Surface Engineering of Nanomaterials
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Lecture - 16
Synthesis, Processing and Characterization of Nano-structured Coatings

Hello, now we are going to discuss about our lecture number 16, which will tells us that about the Synthesis Processing and Characterization of the Nano-structured Coatings. So, here in this particular chapter, we will mainly discuss about that there are several types of synthesis methods, different types of processing techniques on and how to characterize or maybe how to measure that whether these coatings is proper or not or maybe the what are the relations in between them or not.

In our previous lectures, we have actually discussed about a different type of coating methods and now we are going to discuss that how we are going to use those methods for this particular structure. So, first we have to know that why nano structures are important?

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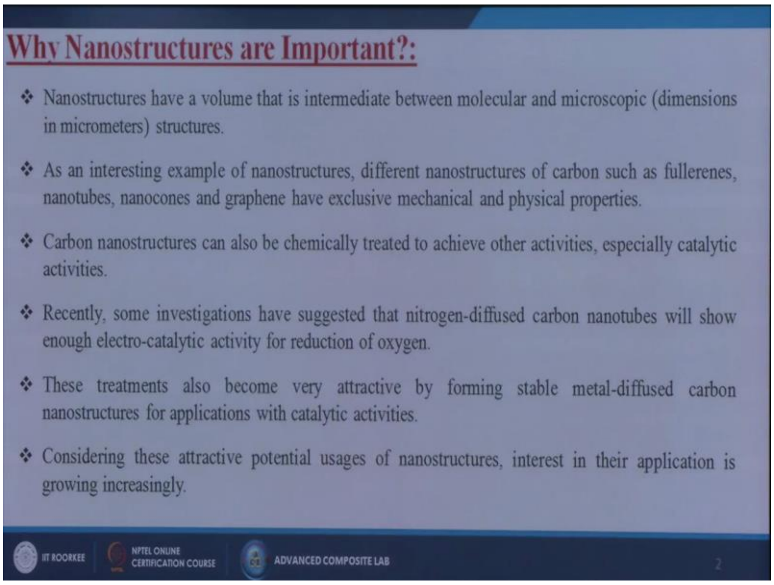

Why nowadays we are talking about the nano structures every time, nanomaterials, nanocomposites, why the term nano is coming each and everywhere, because as we know that when we are talking about the bulk properties or maybe that when you are talking about the micro properties, maybe there is having some kind of saturations of these techniques by which we can enhance the material properties up to certain limit and not only that if we want to increase those properties maybe for 1 or 2 applications we are achieving these results, but if we want a variety of applications for that particular materials, then maybe that bulk properties or maybe that micro composites are not working properly.

Then we are talking about the nanocomposites or maybe the nanostructures by which we can change the material properties up to a big variety; that means, the application will be more. So, first is called the nanostructures have a volume that is intermediate between the molecular and the microscopic dimensions in micrometer structure. So, it is ranging from a small tiny particle which we cannot see by our naked eyes to the macroscopic or maybe the microscopic levels. So, it is in between that maybe from nanometer range to the micrometer range.

As an interesting examples of nanostructures, different nanostructures of carbons such as fullerenes, nanotubes, nanocones and graphene have exclusive mechanical and physical properties, but it is not confined in between the mechanical and physical properties, maybe optical properties, maybe electrical properties, maybe thermal properties and there are several properties, it can increase or maybe the decrease carbon nanostructures can also be chemically treated to achieve other activities especially catalytic activities.

Recently some investigations have suggested that nitrogen diffused carbon nanotubes will show enough electro catalytic activity for reduction of oxygen. So, from these example we can understand that nanocomposites is playing a vital role for enhancing several properties which we cannot get by these kind of micro or maybe the macro or maybe that bulk coatings or maybe that bulk properties. These treatments also become very attractive by forming stable metal diffused carbon nanostructures for applications with catalytic activities, considering these attractive potential uses of nanostructures interest in their applications is growing increasingly. So, these all are the different properties by which we are using these kinds of nanostructures, but here the properties are very few there are N number of properties by which we can prove that nanostructure is the more suitable or maybe that more having more future requirement for our coating techniques.

What is to so interesting about nanostructures that that global researchers attention in recent years.

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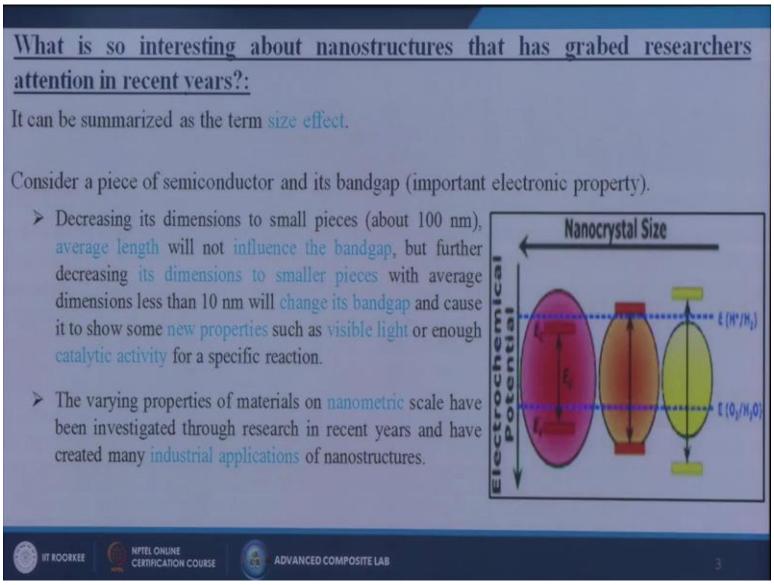

Here we are giving one example, one literature survey just to showing you that, that why we are going for the nanostructures what is the demand for it? Why we are going for these kinds of techniques or maybe why we are adopting these kinds of techniques and what are the logic behind it? It can be summarized as the term called is the size effect. So, consider a piece of semiconductor and it is bandgap important electronic property.

Here we are trying to make you understand in terms of some kind of electronic properties that where you are going for the nanostructure. So, from the term nano, nano is nothing but the 10 to the power minus 9 meter. So, you can see that how much tiny size it is which we cannot see by our naked eyes, for seeing these kind of particles, either we need some kind of microscope, either it may be a scanning electron microscope or maybe the transmission electron microscope.

Next decreasing its dimensions to small pieces about 100 nanometer, average length will not influence the bandgap, but further decreasing its dimensions to smaller pieces with the average dimensionless than 10 nano meter will change its bandgap and cause it to show some new properties such as visible light or enough catalytic activities for a specific reaction.

From these particular sentence you can understand that when we are decreasing the size of the bandgap, size of the particles from 100 nanometer to 10 nanometer, sum of the hidden properties of these particular material is coming out. Like that it is showing some kind of visible light or maybe some kind of enough catalytic activity when the material size is around 10 nanometer. The varying properties of materials on nanometric scale have been investigated through research in recent years and have created many industrial applications of the nanostructures itself.

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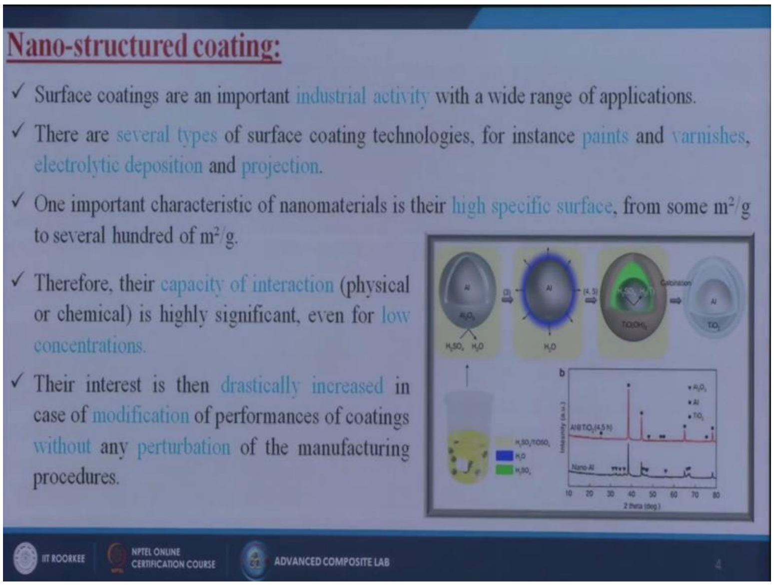

Next nowadays, till now we are talking about the nanomaterials that why we are going to use this kind of nanostructures, but in this particular PPT or maybe the slide we are going to discuss that why we are going to discuss that why we are going for these kind of nanostructured coatings, why we are not going for the bulk coatings or maybe that some micro or macrostructure coatings. So, surface coatings are an important industrial activity with a wide range of applications. So, as we already know that when we are going to do this kind of coatings, just we are changing the outer surface of that particular material, we are not hampering the materials itself or maybe we are not changing the materials inner end property, simple the outer surface of that material property we are going to change so that it cancels the different properties into different manners. These are several types of surface coating technologies for instance paints and varnishes electrolytic depositions and the projections.

One important characteristic of nanomaterials is their high specific surface from some meter square per gram to several 100 of meters cube per gram. So, you can change the wide variety of materials for these particular properties. Therefore, their capacity of interactions physical or chemical is highly significant even for low concentrations their interest is then drastically increased in case of modification of performances of coatings without any perturbations of the manufacturing procedures. That means, we are not going to change the material properties, we are not going to change the material structure or maybe the material chemical structure, rather simply from the outer surface only the physical properties of that materials we are going to change by this kind of techniques.

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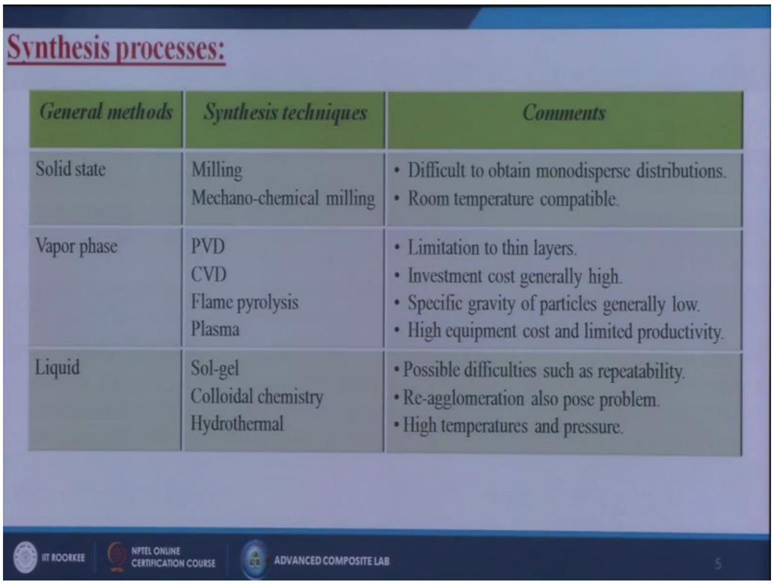

Synthesis process; there are several types of synthesis process, we have discussed some of them in our previous lectures, first one is called the general methods which is known as the solid state, synthesis techniques milling operations, mechano chemical milling comments. There are several types of difficulties or remarks are available, first one is called the difficult to obtain monodisperse distributions, room temperature compatible. So, these all are the different problems, actually we know that if there is no ending of any technology there will not be any new technology will be developed. So, unless and until there will not be any problem for these technology, will not go for the nanostructure or maybe the nanostructure properties of that particular material.

Here when we are talking about the vapor phase we are talking about the PVD; physical vapor depositions, CVD; chemical vapor depositions, flame pyrolysis, plasma. So, these in these particular case suppose for PVD, we are having some limitations to thin layers when we are talking about the CVD, investment cost is generally high, equipment cost is more high and when we are talking about the flame pyrolysis, specific gravity of particles is generally low, when we are talking about the plasma, high equipment cost and limited productivity, when we are talking about the materials in the liquid formations, we are having that sol-gel technology, we are having the colloidal chemistry, we are having the hydrothermal chemistry.

In this particular case, we are having some possible difficulties such as repeatability re agglomerations also pose some problems, high temperature and pressures. So, these all are the different limitations different problems. So, that is why we are going for the newer technology or maybe the near coating methods which is known as the nano structured coatings.

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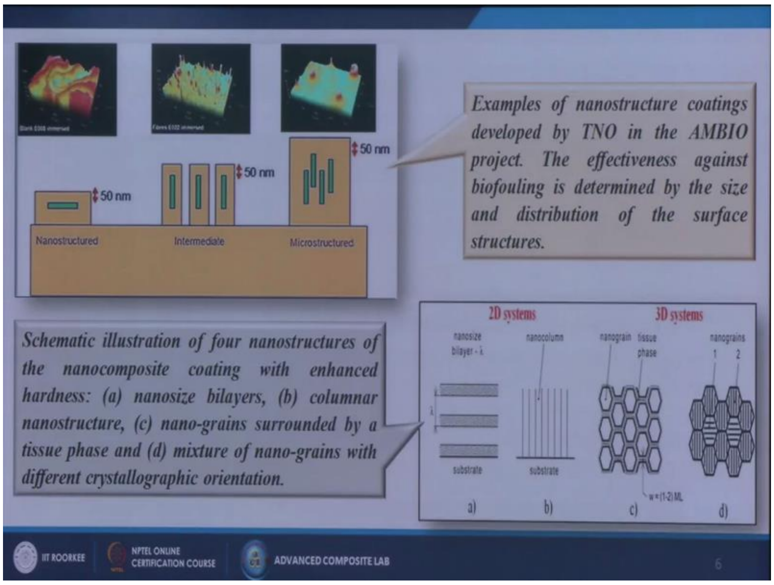

From the left hand side figure, you can see that we are having some kind of nano structured materials, which is having the 50 nanometer size, then we are having that intermediate size, we are having the around 59 nanometer, then we are having some kind of microstructures. So, here from this example, we can see that example of nanostructure coating developed by TNO in the AMBIO project, the effectiveness against biofouling is determined by the size and distribution of the surface structure. So, from this particular case, you can see that nanostructure is into the oriental positions when we are just putting into the longitudinal directions then that properties is gaining the better results.

From this AFM figure, we can see that different types of structures is found, we are getting on to the subtract itself. Here is also some kind of schematic illustrations perform microstructures of nanocomposite coating with enhanced hardness, first one is called the nano sized bilayers. So, here you can see on the substrate, we are giving the different types of layers of coatings on to the materials itself, next one is called the kalamna nanostructure in which the nanoparticles is stacking into the longitudinal directions, then nano grains surrounded by a tissue phase, here the nanoparticles is simply dispersed on to the substrate itself and last one is the mixture of nano grains with different crystallographic orientations - some nanoparticles maybe into the horizontal positions, some nanoparticles into the maybe into the longitudinal positions, so it is a mixing of different nano particles on to the substrate itself.

Next, processing and characterization of the nanostructured coatings that is the main motto of this particular lecture. So, how we are doing? How we are preparing this kind of nanostructures? How we are making this kind of nanostructured coatings on to the substrate itself? What are the methods and what are the advantages and disadvantages of this kind of methods. So, first the characterization is done to confirm the fact that particles are rarely isolated.

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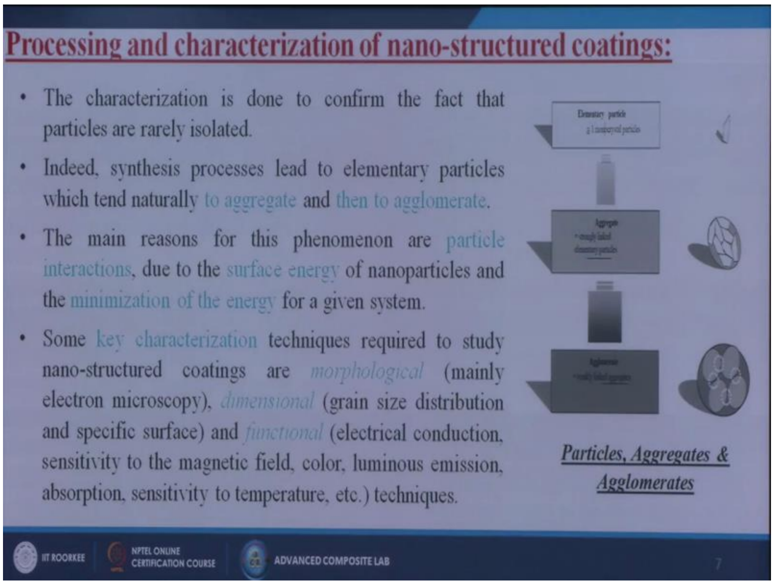

Indeed synthesis of process lead to elementary particles which tend naturally to agglomerate and then to agglomerate. The biggest problem of this nanostructures or nanoparticles is that when we are trying to mix it into some solutions, when we are trying to mix it into some matrix or maybe that blends or maybe the alloys due to its small size and high surface energy, it is tried to agglomerate; that means, the nano particles should not or may be unable to distribute all among the blends or maybe that substrate just it is trying to do the make a separations and it is trying to make a agglomerations and or may be the heap of the particles into a one side into inside the matrix.

The nanoparticles distribution is not the homogeneous, it is making some kind of heterogeneous structure inside the term composites or maybe that blends, the main reason for this phenomenon are particle interactions due to the surface energy of nanoparticles and the minimization of the energy for a given systems. So, these all are the drawbacks for these particular techniques, some key characterization techniques required to study nanostructured coatings are morphological, mainly electro logical microscophy; that means, morphological study of these kind of nanoparticles, dimensional like grain sized distribution and the specific surface geometry and then the functional like electron conduction sensitivity to the magnetic field, color luminous emissions, absorptions, sensitivity to temperature, etcetera; that means, those all are the physical properties of this particular techniques.

From this particular figures, we are giving some kind of elementary particle having 1 size then aggregations is taking place then agglomerations is taking place; that means, stacking of the nanoparticles in a particular phase and they are making heap of the nanoparticles and not mixing properly inside our composites blends or maybe the alloys, what are the applications? These are mainly applications of nanomaterials and it is not relevant there to study them exhaustively.

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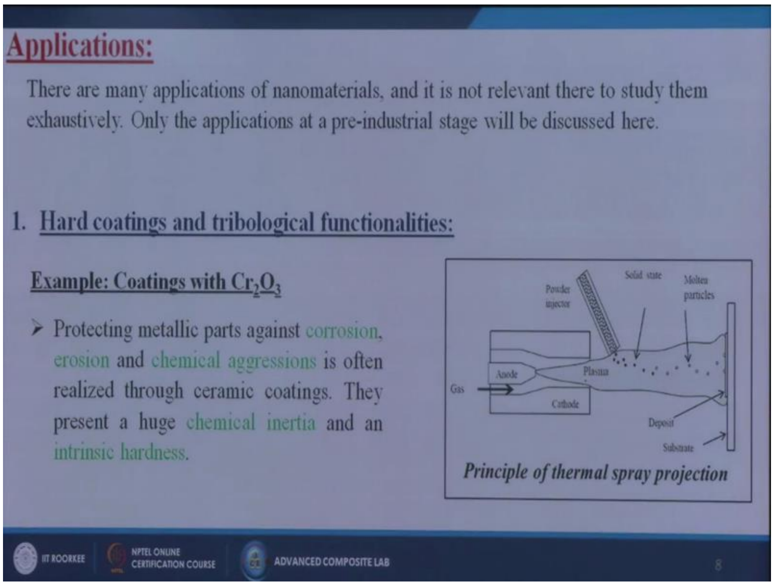

Only the applications at a pre industrial stage will be discussed here because there are N number of applications, if we start this kind of applications may be it can take hour or maybe more than hour. Just here we are keeping our applications for the preindustrial stage or maybe in our laboratory studies or maybe our research base studies.

First one is called the hard coating and the tribological functions. So, just doing this kind of techniques, sorry we can do a hard coating and a tribological functionalities of these particular techniques, first one is called the coatings with chromium oxides. So simple, here we are doing some kind of thermal projections thermal spray projections of our nanoparticles.

We are having the anode and cathode, simply we are applying the gas and then it is making the gas is atomizing into the plus sign and minus sign, then it is atomizing and a high velocity of plasma is forming, in this particular plasma, we are putting the powder; that means, the particle which we are going to coat on to our substrate, simply we are mixing, then through these temperature this powder particle is getting melted and then simply it is depositing on to our substrate itself then it is making a layer form on to the substrate itself like a thin film or some kind of things.

So, protecting metallic parts against corrosions, erosions and chemical aggregations is often realized through ceramic coatings, they present a huge chemical inertia and an intrinsic hardness. So, just applying the chromium oxide on to the substrate itself, we can enhance these kinds of properties on to our substrate. Advance thermal spray makes it possible to inject directly into the plasma a suspension of nanoparticles these techniques was operated to deposit a nanostructural layer of chromium oxide.

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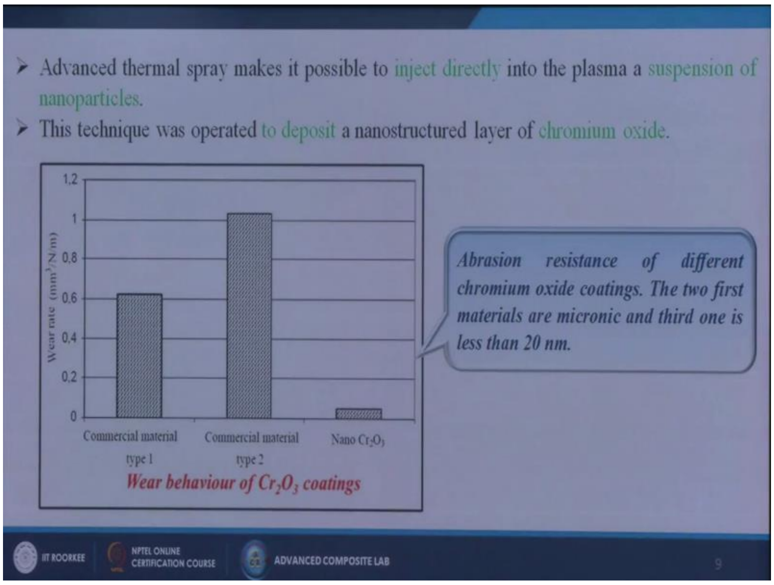

Here just we have given example of the chromium oxide, we can put like this like titanium oxide aluminum oxide. So, there are several types of hard materials which simply use and we can put on to the substrate itself.

Here just it is an example that when we are talking about the wear behavior of chromium coating. So, first for the commercial material type 1 so, first for the commercial material type 1, so we can see that the wear rate is around 0.6 millimeter cube per Newton per meter. But when we are talking about the commercial material type 2, so it is increasing up to 1, but when we are doing such kind of nanocoatings of our material surface, then the wear behavior is around less than 0.1 millimeter cube per Newton per meter. So, this is the things that when we are doing this kind of coatings, the wear behavior of that particular material is totally decreasing and it is coming to almost 0.

Abrasion resistances of different chromium oxide coatings for 2 first materials are micronic and the third one is less than the 20 nanometers. So, from first 2 cases, we have been used the nanoparticles having the micrometer range, now in the third case, we are using this chromium particle into the nano size range. So, that is why it is drastically changing the material properties.

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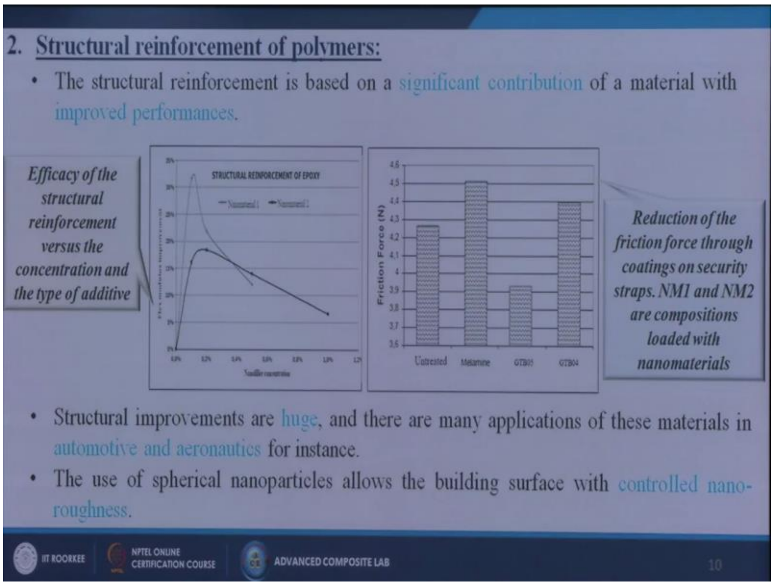

Next one is called the structural reinforcement of polymers, the structural reinforcement is based on a significant contribution of a material with improved performances so; that means, efficacy of the structural reinforcement versus the concentration and the type of additives generally we are applying. So, here we can see that we are applying different kind of nanofiller concentrations; that means, the loading of these nanofillers for a particular systems whether we are going for a 1 weight percent, 2 weight percent, 3 weight percent or different types of loading of the nanoparticles, here it has been given like 0.2, 0.4, 0.6, 0.8, 1 and then here this side, we are getting the modulus of a different particles.

When we are going for a small particle size then that small particle size and small concentrations is equally distributed into the matrix composites which is giving you the better properties, but when you are increasing the concentrations of those nanoparticles then automatically the properties is going down; that means, that nanoparticles is making a agglomerations into the matrix inside the matrix or maybe inside the composites which is reducing the material properties drastically. Here also the friction force so here the example is that reduction of the friction force through coating on security straps NM1 and NM2 are compositions loaded with nanomaterials.

Here some kind of untreated materials, some melamine GTV05, GTV04, so these all are the some kind of you can say that obtained results from the literature review just to show you that if we change the particle size how the material properties is changing, if we change the concentrations of those nanoparticle inside the composites how the material properties is changing. Structural improvements are huge and there are many applications of these materials in automotive and aeronautics for instances the use of spherical nanoparticles allows the building surface with controlled nano roughness.

Next one is called the biocides, from the name itself we can understand that these materials can be used for the bio medical applications or maybe the for the biology purpose.

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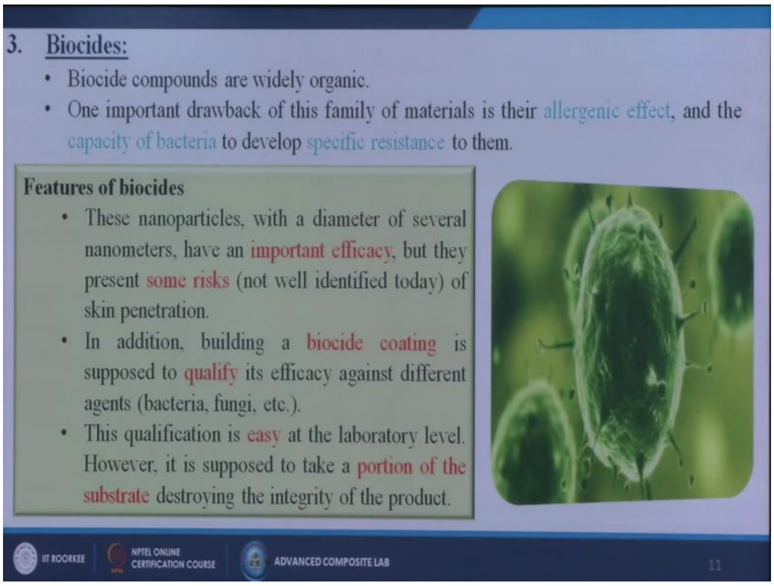

Biocide compounds are widely organic materials, one important drawback of the family of materials is their allergenic effect and the capacity of bacteria to develop specific resistance to them feature of biocides, these nanoparticles with a diameter of several nanometers have an important efficacy, but they present some risks not well identified today of skin penetration.

Here these materials, we are using for the skin material applications or maybe that for the bio medical applications. In additions building a biocide coating is supposed to qualify, it is efficacy against different agents like bacteria, virus, fungi, etcetera. The qualification is easy at the laboratory level; however, it is supposed to take portions of the substrate destroying their integrity of the product. So simple; this kind of materials simply we are using for the bio medical applications.

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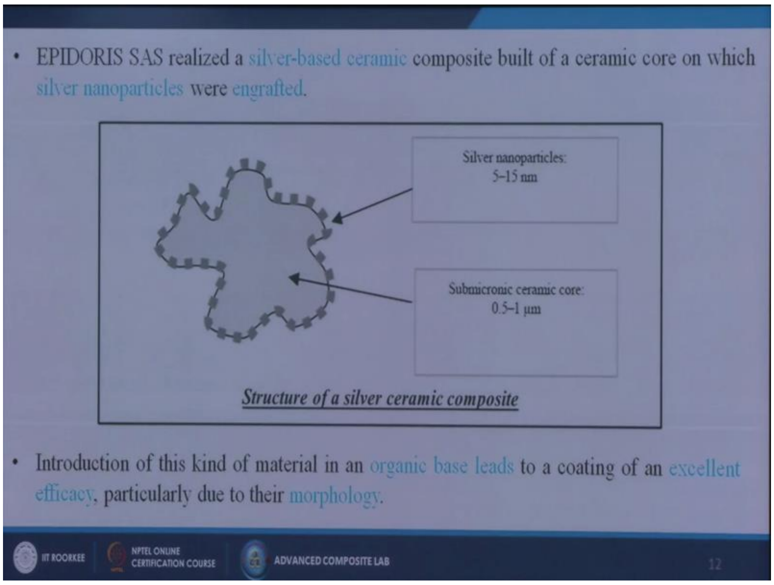

Here one example, just we are trying to show you that EPIDORIS SAS realized silver based ceramic composite built of a ceramic core on which silver nanoparticles were engrafted. So, here the outside material, we are putting some kind of silver nanoparticles ranging from 5 to 15 nanometer and the inside material is submicronic, some kind of ceramic core is around 0.5 to 1 micrometer. So, here it is a structure of silver ceramic composites in where inside is the ceramic material and outside we are putting the silver materials. So, introduction of this kind of materials is an organic base leads to a coating of an excellent efficacy particularly due to their morphology. So, these all are the added advantage for this kind of biocides mechanisms.

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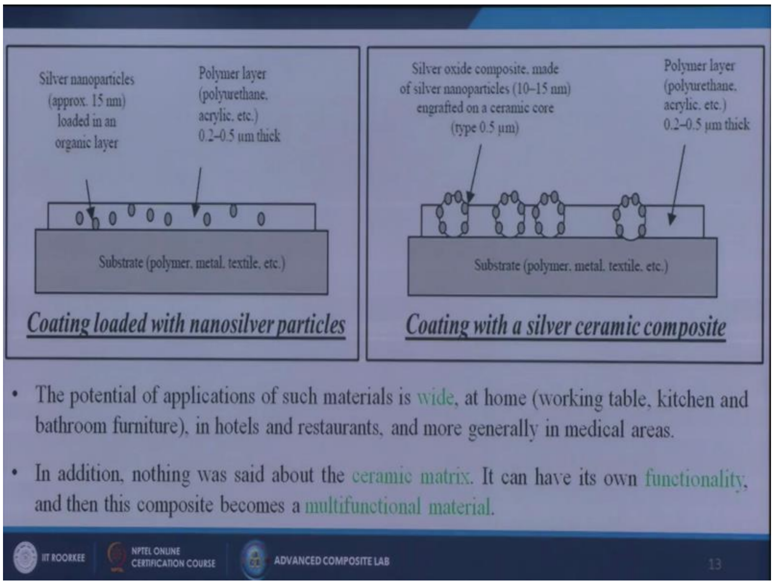

Here also one kind of examples, we are showing that in which we are taking the substrate as may be some polymer, metal, textiles, etcetera then we are incorporating some kind of silver nanoparticles having 15 nanometer diameter loaded in an organic layer, polymer layer like polyurethane acrylic having 0.2 to 0.5 millimeter thickness. So, simple, here we are putting a polymer nanocomposites coating on to our substrate itself and in these particular case, just we are changing some kind of silver oxide composites made of silver nanoparticles having diameter from 10 to 15 nanometers engrafted on a ceramic core type.

This is some ceramic materials in which it is surrounded by some kind of silver nanoparticles and then the whole this silicon with silver nanoparticle is encapsulated into the polymer layer and then this is a coating on to the material itself or maybe the polymer itself. So, the potential of applications of such material is wide at home, working table kitchen and bathroom, furniture, in hotels and restaurants and more generally in the medical areas. So, as I told already, these kinds of nanomaterials is widely used for the biomedical applications. In additions nothing was said about the ceramic matrix, it can have its own functionality and then this composite becomes a multifunctional material. So, these materials are showing different applications for different materials.

Then we are doing the coatings for the fire retardancy. So, simply we can increase or decrease the fire retardant properties of that particular substrate or maybe that particular material by doing this kind of coatings. So, fire protection is widely you required for many applications fire retardant compounds bring often environmental risks as antimonial fluorides for instant.

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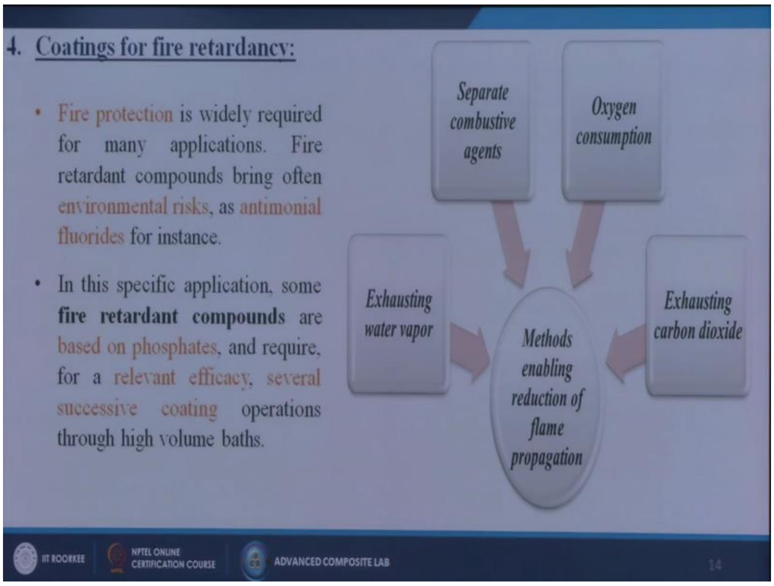

In these specific applications, some fire retardant compounds are based on phosphates and require for a relevant efficacy, several successive coating operations though high volume baths.

Next here, how we are going to do it? Methods of enabling reduction of flame propagations, exhausting water vapor then automatically it will increase the client retardant properties, separate combustive agents, oxygen consumptions, exhausting carbon dioxide. So, these all are the techniques by which we can increase or decrease the fire retardancy for this particular material.

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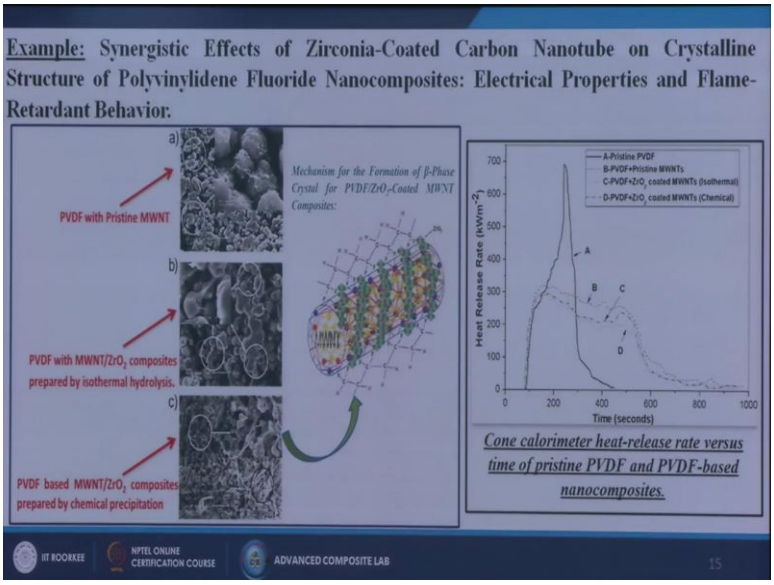

Where is the examples synergistic effect? So this one is the literature study which we have done in our lab itself, so in this particular case, what we have taken? We have taken some kind of carbon nanotubes, then we have done the modification of these kinds of nanotubes by 2 methodology, 2 different methods, one is called the isothermal hydrolizations, one is called the chemical precipitation method. So, by these 2 methods, we have seen that isothermal hydrolization is giving you the better properties because we can control the thickness of zirconia because here we have done the zirconia coating on the carbon nanotubes.

Then we have done for different materials like multiwall carbon nanotubes, for single wall carbon nanotubes, then we have seen that isothermal hydrolization process by which the layer of the zirconia on to the carbon nanotubes can be increased or decreased; that means, it is a control level approach, but while we are talking for the chemical precipitation methods, we have seen that zirconia is totally agglomerated on to the surface, thus it is not giving you the better properties.

Here then this kind of modified carbon nanotubes, we have mixed into the PVDF solutions. So, into the PVDF solutions, we have mixed the composites and then we have tested the fire retardant properties. So, in this particular case, we have seen that first initially we are having the PVDF with the pristine MWNT; then PVDF with MWNT with zirconia composites prepared by isothermal hydrolization process which I have already mentioned and the lower one is called the PVDF based on MWNT zirconia oxide nanocomposites by the chemical precipitation methods.

Here we have shown one kind of schematic diagram by which we have shown that how the mechanism is going on to the MWCNT by coating these kinds of materials and right hand side, we have shown the heat released rate. So, initially when we are talking about the A, A is nothing but the pristine PVDF. So, when we are hitting that material, it is having a high heat releasers around 700 degree and then within 400 second the total material is finished.

But when we are applying these kind of coating materials inside the matrix, we have seen that almost for the D samples, then when we are going for the C samples, it is giving you the maximum time that, that material can sustained and also the heat released rate for these particular material is very very low. So, just the important parameters what we are showing to here that when we are using some kind of coating techniques on to the materials some kind of nanocoatings on to the materials of that CNT, automatically the material heat released rate is decreasing and not only that the sustain temperature for that particular material is increasing.

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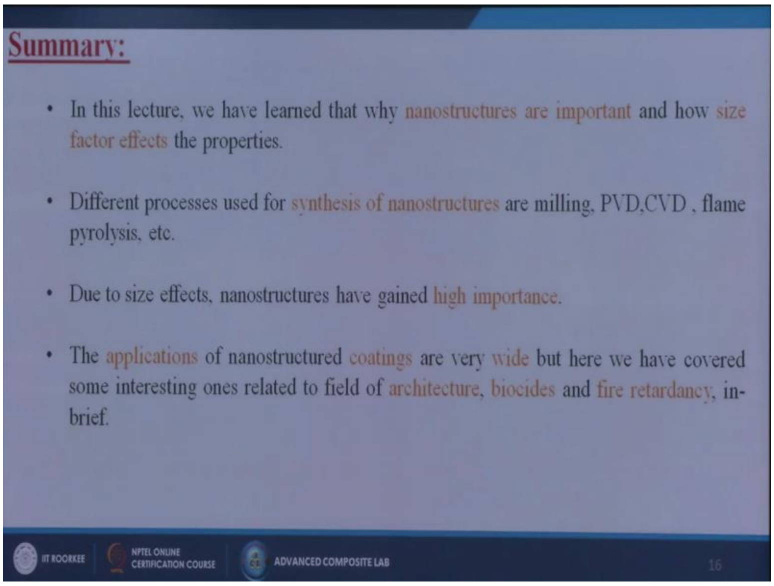

Here now we are coming to the summary that in this particular lecture, we have learned that why nanostructures are important and how size factor affects the properties. So, when you are talking about the macro properties, macro size, then the material is showing some other properties, but when we have same material, we are applying into the nanoscale size; the material property is totally changing. Different process are used for synthesis of nanostructure are milling physical vapor depositions, chemical vapor depositions, flame pyrolysis, etcetera, due to size effects nanostructure have gained the high importance the applications of nanostructured coatings are very wide, but here we have covered some interesting ones related to field of architecture biocides and fire retardancy in brief.

But here we have shown a very few parameters, but by using this kind of nanocomposite coatings, we can change the several material properties of our substrate or maybe as per our requirement.

Thank you.