we again do these measurements. Now, we are looking at sono blending time versus the turbidity, and we can see that the turbidity values for level 1 and level 2 are now much closer, indicating that the particles are now well dispersed in solution. In fact, thirty minutes of Sonication appears to be optimal in this case, and the turbidity values for level 1 and level 2 are virtually equal. And this is an example of doing the same blending with higher frequency ultrasonics and

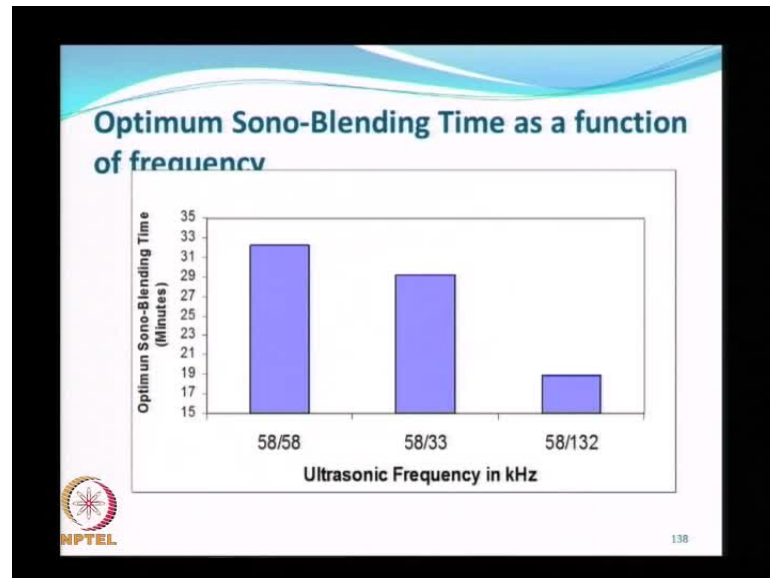
here we see that, even at fifteen minutes of blending, we are able to achieve virtual equality between the turbidity values of level 1 and level 2.

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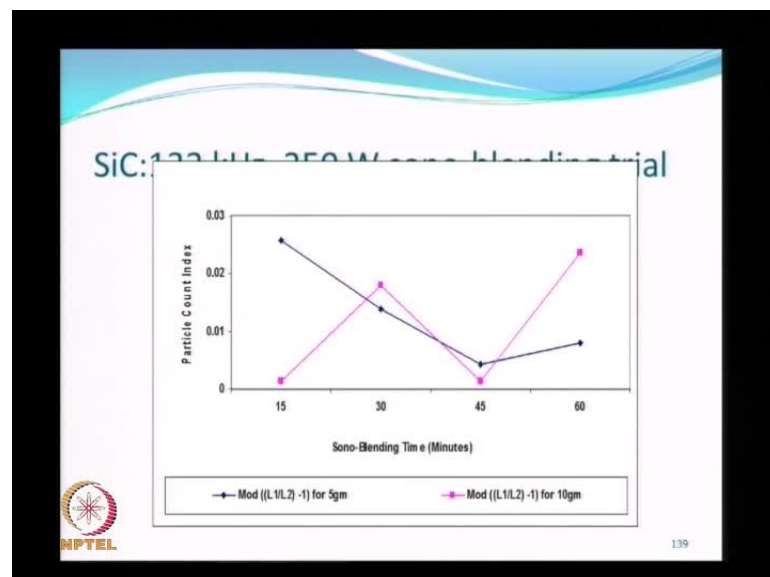
So here, we are simply using turbidity of the suspension as the characteristic of dispersion, and we are able to show that by increasing the frequency of the ultrasound, you can achieve efficient dispersion sooner, compared to lower frequency ultrasound. So, you can actually use this type of data to optimize the sono blending time as a function of frequency, by going to a blending frequency of 132 kilohertz, you can actually achieve blending much faster than trying to do this at a lower frequency. So here, the characteristic of particle dispersion is simply equalizing the turbidity of suspension at various levels.

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And here, we are looking at an optimized sono blending time, again as a function of ultrasonic frequency, the difference between this graph and the previous graph is in the synthesis part. Here we are doing the ultra sound in two parts; we are first using ultrasound to synthesis nano particles, and then again using higher frequency ultrasound to disperse the nano particles.

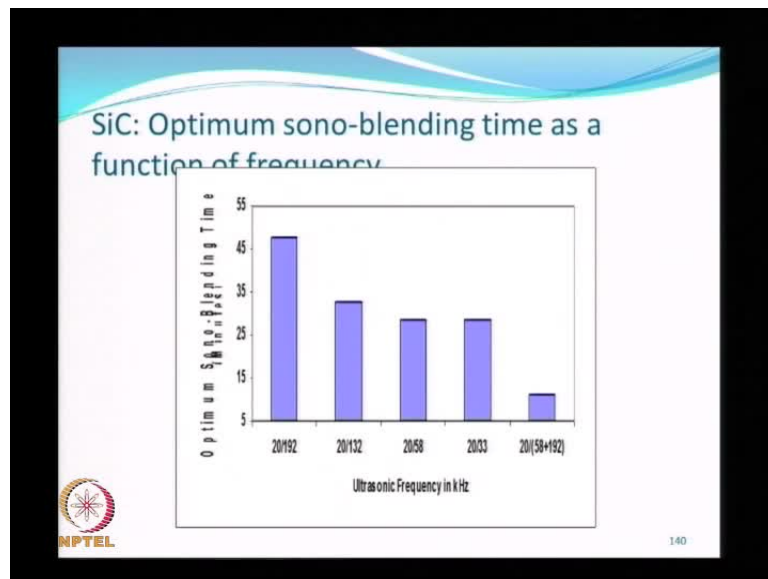
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And it appears from these graphs that 58 kilohertz is optimal for synthesizing nano particles and 132 kilohertz is optimum for dispersing these nano particles.

This is again a way to represent bending efficiency or dispersion efficiency, simply by taking the ratio of the particle concentrations in the two levels. And here we can see that, as we increase the sono blending time, the difference between the turbidities of the suspensions goes to virtually 0 after only fifteen minutes. **This** The index that is shown on the vertical axis here, is actually the difference in concentrations between particles in the two layers, so 0 here is the optimal value, the ideal value, the sooner you can get to 0, the better.

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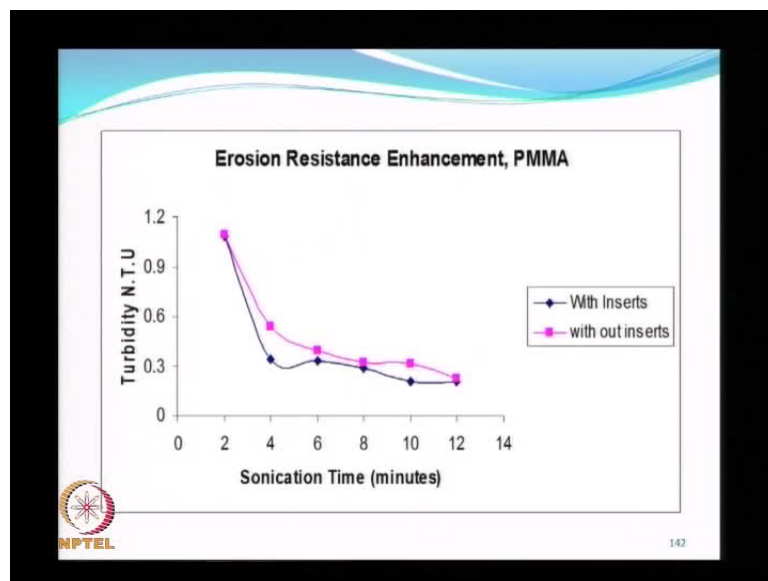


So here you can see that, with sono blending you can achieve uniform dispersion within fifteen minutes. And this is for the case of silicon carbide, again plotting ultrasonic frequency in kilohertz on the x axis, and the optimum sono blending time on the vertical axis. And here we can see that, a combination of frequencies a low and a high; 58 kilohertz and 190 kilohertz, is the optimum setting for achieving a low value in sono blending time.

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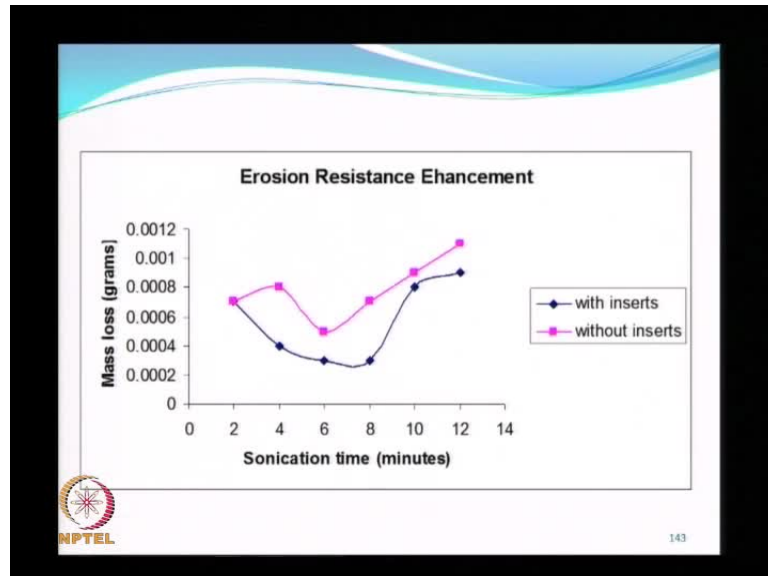
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Now, extending this to the formulation of composites, again what we see is that, when we have nano dimensional particles that are inserted into a polymer matrix, they can certainly enhance erosion resistance. Here again, we are using turbidity as a characteristic of erosion resistance of the material. The way this testing is done is by taking the material, exposing it to ultrasonics for various times, and looking at particles that are generated due to the ultrasonic field, which are reflected in the turbidity values. So, here a lower turbidity value is indicated of higher erosion resistance. So, here you

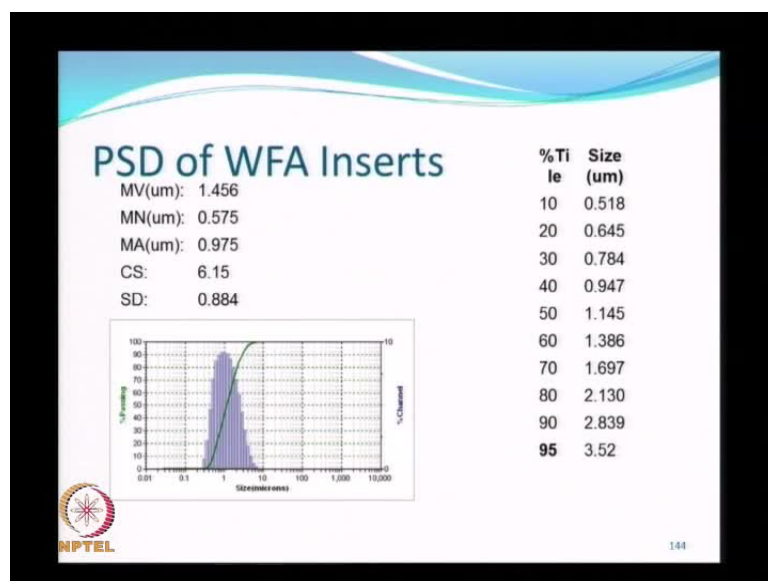
can see that, if you plot turbidity as a function of sonication time, when you have nano particle inserts, the erosion values are lower compared to without the inserts.

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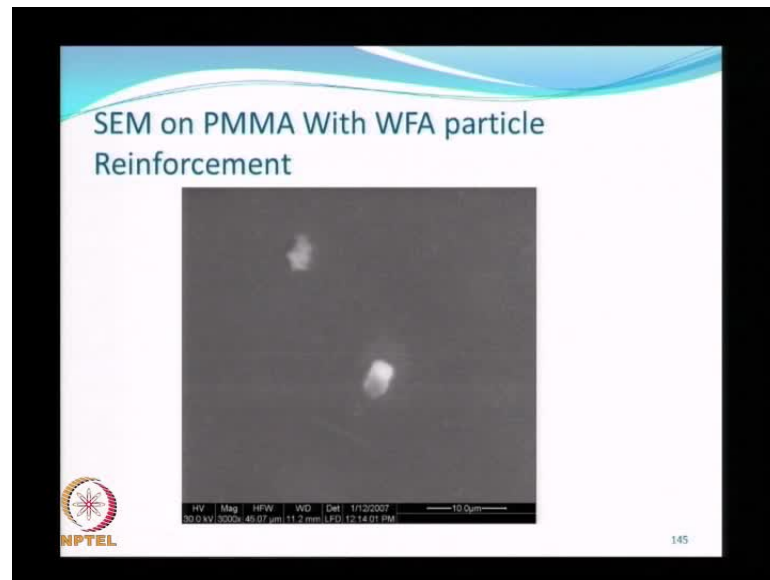
And here, we are looking at erosion resistance in terms of mass loss, which is a more conventional way of measuring erosion resistance of materials. So, here we are looking at mass loss as a function of sonication time, and here again we see that the insertion of nano particles into a polymer matrix increases its erosion resistance significantly.

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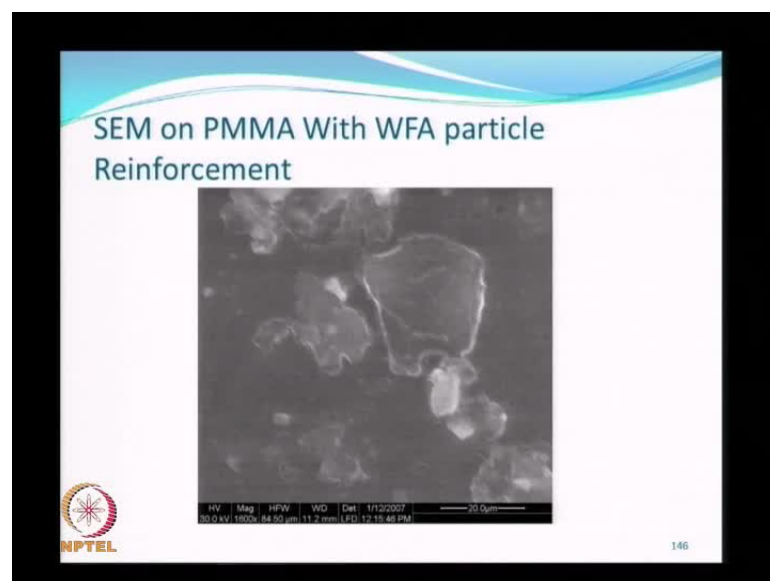
The particle size distribution of these alumina inserts is shown here. The mean size here is of the order of roughly 1.5 microns, and there is a substantial fraction of these particles that are below a micron. As you can see, the lower part of the distribution has a tail that extends all the way to about 0.2 microns.

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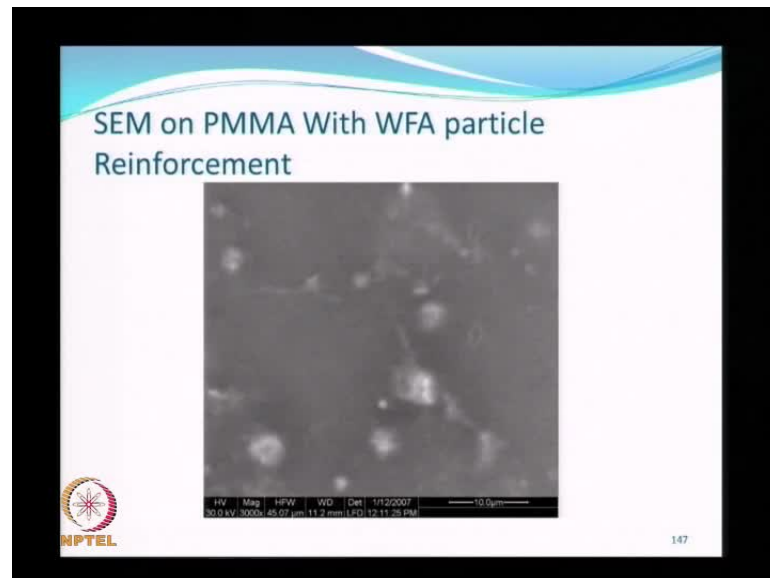
And these are some scanning electron microscopy pictures on how the PMMA polymer matrix looks with particle reinforcement. This is with 10 micron resolution.

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And this again is the same material with particle reinforcement with 20 micron resolution.

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And this is another picture of the material showing the alumina particles dispersed and distributed in the matrix, and this is shown at 10 micron resolution, with a scanning electron microscope.

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Indicator of Dispersion Uniformity in Composites

- Select 50 [1 μm X 1 μm] areas at random from sample
- Examine via microscopy (OM, SEM, TEM)
- Count # of additive particles
- Calculate mean & std dev of #
- If std dev $\leq 10\%$ of the mean, consider dispersion to be adequately uniform
 - i.e., variability coef ≤ 0.1

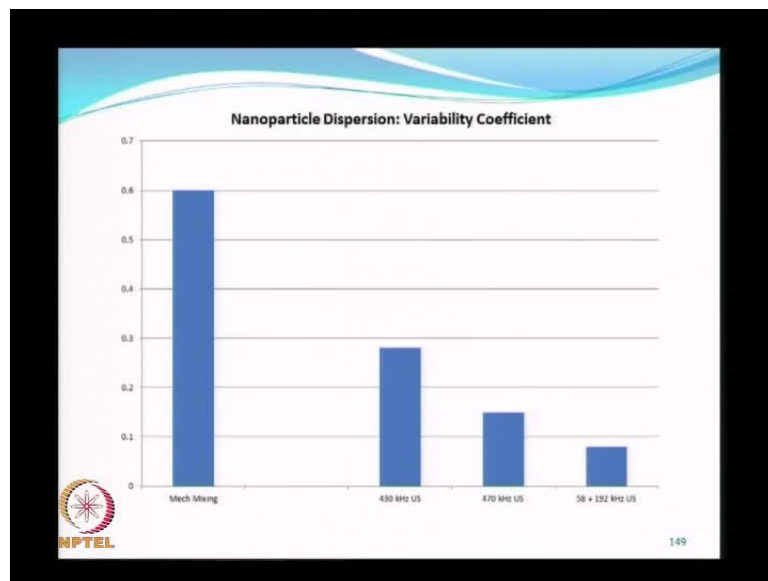
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So, ultimately what is the best indicator of dispersion uniformity in composite materials? How do you assess how uniform is the dispersion? Well the pictures that we

saw in the last three slides are qualitative in nature, by looking at them you can get a feel for dispersion, but you cannot quantify it very well. So, a procedure that is used to quantify dispersion is as follows:

You have to select fifty areas at random from the SEM pictures or from the sample, and then examine these areas using microscopy. So, depending on the size range of the particles, you may choose to use optical microscopy or scanning electron microscopy or tunneling electron microscopy. You count the number of nano particles in each of these areas, calculate the mean number and the standard deviation. If the standard deviation is less the 10 percent of the mean, you can consider the dispersion to be adequately uniform. Because this results in a variability coefficient of less than or equal to 0.1, where variability coefficient is defined as standard deviation divided by the mean.

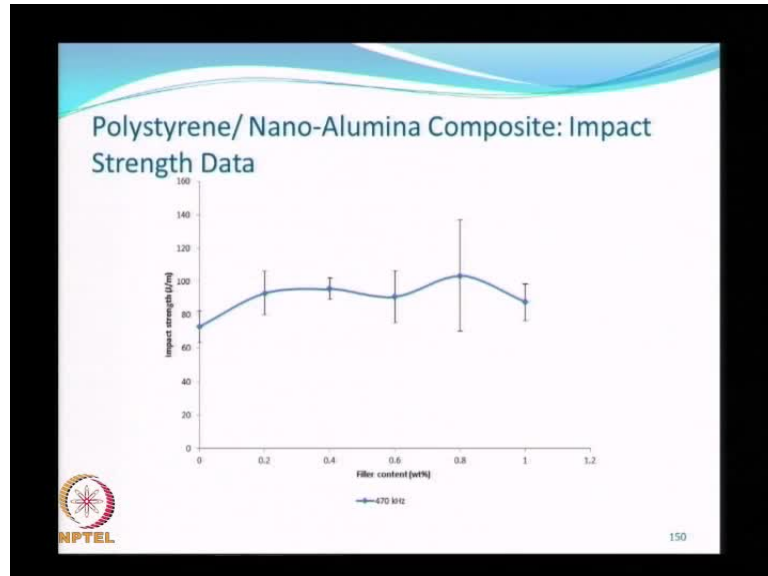
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So, when we quantify nano particle dispersion in terms of its variability coefficient, and we compare various methods of dispersion, now you can start to quantify dispersion much better. So here you see that, mechanical mixing results in a very high variability coefficient, which is indicative of poor dispersion. Whereas, 430 kilohertz ultrasonics and 470 kilohertz ultrasonics show improved dispersion, resulting in lower variability coefficients; however, if you look at our dual frequency mixing, which combines low frequency cavitation mixing with high frequency acoustic streaming based mixing, you can see that the variability coefficient is below 0.1.

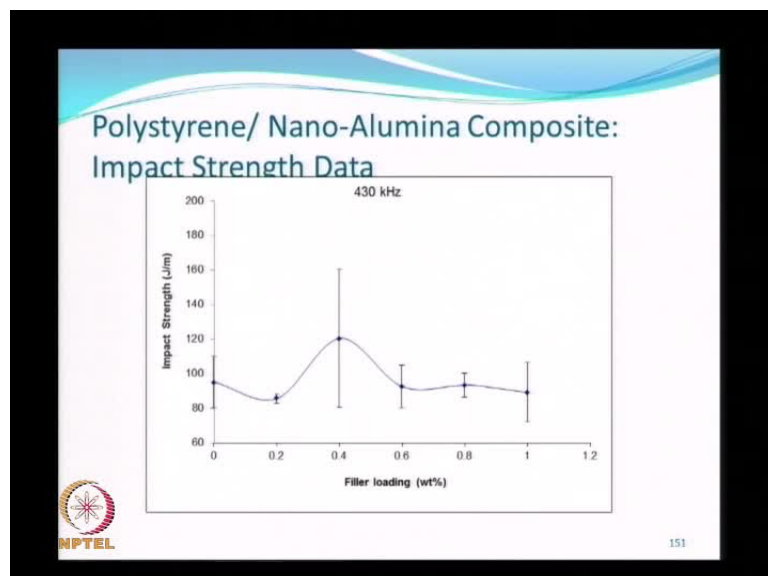
So, in this way we can quantify dispersion efficiency and conclusively show that an ultrasonic dispersion process, which combines elements of cavitation with elements of streaming, is optimum for obtaining a well dispersed solution.

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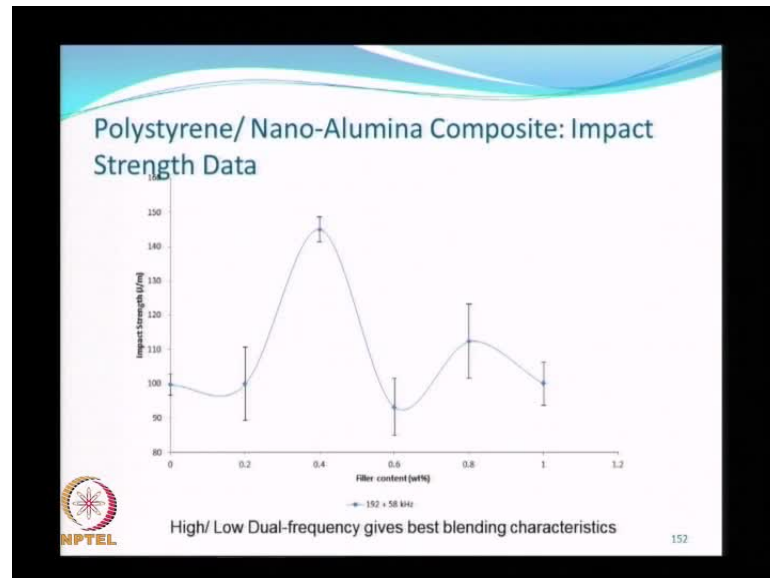
And this is reflected in data as well. For example, if you take a Polystyrene/ Nano Alumina composite, and you study the impact strength, here we are plotting the filler content versus impact strength, and you will see that there is no significant effect when the dispersion is being done using 470 kilohertz as the ultrasonic frequency.

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At 430 kilohertz, you start to see some increased effect of filler loading, it appears that 0.4 percent filler loading is optimal and results in a increased impact strength compared to the virgin material as well as other filler volume percentages.

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But if you do the high/ low dual- frequency, which we had previously quantified as giving the best dispersion, you can see that, based on the impact strength data as well, this has the best functional effect. So, that is good correlation between our dispersion index that we had previously developed, and the functional values that are provided by this additive materials,

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The slide features a blue and white header with a decorative wave pattern. On the right side, there is a small illustration of a person in a red outfit performing a hurdle jump. The main title 'Constraints Overcome' is in a large, bold, blue font. Below the title, the word 'Poly-dispersity' is written in a smaller font. A bulleted list follows, detailing four constraints and their solutions. In the bottom left corner, there is a circular logo with a star-like pattern and the text 'NPTEL' below it. In the bottom right corner, the number '153' is displayed.

Constraints Overcome

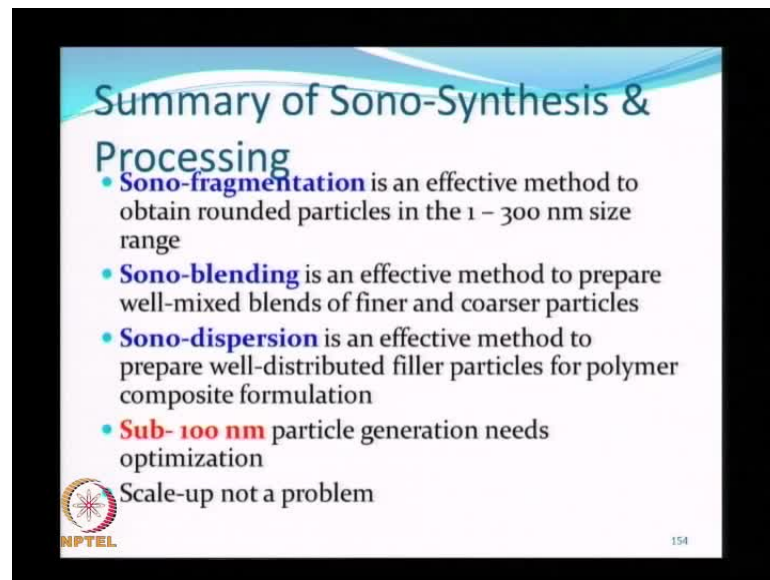
Poly-dispersity

- Separation of the Micron/ Sub-Micron sized particles during post sono-fragmentation period.
- Keeping the lower dimensional particles in dispersed state.
- Post-Blending Period: after drying, particles stick to wall of beaker, since they have lower dimension and hence higher surface area.
 - solved by solvent (eg. CHCl_3) flushing, in turn used as precursor for polymer fabrication.
- Reinforcing the sub-micron particles into polymer matrix

NPTEL 153

So, when we are trying to do dispersion of nano particles, some of the challenges are; Poly-dispersity, particles have very different sizes, separation of micron and submicron size particles is always an issue, keeping the lower dimensional particles in a dispersed state is a challenge, the Post- Blending Period, where when you dry the particles, the particles stick to the wall of the beaker or to each other is again a challenge, and finally, reinforcing the submicron and nano dimensional particles into the polymer matrix is another huge challenge. But it turns out that, by using a combination of low frequency and high frequency ultrasound, you can overcome all these challenges and produce a well dispersed suspension of particles or a well dispersed nano composite material.


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Summary of Sono-Synthesis & Processing

- **Sono-fragmentation** is an effective method to obtain rounded particles in the 1 – 300 nm size range
- **Sono-blending** is an effective method to prepare well-mixed blends of finer and coarser particles
- **Sono-dispersion** is an effective method to prepare well-distributed filler particles for polymer composite formulation
- **Sub- 100 nm** particle generation needs optimization

Scale-up not a problem

 NPTEL 154

So, to summarize what we have been talking about Sono- Synthesis and Processing offers several advantages; Sono-fragmentation can produce well rounded particles in the 1 to 300 nanometer size range, Sono- blending is an effective method to dispersed these particles, and Sono- dispersion is an effective method to prepare polymer composites of very uniform properties. Sub- 100 nanometer particle generation still needs optimization, but scale up is not an issue. One of the big advantages we have is, increase concentration actually increase fragmentation efficiency. So, we will stop this at this point and in the next lecture, we will particularly focus in on the properties of nano particles and how to characterize them. **Any questions? I will see you at the next lecture then.**