

**Surface Engineering of Nanomaterials**  
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**Lecture – 07**  
**Types of Surface Modifications**

Hello. Today we are going to start our next lecture it is called the Types of Surface Modifications. In these particular lectures we are going to discuss about the various types of surface modifications. So, before going to start this I first let me tell you that what is the purpose of doing the surface modifications, what benefits we are going to do, why we are going to do, and then what are the methods generally we are adopting to do the surface modifications.

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**Surface Modification:**

- It is an act of modifying the surface of a material by physical, chemical or biological characteristics different from the ones originally found on the surface of a material.

*Purposes of surface modification*

- Enhancing anticorrosive properties.
- Improving electrical conductivities and optical properties.
- Increasing biocompatibilities.
- Improving adhesion properties.
- Improves component lifetime and resistance to aggressive environments.
- Produce biocompatibility.
- Create permanent wettability.
- Produce hydrophobic characteristics.

First, let us know the definitions of the surface modifications. So, it is an act of modifying the surface of a material by physical, chemical or biological characteristics different from the ones originally found on the surface of a material. From that particular definitions we can understand that when we are talking about the surface modifications so we are doing to modify the surface right, if there is any problem or may be if there is any contaminations or may be if there is any impurities or may be any kind a hazardness on the surface of the bodies so we are trying to modify it. By which method we are trying to modify it that mechanisms is known as the surface modifications method.

And, whatever the materials we are going to deposit or may be your going to put on the surface of the particular material that should be the different from the base material. Now what is the purpose of the surface modifications. So, first one is enhancing the anticorrosive properties. In the last several slides where I was discussing about the abrasions I was discussing about the surface hazardness or may be some kind of chemical vortex. So, when we are making a materials, from a material scientist point of view when we are making certain kind of materials we are using materials for various applications.

So, when we are using those materials may be we dont know that what purpose we are going to use, may be we are keeping that materials into some chemical environment or may be the atmospheres or may be some kind of reactions can be done. So, due to that may be some kind of corrosions can takes place on to the surface of that particular material. So, just to remove or may be delete or may be give some protections on to that surface of that particular materials we are going to do the surface modifications.

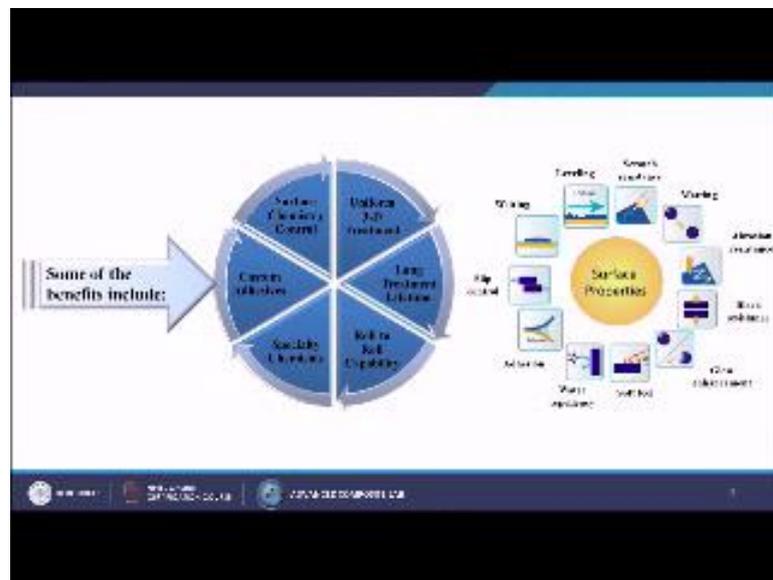
Next, improving the electrical conductivities and the optical properties. Maybe my material is a insulator material, but by doing the coating of any conducting materials we can make that material as a electrical conductor, or maybe we can use it some for some optical purposes too. Next increasing the bioactivities. Maybe that material can be used for some biocompatible material, either I can use that materials for some may be some medical applications. Nowadays we are talking about some kind of metals or may be some kind of polymers which we are going to use for our biomedical applications, like for hip replacement, maybe elbow replacement, maybe any kind of joint replacement. But sometimes what happened maybe that material is not readily accepted by our body. So, what we are going to do, we are trying to do certain kind of coatings on that particular materials by which that material can be accepted to our body.

Next improves adhesion properties. So, that stickiness or may be the rather we can say it may be I am doing the coating on particular material so that it should not be come out like a barrier any kind of barrier layer we can put on to that particular material. Improves component lifetimes resistant to aggressive environments, produce biocompatibility that should be biocompatible nowadays we are very much concern about the pollutions or may be that whatever the pollutions is coming from the material waste. So, we are trying to make certain kind of materials which should be bio comfortable so that when after

finishing its life when we are putting or may be throwing that material into the environment it should not create some kind of toxic gasses. Then create permanent wettability produce the hydrophobic characteristics.

So, these all are the also some kind of applications or may be some kind of purposes which we can get from the surface modifications. So, from the left hand side figure you can understand there are some benefits which can be included for surface modification process, what are those?

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First one is called the surface chemistry control, then uniform 3-D treatment, long treatment lifetime, roll to roll compatibility, specialty chemicals and custom adhesives. So, these all are the different benefits or may be rather we can say advantageous by using the surface modifications method. And right hand side you can see how or by which properties we can analyze a surface modifications.

Say, let us start from wetting, then leveling, scratch resistance, matting, abrasion resistance, block resistance, glow enhancement, soft feel, water repellency, adhesions and slip control. So, there are a numerous applications by which we can control the material properties, we can change the material properties, we can change the acceptance of the particular materials to asks so that it can behaves something totally different than the previous one or may be it can show some better properties in terms of physical properties, chemical properties, or may be the mechanical properties.

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So, in these particular slide we are going to discuss about the different technical resources for the surface modifications. So, in a layman term I can say that there are various types of sources by adopting these sources we can do the surface modification techniques. So, mainly these all are the background of the surface modification techniques. So, first one is called the plasma treatment: maybe that plasma treatment can you can adopt for doing the surface modifications. So, this is a one kind of resource for your perfect module. Or maybe the corona discharge then parylene coating and the photolysis.

So, in the next slide we are going to discuss about these four surface technical resources. Next will discuss about the plasma. So, as we know that plasma is nothing but the fourth state of any material. So, if we hesitate those materials it can show the fourth state, that generally normally we know that solid state, liquid state and the gas state. And plasma is called the fourth state of particular material; that is beyond these three normal states.

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**Plasma:**

- Plasma is a reactive treatment process where positive and negative ions, electrons, and radicals react and collide as long as an electric potential difference exists.
- **Advantages:**
  - ✓ Surface chemistry is highly selective and unique ability to treat a material three dimensionally.
  - ✓ Control the treatment conditions by controlling gas flow, pressure & concentration.
  - ✓ Unique ability to treat a material 3-D.
- **Disadvantages:**
  - ✓ High plasma system price and low rate of production (large chamber size and high power).
- **Plasma treatment helps to:**
  - ✓ Micro-clean to enhance the surface wetting of adhesive.
  - ✓ Functionalize groups to improve surface energy.
  - ✓ Establish hydrophobic & hydrophilic properties.

The slide includes three diagrams of plasma treatment chambers and two photographs showing the results of plasma treatment on various components.

So, plasma is a reactive treatment process where positive and negative ions electrons and radicals react and collide as long as an electronic potential difference exists. What is the surface advantageous? Surface chemistry is highly selective and unique ability to treat a material 3-Dimensionally. So, the simple thing is that I am having some targets, I am ejecting that targets so that it can relies certain kind of ions and or may be the electrons then we have to collect this ions and electrons and we have to do the bombardment to that material surface by which the surface chemistry or may be the surface properties can be changed.

So, what are the disadvantageous? High plasma system price and low rate of productions large chamber size and higher power, because for these particular case we need some controlled atmospheres, we need some innate gas, we need some controlled temperature or may be the ambient conditions so that we have to maintain that constant atmosphere all cover the experimental time. So, that is why it is little bit expensive and the machines also too sophisticated and too large also. Plasma treatment helps to micro clean to enhance the surface wetting adhesives, functionalize groups to improve surface energy establish hydrophobic and hydrophilic properties.

So, by changing the material properties or may be by doing the surface modifications by the ion bombardment or may be the electron bombardment we can change the material properties. So, from this particular figure you can see the before plasma treatment the

poor adhesion of paint on adised device. So, how many times you are putting the paint to that but it is not sticking, means its adhesion properties is very very less it is coming out. So, when we are doing some kind of itching types or may be some kind of scratching type on to that material by the plasma treatment after that we find that the simply the paint sticking with the materials. That means, adhesion properties of that particular materials has been enhanced.

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**Corona Discharge:**  
Corona discharge is plasma at standard atmospheric pressure. This plasma is produced by high voltage and the close proximity of two metal plates (electrodes) in atmosphere.

**If modifies the properties of a surface to:**

- provide a longer lifespan
- Improve surface bonding
- improve corrosion-resistance.

**Drawbacks:**

- Lack of surface chemistry selectivity
- Most corona systems are designed to operate in open-air conditions.
- Limited polymer choice
- Treatment is two-dimensional

**Advantages:**

- Price of purchasing a system for in-house treatment
- Systems are robust and easy to maintain.
- Ease of use

The diagram shows a 'Positive Electrode' on the left and a 'Negative Electrode' on the right. A 'High Voltage' source is connected between them. A 'Target Material' is placed between the electrodes. The diagram illustrates the 'Corona Discharge' process where ions are generated and interact with the target material.

Next one is called the corona discharge, rather we can say it is little bit kind of modified versions of the plasma treatment. So, from these particular things we can understand that corona discharge is plasma at standard atmospheric pressure, this plasma is produced by high voltage and the close proximity of two metal plate in atmosphere.

So, from these particular case you can understand that we are having one electrode rather we are having two electrodes; one is acting as a positive another one is acting as negative in between that we are generating the high voltage difference or may be the potential difference. And we are having some target materials that target materials is divided into two ions and then one of the ions is just coming to a surface that opposite materials, just like that opposite magnetic fields can attract each other something that plus ions that goes to the minus ions and they are doing the surface modifications.

Here, it improves the properties of a surface to provide a longer life span, improves surface bonding, improve corrosion resistance. But there are certain drawbacks too, what

are those? Lack of surface chemistry selectivity, most corona systems are designed to operate in open air conditions, limited polymer choice treatment in two dimensional. That means, whatever the target material I am taking that should have the comparability with the best materials. If there is should not be any comparability in between that or may be there should not be any reactions in between that that material will not stick with the base material so that the material adhesion properties will not be increased or may be not going to be changed.

Advantages: price of purchasing system fir in house treatment, systems are robust and easy to maintain, and easy of use.

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**Parylene coating:**

- It is a conformal surface coating that protects sensitive devices by providing a barrier layer against environmental contaminants
- It significantly improves the performance and durability of manufacturing components by extending lifetime coating to a decade or even longer
- Parylene coating improves device longevity due to:*
  - Resists flaking, abrasion, chemicals, solvents and moisture
  - Reduces surface tack and stickiness
  - Strengthens molded plastic magnetic components
  - Provides a barrier against leaching or bleeding
  - Improves tribology through a low friction
  - Offers excellent thermal stability at high temperatures
  - Remains chemically and biologically inert

The diagram on the right shows a cross-section of a coating chamber. It features a central cylindrical chamber with a rotating drum inside. Gas enters from the top and flows through the chamber, coating the drum and any components placed inside. The diagram is color-coded with red and blue sections.

Then next one is called the parylene coatings. So, parylene coating it is also a one kind of rather we can say that one kind of chemical type of modifications methods by which we are trying to do some kind of chemical reactions over there. Then we are having some sub strict that is known as solid dyma. And we are taking the gas molecules of or may be some inner gas or may be the inner gas we are generally here taking or maybe you are trying to do some kind of chemical reactions in between that, so that some gas is generating; that gas is directly coming through this chamber and it is coating your materials. So, by doing this methods we are calling it has a parylene coating.

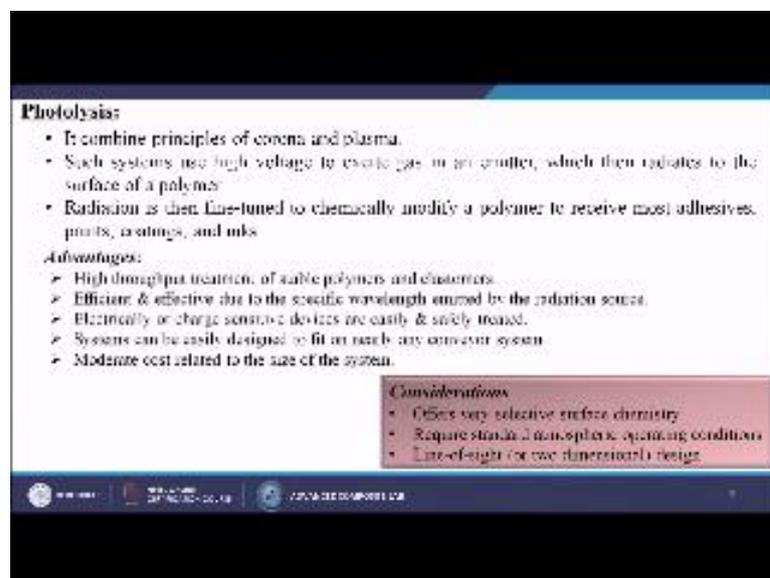
So, it is a conformal surface coating that protects sensitive devices by providing a barrier layer against environmental containments. So, simply it is doing one kind of a rapping on

to the material surface. It significantly improves the performance and durability of manufacturing components by extending lifetime coating to a decade or even longer. So, parylene coating improves device longevity due to resists flaking, abrasion, chemicals, solvents and moisture.

So, just it is giving a layer so that any chemical environment or may be the environmental moisture can react with your base material. Strengthens molded plastic magnetic components. Provides a barrier against leaching or blooming. Improves lubricity through a low frictions, because it may be some kind of sleepy nature so that it can be used for as a lubricating in between the surfaces. Offers excellent thermal stability in high temperatures that material is having that capacity or may be the capability that it can withstand the higher temperature so that it can be used into the high temperatures. Remains chemically and biologically inert.

So, these all are the different properties for parylene coating. And the next one is called the photolysis. So, in a single word I can say that this is the combinations of plasma as well as the corona.

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**Photolysis:**

- It combine principles of corona and plasma.
- Such systems use high voltage to excite gas in an emitter, which then radiates to the surface of a polymer.
- Radiation is then fine-tuned to chemically modify a polymer to receive most adhesives, paints, coatings, and inks.

**Advantages:**

- High throughput treatment of stable polymers and elastomers.
- Efficient & effective due to the specific wavelength emitted by the radiation source.
- Electrically or charge sensitive devices are easily & safely treated.
- Systems can be easily designed to fit on nearly any conveyor system.
- Moderate cost related to the size of the system.

**Considerations:**

- Offers very selective surface chemistry.
- Require standard non-spheric operating conditions.
- Line-of-sight (or two dimensional) design.

So, it combine principles of corona and plasma. Such systems use high voltage to excite gas in an emitter, which then radiates to the surface of a polymer. Radiation is then fine turned to chemically modify a polymer to receive most adhesives, paints, coatings, and links. So, from these particular slide you can understand that is controllable. That means,

the thickness of particular coating can be controlled by us not only that the reactions in between the coating materials and the base materials that also can be changed. Means, if you are going for different materials that you have to change the precautions.

So, advantageous: high throughput treatment of stable polymers and elastomers, efficient and effective due to the specific wavelength emitted by the radiation source, electricity or charge sensitive device are easily and safely treated, systems can be easily designed to fit on nearly any conveyor systems, moderate cost related size and shapes. So, it depends upon what type of applications we are going to do, so based on that you can choose any of them.

So, considerations: offers very selective surface chemistry, require standard atmospheric operating conditions, line-of-sight or may be the two dimensional things we can do it over there. Next it is a just rather we can say that this is a one kind of examples that by which adopting functional groups or may be solving which problems we can do the surface modifications. And what are the characteristics or may be the what are the remedies or may be what are the results we can get by adopting this kind of functional groups.

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**Functional groups for modification towards polymeric materials:**

Functional Group	Class name	Examples	Characteristics
-OH (hydroxyl)	Alcohols	Ethanol, Glycerol, Sugars	Polar, Hydrophilic
-COOH (carboxyl)	Carboxylic acid	Ascorbic acid, Amino acid, Fatty acid	Polar, Hydrophilic, Weak acid
NH <sub>2</sub> (amino)	Amines	Amino acid	Polar, Hydrophilic, Weak base
PO <sub>4</sub> <sup>3-</sup> (phosphate)	Organic phosphate	DNA, ATP, Phospholipids	Polar, Hydrophilic, Acid
-C=O (carbonyl)	Aldehydes	Acetone, Sugars	Polar, Hydrophilic
-C(OH) (enol)	Aldehydes	Formaldehyde, Sugars	Polar, Hydrophilic
-CH <sub>3</sub> (methyl)	-	Fatty acids, Gels, Waxes	Nonpolar, Hydrophobic

Let us take one examples; suppose we can adopt the hydroxyl functional groups generally we can get it from the alcohols itself. Examples is; ethanol, glyccorol, sugars. The characteristics is we can polar characteristics or may be the hydrophilic

characteristics of the particular material. Or rather we can say if we take the amino NH<sub>2</sub>, so generally we are getting a class names is amines we are getting this materials form the amino acid. So, what kind of materials properties we can get, we can get the polar, hydrophilic and weak base.

Then like that methyl. So methyl, generally we can get from the fatty acids, oil, waxes. So, we can transfer the material from to nonpolar and hydrophobic. So, from these particular example you can understand that suppose I am having some materials which is polar easily I can make it into a non polar materials. Or maybe I am having the materials which is showing the hydrophobic nature I can make that materials into the hydrophilic nature.

Now there are certain common problems and remedies by which we can do some kind of modifications or may be by surface modifications we can repair some material surfaces or maybe we can change the material properties.

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Common problems and remedies by surface modification		
Application	Problem	Solution
 Polymer array of DNA and proteins	Polymer properties inhibit or interfere with reagents or cultures	Polymers can be surface modified to get the desired nature through polymer
 Microfluidic device	Pre-adhesion of particles and/or specific molecules	Modification to create a control bond between the polymer and the particles, like surface coating
 Microarray chip	Polymer properties inhibit or interfere with reagents or cultures	Modification to enhance or change properties through surface modification
 Biosensor	Pre-adhesion of particles and/or specific molecules	Modification to alter the molecule's polarity and/or other changing its hydrophobic properties of the molecule
 DNA microarray printing and encapsulation	Non-adhesion and/or adhesion, excessive coating and/or poor resolution	Hydrophobicity to promote adhesion and wetting coatings to a specifically chosen surface
 Microfluidic chip	Pre-adhesion of captured fluid or particles	Modification to make the surface of the polymer hydrophobic from the surface through surface coating

What are those? Like polymeric well plates and cell culture trays, what is the applications of that particular material? What type of problem generally we are getting? We are facing the problems like polymer properties inhibit or interfere with reagents or cultures. Yes of course, because polymer is having a high affinity to react with the chemicals or maybe to react with any kind of chemical environment. So, just try to do some kind of modifications we can observe or maybe we can stop that problems so that

the polymer will not be reacted with the any chemical environment or maybe with the chemicals.

So, enhancement in surface properties by grafting carboxyl, amine or may be the hydroxyl groups. Same thing we can go for some kind of semi conductor materials on electronic devices like PCB boards, flexible circuits, potting or some kind of encapsulations. So, non uniform anti shock and anti corrosion coatings or poor wire bonds these all are the problems generally we are facing in our day today life. So what we are going to do, we are going to do some kind of plasma cleaning to promote uniform and consistent coating on an atomically clean surface.

So, first we have to see the problems, then we have to know the remedies, then we have to do it accordingly. In the next slide we are going to discuss some kind of latest techniques generally we are adopting for doing the surface modifications.

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**Surface modification of bio-materials:**

**1. Attachment of bioactive functionality**

- ❖ Surface modification techniques enhance biocompatibility of the material without changing bulk properties
- ❖ Biocompatibility is heavily dependent upon surface properties as well as interaction between the surface and cells and/or proteins, or between cells themselves
- ❖ Bioactive functionality can be attached through
  - Large ECM protein/Fibrillar Bioactive Coatings
  - Covalently Bound Short Signaling Domains
  - Chromopeptide Short Signaling Domains
  - Physico-physical Short Signaling Domains

**Attachment of Bioactive Functionality**

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Attachment of Bioactive Functionality

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So, what are those? First one is called the attachment of bioactive functionality. Generally we are doing this kind of modifications for the bio materials. So, what we are doing? We are having some kind of materials, bio materials. So, bio materials is having some kind of functional groups on the top of that right at the surface. So, if we keep that material for a particular time either that material will degrade or may be that material will react with the environment and its properties can be changed.

So, by solving these problems we are going to act some kind of bio degradable or maybe bio active materials to the surface so that by chemical reactions that material can react with that materials and that can do certain kind of coatings on to that material. So, surface modification techniques enhance biocompatibility of the material without changing the bulk properties.

Biocompatibility is heavily dependent upon surface properties as well as the interactions between the surface and cells and or proteins or between cells themselves. Bioactive functionality can be attached through: large extra cellular matrices, protein or may be fragment bioactive coatings, covalently bound short signaling domains, chemisorptive short signaling domains, physisorptive short signaling domains.

So, these all are the different or rather we can say the various techniques generally the biotechnology people are adopting. And from that particular figure you can understand that that we are having the base materials and top of that we are attaching some kind of bioactive molecules or may be bioactive materials so that the material can be coated or maybe it should be insulated from the any kind of environmental attack.

Next is called the intensify porosity surface. Generally, we are doing this kind of techniques for the drop delivery. Nowadays people are talking about the targeted drop delivery right, we are trying to adopt some kind of materials and we are trying to put those through the medicines and then we want to see that what is the effect in it. Nowadays people are using some kind of nano fillers, so when we are adopting those materials we are trying to do that that material should have different pores or may be that different holes, so that the medicine can be easily absorb in between the pores and holes. And when it will go into our stomach, so automatically that medicines or maybe that drugs can be realized easily so that it can go to the affected portions.

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**2. Intensifying porosity of surface (Drug Delivery)**

- The purpose of a drug delivery system is to devise a method that enables delivery of a therapeutic agent that may have sub-optimal physicochemical properties in biological tissue.
- The formation of temporary pores in the cell membrane achieved through the application of various physical energies.
- Drug-carrying NP (smart nanoparticles) or smart drug carriers (SDC) enter through pores to the cells where the drug/gene is further released and activated.

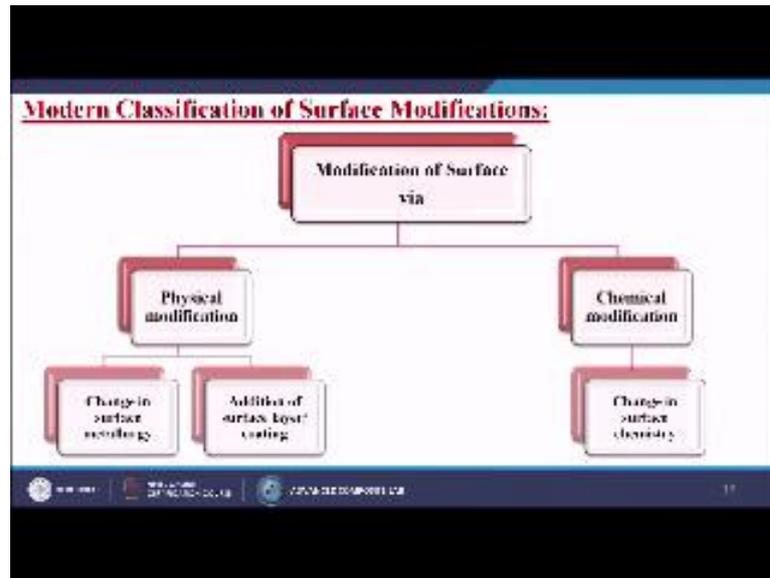
*Few Techniques associated with physical energy are listed below:*

Technique	Electroporation	Magnetoporation	Thermoporation	Sonoporation
Principle	Electric field	Magnetic field	Temperature	Ultrasound
Disadvantages	Irreversible electroporation cell death (high electric field)	Overheating, magnetic field, mechanical stress (MNP/SDC)	Excessive heating (high temperature)	Excessive heating, cell damage (high frequency)
Advantages	Reversible electroporation	Non-thermal, non-invasive, low electric field	Non-thermal, non-invasive, low temperature	Reversible, non-invasive, low frequency

So, the purpose of a drug delivery system is to devise methods that enables delivery of a therapeutic agent that may be have sub optimal physicochemical properties in biological tissues. Drug carrying nano particles or smart drug carries enter through pores to the cells where the drug or gene is further released and activated. So, some cases that a maybe drug cannot reach properly, so what you are doing? We are trying to make certain kind of microspheres which is having some pores, so we are injecting the medicines in between that pores and that microspheres can easily go to the affected parts. And while it is reaching to the affective parts easily it can relies the drugs so that it can to the remedy at the particular point.

So, few techniques associated with physical energy are listed below: so like these electroporations, magnetoporations, thermoporations and the sonoporations. So, physical energy like electric field, magnetic field, temperature, ultrasound. There are certain disadvantage also irreversible electroporation cell dealt with high fields. So, still now these all are the methods which were using from the past, but now we are trying to modify those methods by doing some kind of material or maybe preparing some kind of materials which is having the higher porosity.

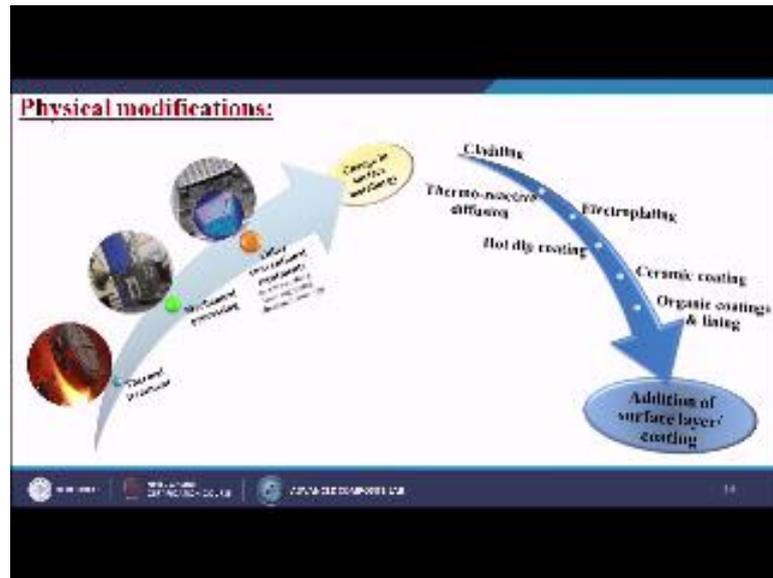
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Next, we will discuss about the classification techniques which generally we are going to adopt for the surface modifications. What are those? It is divided into two parts one is called the physical modifications another one is called the chemical modifications. Then physical modification also divided into two parts change in surface metallurgy and addition of surface layer and coating and chemical modifications is change in surface chemistry. So, these is the whole idea about the surface modifications.

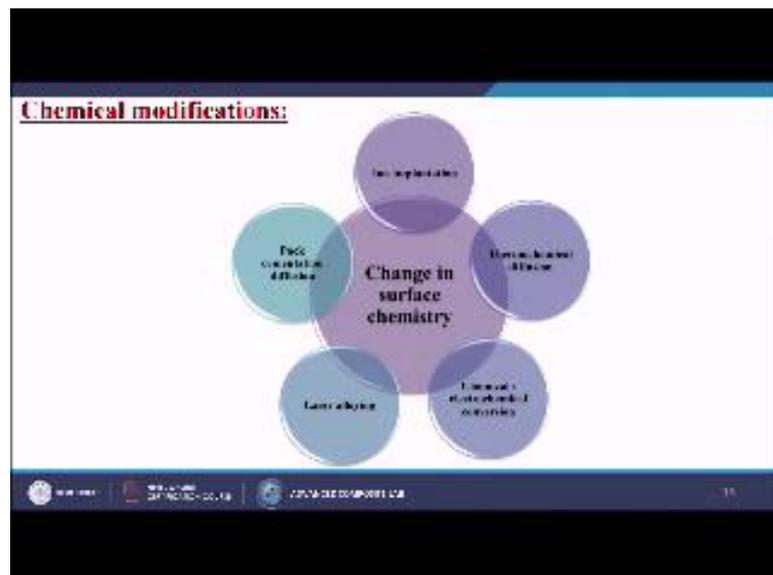
So, in our coming slide we are going to see that what are the physical modifications and what are the chemical modifications generally we are going to do.

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So, like thermal treatment mechanical processing other environmental treatment treatments by adopting all these methods we are going to do the surface modifications. And the right hand side you can see some kind of cladding, thermo reactive diffusions, electroplating, hot dip coating, ceramic coatings, organic coating and lining by changing the surface layer or may be the surface chemistry we are going to do the surface modifications. And also the chemical reactions is like that.

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That we are going to do by pack cementation diffusions, ion implementation, thermochemical diffusion, chemical electrochemical conversion, laser alloying. So, these all are the different techniques generally we are adopting for the surface chemistry by changing the surface or may be rather we can say that by changing the surface chemistry we are doing the surface modifications.

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And in summary if we discuss about the whole slide what we have discussed till now so the thing is that, here we have discussed into two parts one is called the surface modifications is mostly done through by which method; change in surface metallurgy, change in surface chemistry, additions of a layered surface coating, attachment of bioactive functionality, intensifying porosity of the surface. Then these surface modification results for improvement in physical chemical property.

So, these is the applications or may be this is the things why we are going to do the surface modifications, improvement in electrical and electronics properties, enhancement in durability and reliability of the work pieces, applications in various fields like aerospace, automobile, electronic, device and biomedical applications etcetera.

So, there are n number of applications generally by we can do by these surface modifications or may be the we can change the surface properties by that our material can be accepted to any environment.

Thank you.