Surface Engineering of Nanomaterials

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Lecture - 38
Current Trends In Surface Modification of nanomaterials (Part - 3)

Hello, this is the new lecture, in this particular lecture actually you were going to discuss about the current trends and surface modifications of the nanomaterials or maybe about the nanocomposite coatings. So, here actually this is called the part 3 because in the first part 1 lecture, we have discussed about the doping, part 2, we have discussed about the functionalizations and part 3 we have trying to discuss the rest of the modification methods by which nowadays, we are going to modify our nanocomposites maybe the nanofillers or maybe the nanocoatings.

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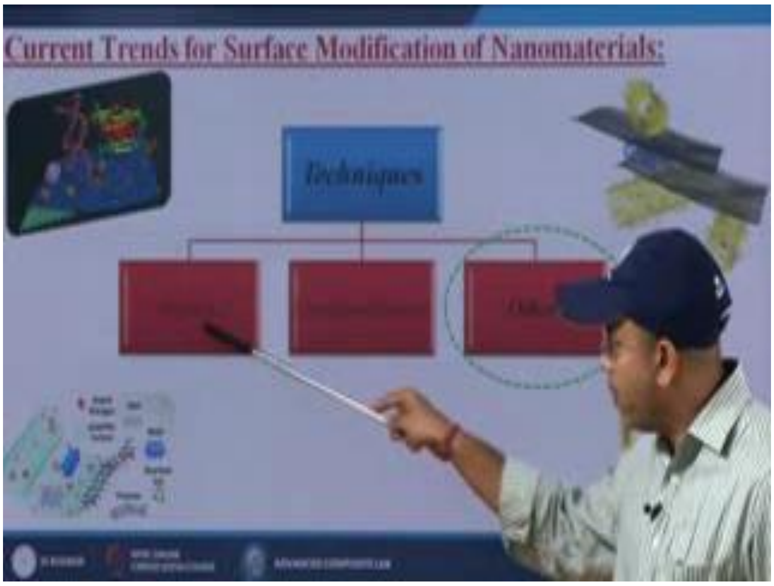

Current Trends for Surface Modification of Nanomaterials:

Techniques

Here if you remember that in our last 2 lectures, last 2 last lectures, we have discussed about the doping, then last lectures we have discussed about the functionalizations and this particular lectures, we are trying to go for the other properties, maybe some kind of grafting will come or maybe some kind of chemical reactions will come. So, these all are the different types of the methods which is not included into the doping part or maybe which is not included into the functionalization part that part actually we are going to discuss into the others.

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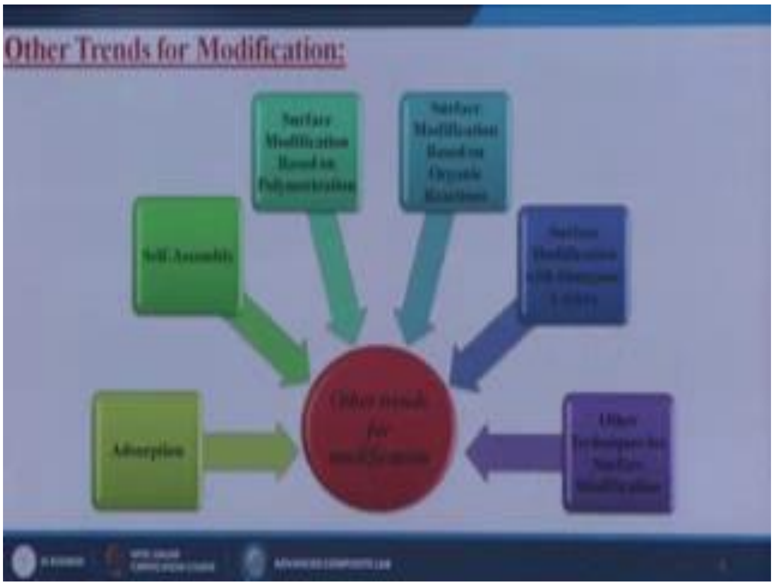

Other Trends for Modification:

Adsorption

Self Assembly

Surface Modification Based on Polymerization

Surface Modification Based on Organic Reactions

Surface Modification with Inorganic Layers

Other Techniques for Surface Modification

Other trends for modification

Here what are the other trends? Actually when we are talking about the other trends, it is only divided or maybe sub divided into several parts. So, first one is called the adsorptions, so by adsorption technology, how we are going to modify our surface or maybe the nanoparticles. Then second one is called the self assembly, so by self assembly materials we are going to modify our nanoparticles, then surface modification based on polymerization. So, actually we are going to do some kind of polymerization techniques. So, what there by which we can modify a nanoparticles then the fourth one is called surface modification based on organic reactions.

So, here by these organic reactions by some doing some chemical reactions we are trying to modify the surface of one nanomaterials and then surface modification with inorganic layers. So, one case we are doing the organic, another case we are trying to do is it inorganic, then other techniques for the surface modification stills, there are some residual application or maybe the functions and processes are left which we are trying to discuss in this particular section.

First is that adsorptions. So, before going to start that how we are doing the modification of that adsorption, first let us know that what is the principle of the adsorptions and how we are classifying the adsorption process or maybe the how adsorption process is going on into the materials and how we are denoting all these things.

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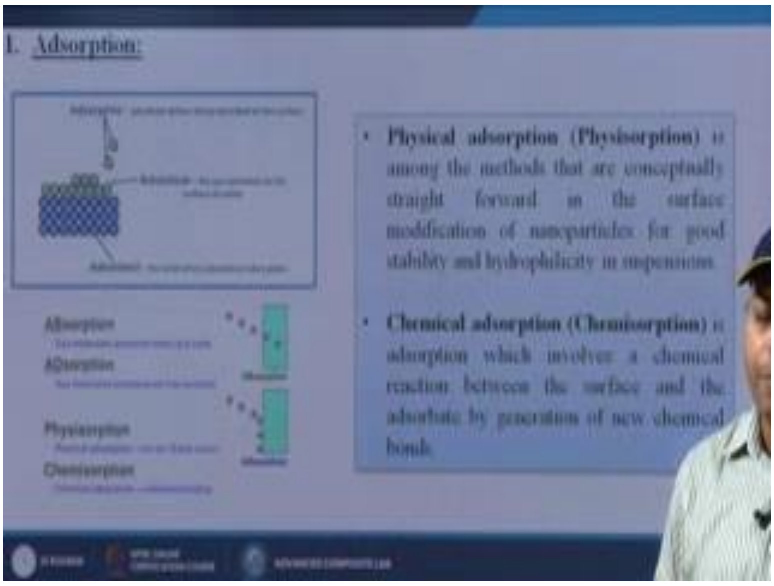

1. Adsorption:

- **Physical adsorption (Physisorption)** is among the methods that are conceptually straight forward in the surface modification of nanoparticles for good stability and hydrophilicity in suspensions.
- **Chemical adsorption (Chemisorption)** is adsorption which involves a chemical reaction between the surface and the adsorbate by generation of new chemical bonds.

Adsorption is a material properties as simple as that, it is a material physical properties by which a material can attract some impurities or maybe some other materials towards its. So, know there are 2 things one is called the absorption, another one is called adsorption. So, there are 2 distinct difference in between these 2 that is absorption and adsorption.

First when we are going to discuss about the absorption. So, absorptions means this is our substrate materials or maybe this is our parent materials then when we are putting certain kind of gas molecules or maybe when we are keeping those substrate materials into some medium maybe either some gas medium or maybe some gas environment. So, that gas molecules may go inside the parent material through its pores. So, that techniques or maybe the technology is known as the absorption, but adsorption is totally different, adsorption is that that through pores the material or maybe the gas molecule they will not go inside simple it will convince on the free surface on to the material substrate itself so; that means, it will make a one kind of coating on to the substrate material.

Now when we are talking about the adsorption, first let us know that which material we are using a parent material that is known as the adsorpment, the solid were adsorption takes place. So, actually the gas molecules or maybe some other functional molecules are trying to stick on to the surface of these material. So, this is our base material which is known as the adsorbent then what is the molecules are going to stick or maybe are going to sit on to the base material, that is known as the adsorbate that gas absorbed on the surface of the solids. So, these gas molecules which is already stick together on to the surface is known as the adsorbate and before that which gas molecules can stick on to the surface. So, before sticking those particles or maybe the molecules is known as the adsorptic materials, adsorbate before being absorbed on the surface.

Before sticking the material or maybe that particle is known as the adsorptive, when it is sticking or maybe we it is a depositing on to the surface, then it is known as the adsorbate and on which material it is depositing it is known as the adsorbent.

Now, there are 2 types of depositions, generally adsorptions is taking place on to the material, one is called the physisorptions were the physical adsorptions due to the banderol spots is taking places because you know that when the molecules molecules will come together. So, there will be a banderol spots will be acting in between that. So, outside of the surface always there is having some kind of banderol force, due to that banderol spots some molecules or maybe the some gas molecules will be attracted towards a substrate, due to that the physisorption will be taking place and another one is called the chemisorptions whereby it is doing by the chemical bonding; that means, some kind of chemical reaction is going so that the material is coming and it is depositing on to the surface itself and in between that some kind of chemical bonding formations is taking place by which the material or maybe that gas molecule is staying on to the surface itself.

If we are going in elaborately for these physisorptions and chemisorptions so, first is called the physical adsorptions is among the methods that are conceptually straight forward in the surface modification of nanoparticles for good stability and hydrophilicity in suspensions. So, that is the property. So, when we are going for the physical adsorption that is the good stability can be observed and hydrophilicity can be observed. But when we are talking about the chemical adsorption process or maybe the chemi absorption process is adsorption which involves a chemical reaction between the surface and the adsorbate by generation of new chemical bonds.

So, what I am telling that simple due to the banderol force if some material will come and stick on to the surface or maybe some gas molecules can stick on to the surface that is known as the physical adsorption, where the stability is good and the hydrophilicity can be achieved and due to that chemical adsorption process when that materials or maybe that third materials or maybe the extra impairer materials is gain is doing some kind of reactions on to the surface and due to the chemical bonding that material is sticking with the substrate. So that is known as the chemical adsorption process.

Now here actually we have given some comparisons between the physical and chemical adsorption process.

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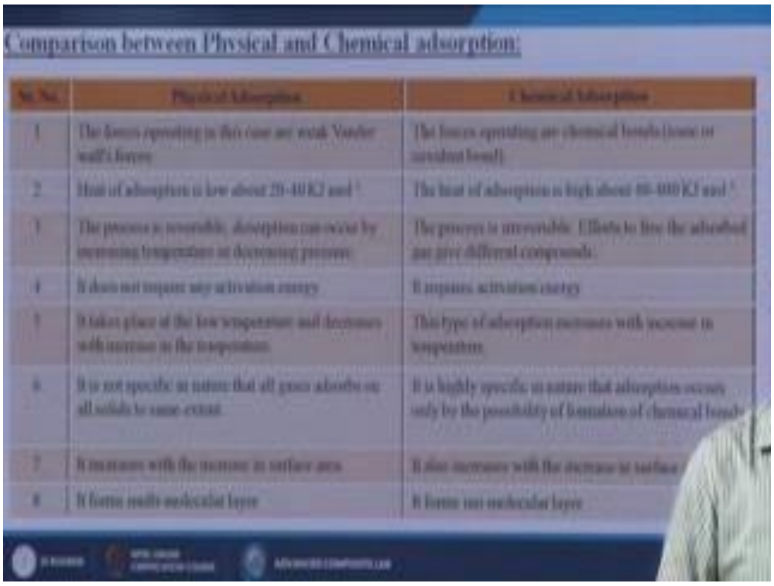

Comparison between Physical and Chemical adsorption:

First one is called the physical adsorptions. So, what does it means? The forces operating in this case are weak banderol force as I already discussed that when the material is coming nearer to the base material. So, there are is weak banderol force is acting in between that by which that gas molecule is sticking on to the substrate itself, but when we are talking about the chemical adsorption process, the forces operating are chemical bonds maybe ionic or maybe the coaler bond is forming in between your gas molecules or maybe that functional materials and the substrate itself.

Then heat of the adsorptions is low about 22 to 40 kilo joule per mole, in this particular case because it is simply coming and sticking by the weak banderol force. So, heat is very very less heat generations, but in this particular case, we are doing some kind of chemical reactions. So, due to that chemical reaction the heat generation is more. So, the heat of adsorptions is high about 40 to 400 kilo joule per mole.

Then the process physical adsorption process is totally the reversible process, desorption can occur by increasing temperature or decreasing the pressure, yes of course, because a simple molecule it is coming and to the surface and it is sticking on to the surface of that parent material. So, if we heat that material if we heat that material then automatically that can be physical modifications can be done. So, the process is reversible; that means, if we simply heat that material then the material can or maybe that monomial or maybe that gas molecule can simply evaporate and not only that dipole desorption can occurred by increasing the temperature or the decreasing the pressure.

The process is irreversible because this is the chemical reaction process. So, it is the irreversible process, we cannot take out that functional material from the parent body. Easily efforts to free the adsorbed gas give different compounds because it can change the parent body properties too then it does not require any activation energy because it is the simple methods it requires some kind of activation energy to starts the chemical reaction because chemical reaction is a vital parameter for the chemical adsorption.

Then it takes place at the low temperature and decrease with increase in the temperature. So, it takes place at low temperature because we simply due to the banderol force, it is sticking. So, we know need to put any extra added temperature at that particular system and decrease with increase in the temperature because that that temperature also we reduced because when the pressure of the system will be increased and same thing these type of adsorption increases with increase in temperature. So, absorption process increases because the chemical reaction is going on. So, if we put any extra added temperature to that particular system automatically the adsorption process will be increased.

Then it is not specific in nature that all gases adsorbs and all solids to the same extent yes of course, because it is depend upon the compatibility in between the gas molecule and in between the substrate itself. So, it is not specific in nature that all gases because all gas molecules and in between the parent body or maybe the substrate, there will be some banderol force will be acting. So that, that gas molecule can stick on to the substrate itself, but it is highly specific in nature that adsorption occurs only by the possibility of formation of chemical bonds. So, this is the more conformal because we are trying to do that certain kind of chemical reactions. So that due to that high chemical bonding that material will stick on to the surface itself. So, the failure of chemical adsorption is very very less.

Then for physical adsorption, it increases with the increase in surface area and the thing is that if the surface area will be increase. So, automatically the banderol force all will be also increase. So, the gas molecule it can be trapped more easily, but in the chemical adsorption process it also increases with the increase in the surface area and for physical ad adsorption it forms multi molecular layer because the gas molecules, it is sticking on to the surface then again that molecule gas molecule also generating little bit of banderol force due to that the other gas molecules are we can be observed. So, like that it multi layer can be formed for these physical adsorption process, but chemical adsorption process it is only the chemical reactions is going on due to that the material is sticking on to the surface. So, that it should be the unique molecular layer can be formed.

Now, the next technology is known as the self assembly. So, it is the method of making 1, 2 or maybe the 3 dimensional structures of nanomaterials.

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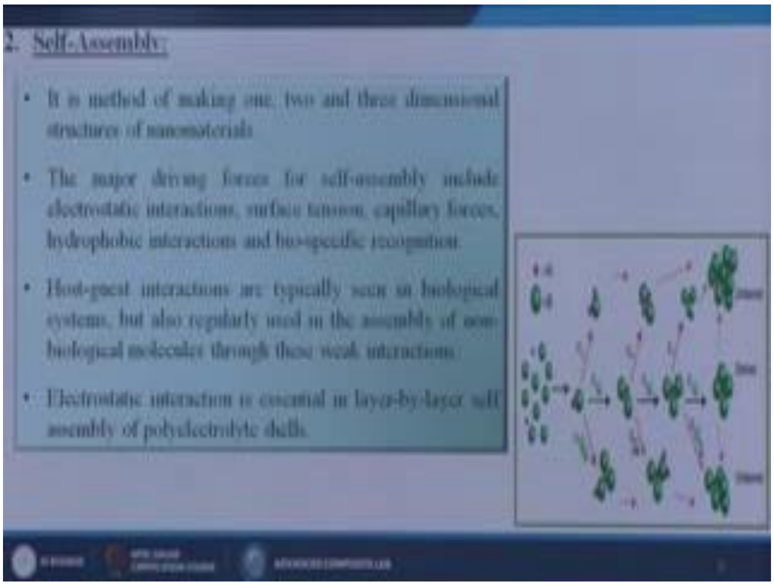

2. Self-Assembly:

- It is method of making one, two and three dimensional structures of nanomaterials
- The major driving forces for self-assembly include electrostatic interactions, surface tension, capillary forces, hydrophobic interactions and bio-specific recognition.
- Host-guest interactions are typically seen in biological systems, but also regularly used in the assembly of non-biological molecules through these weak interactions.
- Electrostatic interaction is essential in layer-by-layer self assembly of polyelectrolyte shells.

The major driving force for self assembly includes electrostatic reactions. So, generally for the electric bath depositions generally we can see this kind of technology over there.

Then the major driving force for self assembly includes electrostatic interactions, surface tension, capillary forces, hydrophobic interaction and biospecific recognition. So, by this technology we can make both the samples desired one and the undesired one. So, undesired one simply we can take it out and we can go for the desired one how to host guest interaction are typically seen in biological systems, but also regularly used in the assembly of non biological molecule through these weak interactions.

Electrostatic interactions are essential in layer by layer self assembly of polyelectrolyte shells. So, generally this kind of deposition is taking place on to the layer by layer. So, the thing is that whatever the material we are trying to put or maybe we are trying to attach on to the substrate itself. So, either we can see that material can be trapped by the parent body. So, that it cannot easily come out because the interaction in between these parent bodies and in between these gas molecules is very very low. So, any time they can come out. So, if we preferred that always that small gas molecule should be trapped inside the system. So, that it not easily come out and the of course, there is some kind of undesired systems where on to the surface that molecules can stick together, but due to the very very weaker bonding maybe that material can be come out from the system itself.

That is why this technology is called the self assembly and another added advantage of these systems is that suppose I am having some electrostatic bath. So, were I am putting the samples then I can start the chemical reactions and no need to add anything extra. So, if I can keep that system for a longer time. So, the chemical reaction is going on going on in between that and that will be occur maybe due to the electrostatic interactions or maybe the surface tensions or maybe the capillary forces or maybe the hydrophobic interactions or maybe the biospecific recognitions no need to add any extra heat no need to add any extra added environment to the system. So, just I have to keep that system for a longer time into the environment. So, the chemical reaction is going on. So, that is why it is called the self assembly treatment.

Next we are trying to discuss about the surface modifications based on the polymerization.

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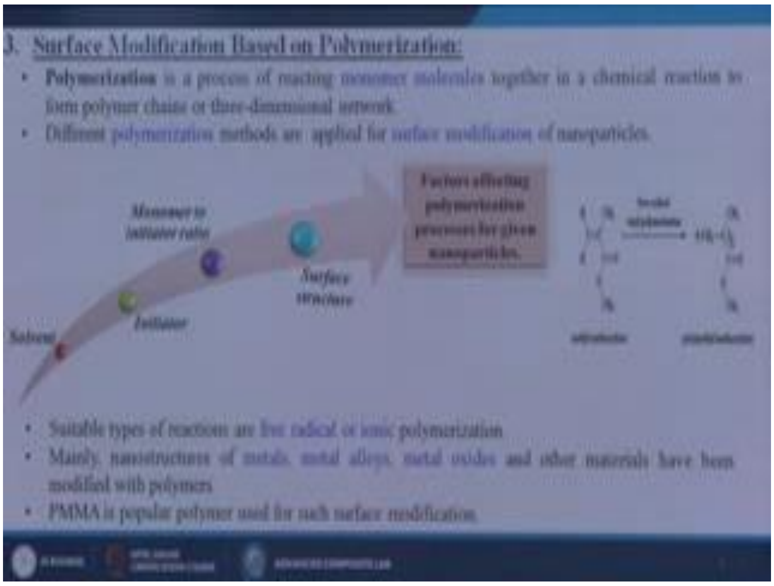

3. Surface Modification Based on Polymerization:

- **Polymerization** is a process of reacting monomer molecules together in a chemical reaction to form polymer chains or three-dimensional network.
- Different polymerization methods are applied for surface modification of nanoparticles.

- Suitable types of reactions are free radical or ionic polymerization
- Mainly, nanostructures of metals, metal alloys, metal oxides and other materials have been modified with polymers
- PMMA is popular polymer used for such surface modification

From this particular heading, we can understand that here we are trying to modify the surface, but we are trying to introduce some kind of polymer on top of that by which it is forming some kind of polymerization techniques or maybe some kind of polymeric chain and by that polymer we are coating that nanocomposites or maybe that nanofillers.

Polymerization is a process of reacting monomer molecules together in a chemical reaction to form polymer chains or 3 dimensional networks. So, simple I am having a monomer when I am doing the chemical reactions by this chemical reactions these monomer will attach with another monomer this monomer will attach with another polymer like that they will make a cloud which is nothing, but the polymer. So, this method is known as the polymerization process.

Here the factors that affecting the polymerizations is called fastest solvent then initiator who is which is initiating the experiment then monomer to initiate a ratio and the surface structure. So, any how I am having the monomer first, I have to agitate that monomer by some initiator then that monomer initiate a reaction will be taking place due to that it will be activated and it will form the polymer.

Here these all are the factors affecting polymerization process for given nanoparticles, here we have given one empirical examples of these polymerization process. So, initially I am having methyl methacrylate then by free radical finial polymerization process, we are making it as a poly methyl methacrylate or maybe which is known as the PMMA which we are using for the bio material purposes which we are using for our contact lance purposes. So, like this polymerization process we are making that methyl methacrylate to the poly methyl methacrylate.

Suitable types of reactions are free radical or maybe the ionic polymerizations. So, by free radical reactions or maybe the ionic polymerization, we can changes from monomer to polymer mainly nanostructures are metals metal alloys metal oxides and other materials have been modified weak polymers.

Sometimes while doing the polymers we can do the modification of that polymerization also. So, while doing the polymerization we can add some kind of extra nanoparticles which can add to the systems and which can make a hybrid polymer over there. So, PMMA poly methyl methacrylate is popular polymer used for such surface modifications and that is also a very nice promising polymer which we can used for the biomaterial purposes and which can acts or maybe in while making this ma methyl methacrylate to the poly methyl methacrylate, we can add some kind of metal some kind of metal alloys, some kind of metal oxides to the systems so that it can make certain kind of hybrid polymer structure at that particular time.

Next we are going to discuss about the surface modifications based on organic reactions. So, here we are trying to do the actually the grafting. So, there are 2 types of grafting or maybe one is called the direct grafting and another one is called indirect grafting, but basically here we are going to discuss about the direct grafting.

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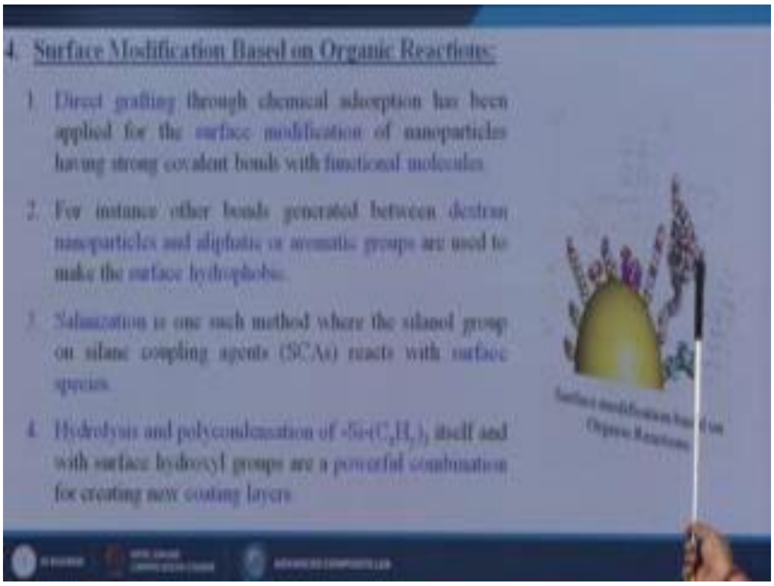

4. Surface Modification Based on Organic Reactions:

1. Direct grafting through chemical adsorption has been applied for the surface modification of nanoparticles having strong covalent bonds with functional molecules.
2. For instance other bonds generated between dextran nanoparticles and aliphatic or aromatic groups are used to make the surface hydrophobic.
3. Salinization is one such method where the silanol group on silane coupling agents (SCAs) reacts with surface species.
4. Hydrolysis and polycondensation of $-Si-(C_2H_5)_3$ itself and with surface hydroxyl groups are a powerful combination for creating new coating layers.

The direct grafting through chemical adsorption has been applied for the surface modification of the nanoparticles having strong covalent bonds with functional molecules. So, here from this particular figure you can understand that we are having some parent materials or maybe that nanofillers or maybe that nanoparticles on which due to the grafting methods or maybe due to some other organic reaction methods we are attaching some kind of functional groups on top of that.

These attaching groups or maybe that organic reactions can be done by 4 distinct methods, one is called the direct grafting where the chemical adsorption process is taking place; that means, chemical reaction is taking place due to that chemical reactions some chemical bonding is occurring, some kind of covalent, non-covalent or maybe some kind of pi pi bonding is taking place by which the material is sticking on to the surface itself.

Then for instance other bonds generated between the extra nanoparticles and aliphatic or aromatic groups are used to make the surface hydrophobic. So, sometimes generally we can change the surface modification survive the surface properties of that particular material by adding the suitable material to that system. Suppose that I want make the system to the hydrophobic then I can use certain kind of materials which can show the hydrophile phobicity into the nature or maybe the hydrophilicity into the nature.

Then salinization is one such method where the silanol groups on silane coupling agents SCAS reacts with the surface species. So, salinizations is also another techniques by which we can make our material that it can source some kind of silane groups on top of that because that material is very very environmental friendly and it can with stand with the higher temperature. So, by doing the chemical adsorption process, we can attach some kind of silicon group into the system itself.

Then another example is that hydrolysis and polycomlensation of silicon CH group itself and with surface hydroxyl groups are a powerful combination of creating new coating layers. So, for getting some also some advanced properties by hydrolysis and polycomlensation method we can attach the CH group with silicon itself and for the betterment or maybe the enhancement of some properties. Here what actually we are trying to show you that by some doing the organic reactions we can do the modification of our surface properly.

So, next slide actually we are going to discuss the surface modifications by the inorganic layers. So, in the previous cases we had added that a material which is organic in nature here we are adding some materials which is inorganic in nature.

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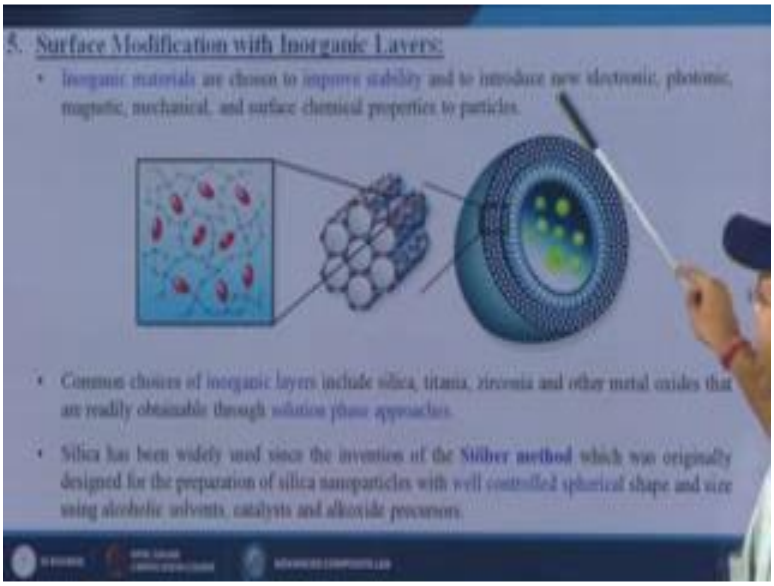

5. Surface Modification with Inorganic Layers:

- Inorganic materials are chosen to improve stability and to introduce new electronic, photonic, magnetic, mechanical, and surface chemical properties to particles.
- Common choices of inorganic layers include silica, titania, zirconia and other metal oxides that are readily obtainable through solution phase approaches.
- Silica has been widely used since the invention of the Stöber method which was originally designed for the preparation of silica nanoparticles with well controlled spherical shape and size using alcoholic solvents, catalysts and alkoxide precursors.

Inorganic materials are choosing to improve stability and to introduce new electronic photonic magnetic mechanical and surface chemical properties to particles. So, this is the figure actually, here where we are having some kind of nanoparticles or maybe some kind of nanofillers on top of that or maybe like a course and structure we are adding some kind of coating materials or maybe some kind of other materials by some inorganic materials.

Here common choice of inorganic layers includes silica, titania, zirconia and other metal oxide that are readily obtainable through solutions phase approaches. So, there are different types of approaches as I have already discussed earlier sol gel method some kind of different techniques like PBD CBD. So, what we are trying to do? I am having that nanocomposites or maybe the nanoparticles, I am trying to coat that nanoparticles by some inorganic materials, what are those inorganic materials. That maybe the silica, that maybe the titania, that maybe the zirconia, we are gone through some silicon coating or maybe that silica coating, we are gone through some zirconia coating or carbon nanotubes, we are gone through some titania coatings or tungsten carbide, we are gone through some other metal oxides like alumina or some kind of hardest material silicon carbide coating or to some aluminum metals irons or maybe metals or maybe that magnesium materials for implied purposes. So, there are n numbers of applications where we are trying to modify our nanoparticles or maybe that nanofillers by using some inorganic materials.

Silica which has been widely used since the invention of the Stober methods which was originally designed for the preparation of silica nanoparticles with the well controlled spherical shape and size using alcoholic solvents catalysis and allcoxide precursors. So, in this particular case, we can see that the cordial is also trapped by some small small molecules or maybe a single molecules can be trapped and then top of that by layer by layer technique, we can do that coating of different inorganic materials on top of that. So, that is why these particular things is known as the surface modifications with inorganic layers.

Then we are going to discuss about several other techniques, first one is called the grafting of silanes, then polymer grafting and the third one is called the grafted polymer.

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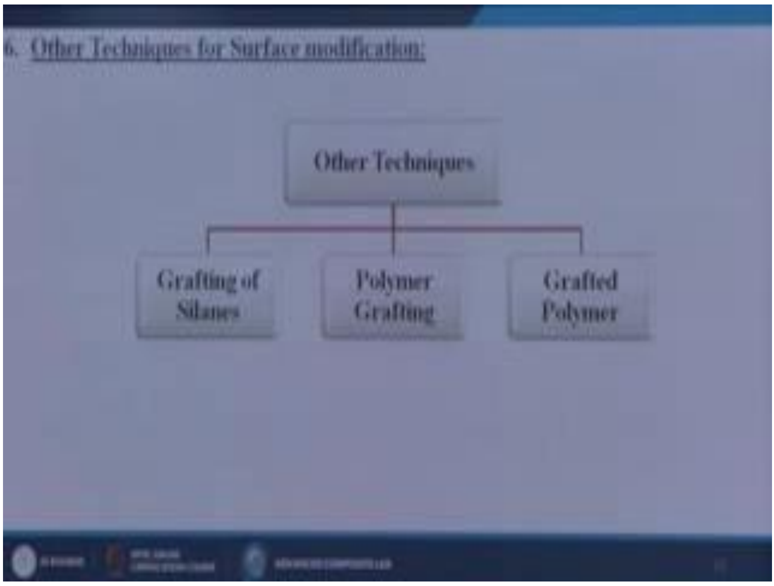

6. Other Techniques for Surface modification:

Other Techniques

Grafting of Silanes

Polymer Grafting

Grafted Polymer

These all are the also 3 different advance techniques by which we can modify our nanofillers by which we can modify our nanocomposites and then that nanofillers are maybe the nanoparticles can be used for advanced surface engineering purposes. So, first is called the grafting of silanes. So, generally oregano silanes here consist of silane with at least 1 silicon carbide or maybe that silicon carbon bond is present.

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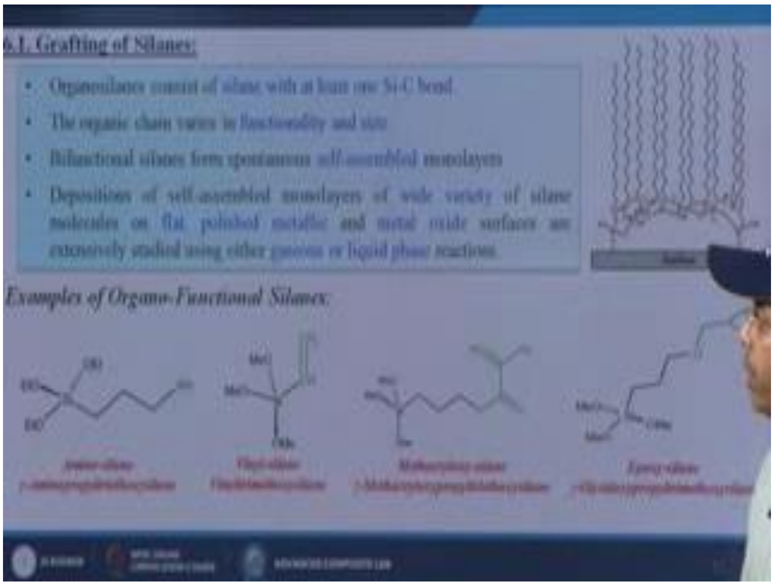

6.1. Grafting of Silanes:

- Organosilanes consist of silane with at least one Si-C bond
- The organic chain varies in functionality and size
- Bifunctional silanes form spontaneous self-assembled monolayers
- Depositions of self-assembled monolayers of wide variety of silane molecules on flat polished metallic and metal oxide surfaces are extensively studied using either gaseous or liquid phase reactions

Examples of Organo-Functional Silanes:

Generally we are trying to use these oregano silanes for modification of these nanoparticles. So, here the organic chains varies in functionality and size and then bifunctional silanes from spontensious self assembled mono layers can be achieved then deposition of self assembled mono layers of wide verity of silane molecular or flat polished metallic and metal oxide surfaces are extensively started using their gases or maybe the liquid phrase reactions. So, what we are trying to do? We are trying to modify our nanoparticles, then nanoparticles we are trying when we it is modify by the silanes; then we are trying to agglomerate of all the nanoparticles together, so that we can do the modification of these materials.

Suppose I am having some surface group on which we are attaching some kind of silanes saline group over there then top of that also by layer by layer technique we can add so many silanes layer of that, so that we can do the modifications or maybe which is known as the organosilanes. So, example of organo functional silanes group of here. So, in this particular case, I am having the silane groups in which I am adding that gamma amino propile thrioxide silane over there. So, I am attaching these materials in this particular case I am having that silane group where I am having that biennial trimethoxide silane over there, then I am having some methacryloxy silane group over here, then in which I am trying to attach the gamma methacryloxy propile tiroxin methyl silane and then I am having some epoxy silane group where I am trying to add this kind of gamma glycidyl oxi propile trimethoxy methyl silane. So, these all are the different silane groups.

The main motto of these particular techniques is that I am having one silane group and also the different silane groups can be attached with that particular materials because that the difference silane groups are having different principle properties. So, when I am trying to attach those silane groups together. So, they will give a number of added applications or maybe the added properties to the system itself. So, by choosing the proper silane groups easily we can modify our systems and maybe we can get proper properties. So, here is the gamma grafting mechanisms of oregano silane.

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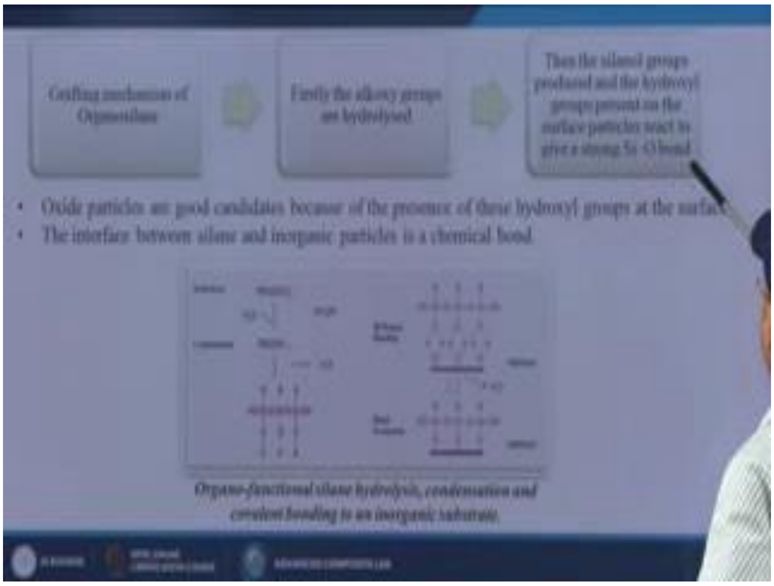

Grafting mechanism of Organosilane

Firstly the alkoxy groups are hydrolysed

Then the silanol groups produced and the hydroxyl groups present on the surface particles react to give a strong Si-O bond

- Oxide particles are good candidates because of the presence of these hydroxyl groups at the surfac
- The interface between silane and inorganic particles is a chemical bond

Organo-functional silane hydrolysis, condensation and covalent bonding to an inorganic substrate.

First then after that we are going to do that elcoxy groups are hydrolyzed over here then the silane groups produced and the hydroxyl groups present on the surface of the proper particles react to give a strong SIO bonding silane and oxine bonding can be observed in this particular case.

First the oxide particles are good candidates because of the presence of these hydroxyl groups at the surface. So, this is the first requirement the interface between the silane and inorganic particles is a chemical bonding process at the chemical bonding is taking place in between the silane and the inorganic particles group. So, my main motto of this particular system is that I am having some silane groups either I can attach some kind of inorganic particle to that system or maybe I can attach certain kind of silane groups to that system so, by do a simply doing the chemical reactions.

Here bihydrolysis and condensation methods so, I am making some kind of silane groups over there are from that I am talking out the water molecules and I am getting the silane groups present in that particular system and also in these particular system I am having the substrate on top of the substrate due to that hydrogen bonding, I can attach some kind of the silane groups to the particular systems or maybe some kind of bond formations can be taking when I am taking the water particles and I can put certain kind of heat over there are. So, just giving some kind of heat and taking out the water or maybe the hydroxide group from the parent body I can do the modifications of this silane on to the substrate itself.

Organic functional in a hydrolysis condensation and covalent bonding to an inorganic substrate group so, finally, we can see that covalent bond has been formed in between the substrate and in between the silane groups next we are going to discuss some polymer grafting using grafted silanes.

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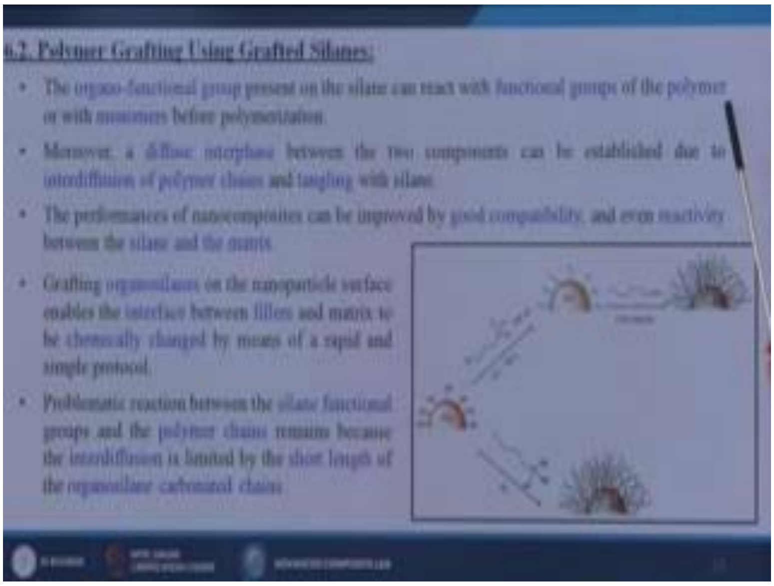

6.2. Polymer Grafting Using Grafted Silanes:

- The organo-functional group present on the silane can react with functional groups of the polymer or with monomers before polymerization.
- Moreover, a diffuse interphase between the two components can be established due to interdiffusion of polymer chains and tangling with silane.
- The performances of nanocomposites can be improved by good compatibility, and even reactivity between the silane and the matrix.
- Grafting organosilanes on the nanoparticle surface enables the interface between fillers and matrix to be chemically changed by means of a rapid and simple protocol.
- Problematic reaction between the silane functional groups and the polymer chains remains because the interdiffusion is limited by the short length of the organosilane carbonated chains.

Here the organic functional group present on the silane can react with functional groups of the polymer or with monomers before polymerizations. So, in this particular case what we are trying to do? I am having the silane groups. So, before polymerizations I am trying to attach some kind of functional groups of there are or maybe some kind of inorganic materials over there onto that silane groups and after that we are trying to do the modification of these particular materials.

Here moreover a diffuse interface between the 2 components can be established due to inter diffusion of polymer chains and tangling with the silane. So, this is the main parameters for this particular case the performance of the nanocomposites can be improved by good compatibility and even reactivity between the silane and the matrix yes of course. So, first initially what you are doing we are trying to may add the silane with our polymer matrix or maybe that with our parent material then again we are trying to attach some kind of inorganic materials with that silane itself, but now this is totally different methods. So, now, first we are taking the silane materials then on that we are adding the inorganic materials then the whole materials we are doing for the polymerization process.

That is why this is giving the more good compatibility and reactivity in between your silane and the matrix itself then grafting organosilanes on the nanoparticle surface enables the interface between fillers and matrix to be chemically changed by means of a rapid and simple protocols. So, the interaction in between your filler material and your substrate material are more stable and more good.

Then problematic reactions between the silane functional groups and the polymer chains remains because of interdiffusion is limited by the short length of the organosilanes carbohydrate chains - yes of course, there is a small disadvantage has been presented over there are which is due to the having the short length of the organosilanes carbohydrate chains, if the chains size will be bigger then maybe this problem can be solved.

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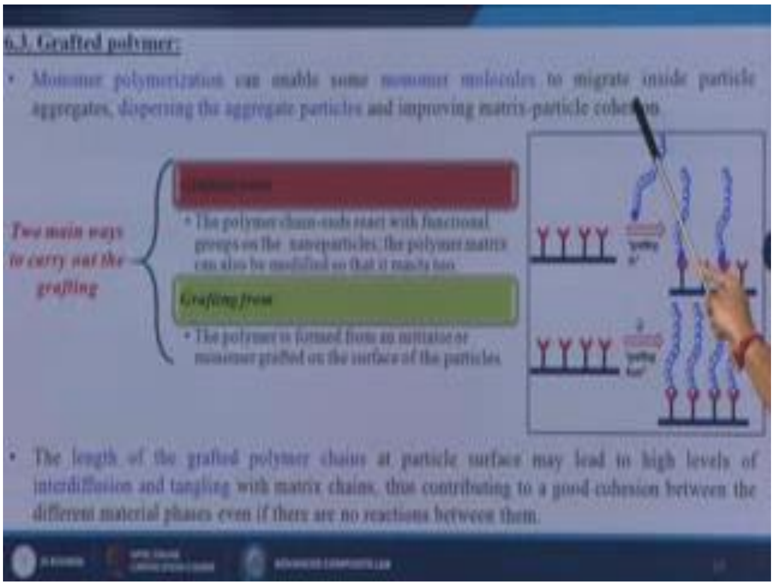

6.3. Grafted polymer:

- Monomer polymerization can enable some monomer molecules to migrate inside particle aggregates, dispersing the aggregate particles and improving matrix-particle cohesion

Two main ways to carry out the grafting

[illegible]

- The polymer chain-ends react with functional groups on the nanoparticles; the polymer matrix can also be modified so that it reacts too

Grafting from

- The polymer is formed from an initiator or monomer grafted on the surface of the particles

- The length of the grafted polymer chains at particle surface may lead to high levels of interdiffusion and tangling with matrix chains, thus contributing to a good cohesion between the different material phases even if there are no reactions between them.

Then next one is called the grafted polymer. So, those in that particular case, the monomer polymerizations can enable some monomer molecules to migrate inside particles aggregates dispersing the aggregate particles and improving the matrix particle cohesion. So, there are actually 2 theories, one is called the grafting to and one is called the grafting from. So, before going to know that about that what is going on first we have to know that 2 main words to carry out this grafting technology because this grafting technology has been divided into 2 parts - one is called the grafting to or maybe the grafting on to another one is called grafting from.

We are talking about the grafting to the polymer chain ends react with functional groups on the nanoparticles the polymer matrix can also be modified so that it reacts too. So, in that particular case, I am having that substrate then I am having some polymer chain that chain is react with the nanoparticles itself. So, that is why it is called the grafting to. So, and for the grafting from the polymer is formed from an initiator or monomer grafted on the surface of the particles. So, in that particular case this polymer chain it is forming from these inorganic materials or maybe whatever material is attached to the substrate.

One case, the polymer chain is attached to the system that is why it is called the grafted to another case from those inorganic materials the polymer chain is forming that is why it is called the grafting form. So, by these 2 methods we can do the modification of that surface itself.

The length of the grafted polymer chains at particles surface may lead to high levels of inter diffusion and tangling with matrix chain thus contributing to a good cohesion between the different material phases even if there are no reactions between them. So, always we prefer that this polymer chain should be little bit bigger. So, that it can be attached with several functional groups. So that the modification of this nanoparticles are more good or even if we can get the better properties in terms of some kind of physical properties or chemical properties of that particular nanofiller.

First one is called the grafting onto. So, polymer end chain can be modified after polymerization to enable the grafting on the particle.

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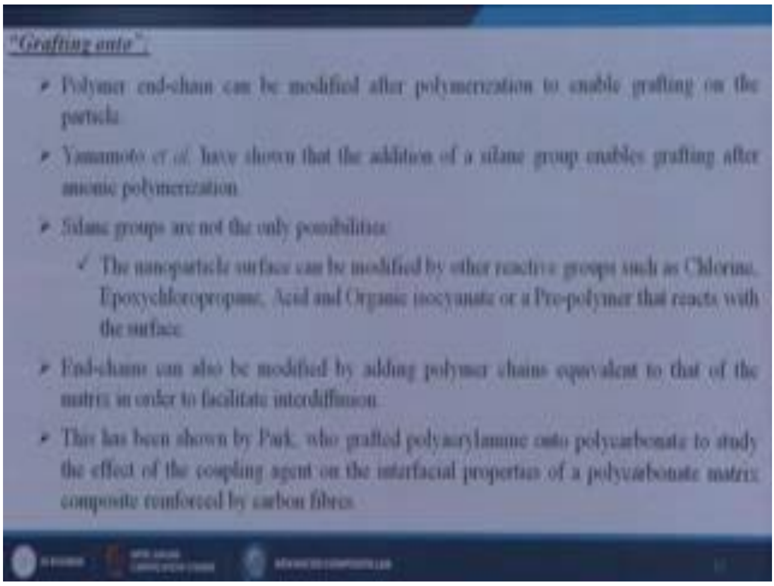

"Grafting onto":

- Polymer end-chain can be modified after polymerization to enable grafting on the particle
- Yamamoto *et al.* have shown that the addition of a silane group enables grafting after anionic polymerization
- Silane groups are not the only possibilities
    - ✓ The nanoparticle surface can be modified by other reactive groups such as Chlorine, Epoxychloropropane, Acid and Organic isocyanate or a Pre-polymer that reacts with the surface
- End-chains can also be modified by adding polymer chains equivalent to that of the matrix in order to facilitate interdiffusion
- This has been shown by Park, who grafted polyacrylamine onto polycarbonate to study the effect of the coupling agent on the interfacial properties of a polycarbonate matrix composite reinforced by carbon fibres

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Yamamoto et al have shown that the addition of a silane group enables grafting after anionic polymerization. So, that particular case the polymer chain is directly attaching with the inorganic particles or maybe the substrate directly. So, that is why it is called the grafting to.

Silane groups are not the only possibilities there are some other possibilities also present. The nanoparticle surface can be modified by other reactive groups such as chlorine epoxychloropropane; acid and Organic isocyanate or a pre-polymer that reacts with the surface. So, accept the silane group also we can attach this kind of material to the systems also.

End-chains can also be modified by adding polymer chains equivalent to that of the matrix in order to facilitate the interdiffusion; that means, here we can add some materials in between the polymer chains in between the silanes which can acts as a binder that in between these 2 which will help you to facilitate some interdiffusion over there and also this has been shown by park who grafted polyacrylamine onto polycarbonate to study the effect of the coupling agent on the interfacial properties of a polycarbonate matrix composites reinforced by carbon fibers. This is also a very very good examples where we have seen that grafting onto of the polymer chain or maybe that silane groups or maybe some inorganic materials has been done on to that polymer substrate itself.

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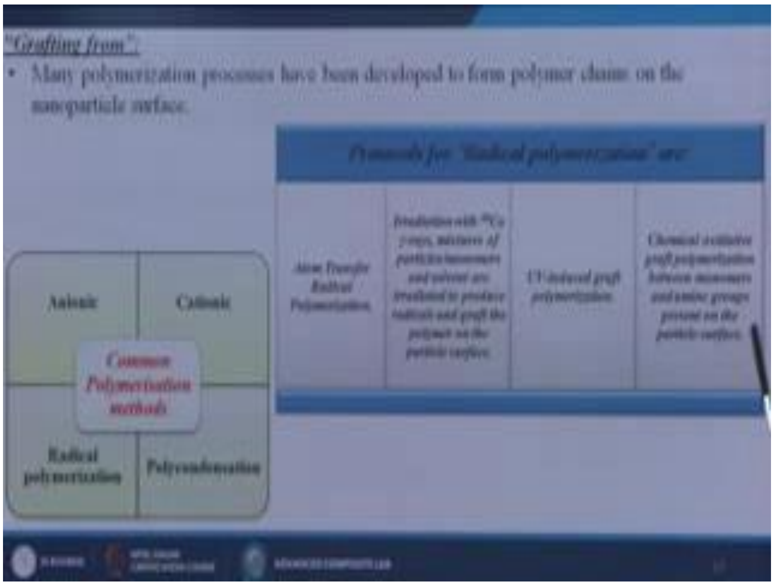

"Grafting from":

- Many polymerization processes have been developed to form polymer chains on the nanoparticle surface.

Protocols for "Radical polymerization" are:			
Atom Transfer Radical Polymerization	Irradiation with ^{60}Co γ-rays, mixtures of particles/monomers and solvent are irradiated to produce radicals and graft the polymer on the particle surface	UV-induced graft polymerization	Chemical oxidative graft polymerization between monomers and amine groups present on the particle surface

Then the next one is known as the grafting form. So, in that particular case, many polymerization processes have been developed to form polymer chains on the nanoparticles surface. So, here the common polymerization methods and anionic polymerization methods, cationic methods, polycondensation methods and the radical polymerization methods, when we are talking about the protocols for radical polymerization that atom transfer radical polymerization is taking place then irradiation with CS cobalt 60 gamma rays mixture of particles and monomers and solvent are irradiated to produce the radicals and grab the polymer onto the particle surface. Then you be induced the graft polymerization is taking place chemical oxidative graft polymerization between monomers and silane groups present on the particles surface.

This is the simple one, simple what I am doing? I am trying to use my substrate on top of that I am trying to put one material then from the outsource I am giving some energy that energy maybe some UV light or maybe some other things by which the polymer chain is going or maybe that silane group or maybe some other reactive functional groups is going at that particular point. So, that is why it is called the grafting from.

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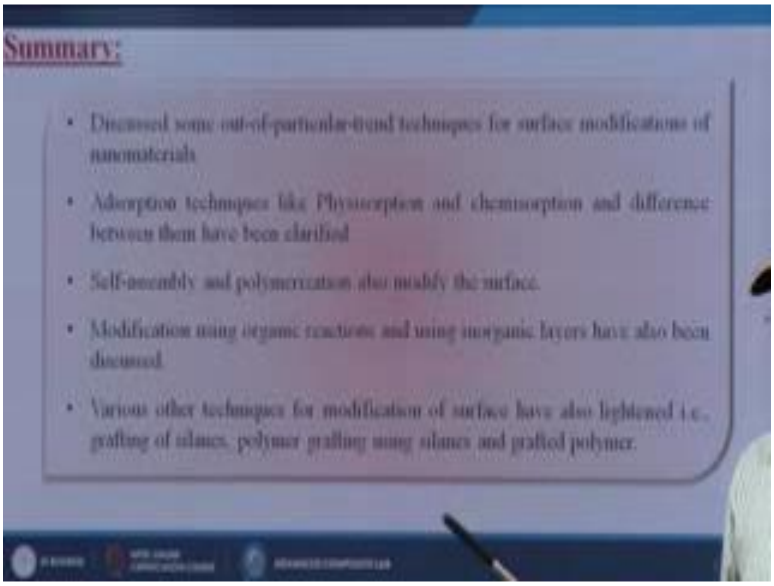

Summary:

- Discussed some out-of-particular-trend techniques for surface modifications of nanomaterials
- Adsorption techniques like Physisorption and chemisorption and difference between them have been clarified
- Self-assembly and polymerization also modify the surface.
- Modification using organic reactions and using inorganic layers have also been discussed.
- Various other techniques for modification of surface have also lightened i.e., grafting of silanes, polymer grafting using silanes and grafted polymer.

Now, we have come to our last slide which is nothing, but the summary that in home if you are going to summaries the study that we have already discussed some out of particular trained techniques for surface modifications of the nanomaterials, some adsorption techniques like physisorption and chemisorption and difference between them have been clarified and detailed, we have explained.

Self assembly and polymerization also modify the surface, modification using organic reactions and using inorganic layers have also been discussed, in this particular lecture. Various other techniques for modification of surface have also lightened that is grafting of silanes polymer, grafting using silanes and grafted polymers. So, by telling all these discussions we have tried to give you a overall glimpse that how are the different latest techniques or may be the latest approaches by which we are trying to modify our nanoparticles and that can give the better surface properties.

Thank you.