Biomedical Ultrasound: Fundamentals of Imaging and Micromachined Transducers

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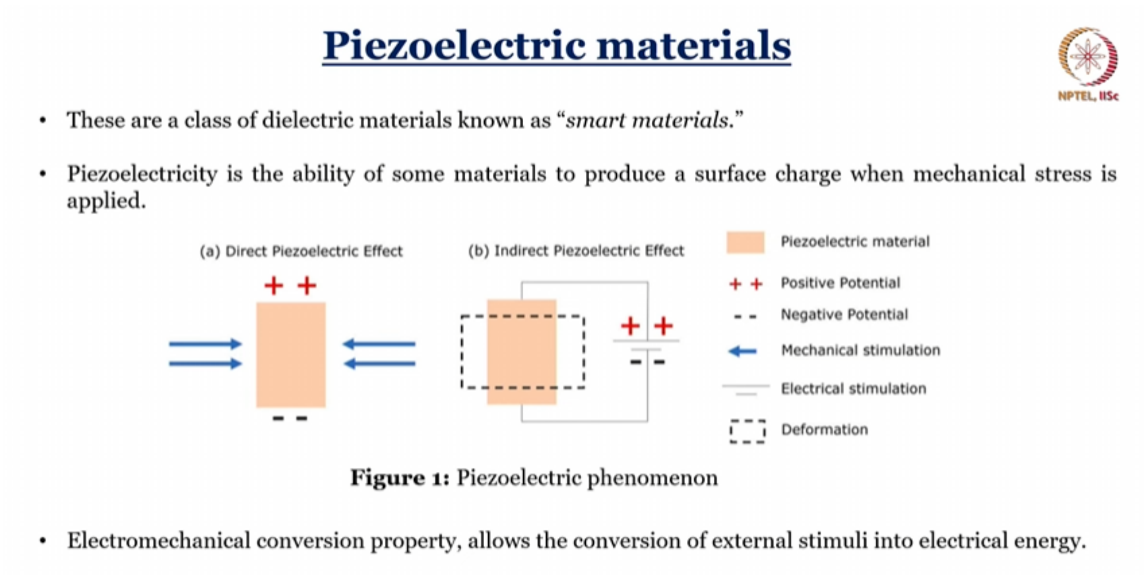
Lecture: 59

Piezoelectric Polymers

Hello everyone, welcome to today's lecture. I am Rashmi HS, Research Associate, BEES Lab, DESC, Indian Institute of Science, Bangalore. So, in today's lecture we are going to learn about piezoelectric polymers. Before we start with the actual piezoelectric polymers, we need to know some basic concepts related to piezoelectric materials. So, these piezoelectric materials, are a class of dielectric materials which are also known as smart materials. Smart material means these materials will be showing reproducible, significant as well as stable variation with only one property under applied stress condition.



This piezoelectricity can be defined as the formation of surface charge on the material whenever some stress is applied on the material. So, this piezoelectric effect can be either direct piezoelectric effect or indirect. So, from the figure, you can see here in case of direct piezoelectric effect, the material it is subjected to electrical field or electrical stress under which it will develop a surface charge that leads to the piezoelectric effect. Here there will be a conversion of electrical energy into mechanical energy.

And in case of indirect piezoelectric effect, some sort of mechanical stress is applied on the material under which the deformation in the material takes place that leads to the piezoelectricity. And in indirect piezoelectric effect, the conversion of mechanical energy into electrical energy takes place. So, this piezoelectricity, was first discovered by two scientists Jacks and Perry Curie in 1880 when they were working with quartz crystal. So this piezoelectric materials will be having a non centrosymmetric structure because of which these materials are able to show the piezoelectric property. Apart from that, these piezoelectric materials they also have electromechanical conversion properties. So, this property allows the material to convert any kind of stress applied on the material such as pH, temperature, pressure or ultrasonic waves etc. into electrical energy. So, because of this good electromechanical behavior of these piezoelectric materials, these materials are capable of regulating multiple physiological functions such as apoptosis, cell migration, cell proliferation, etc. Hence, these materials have found widespread application in biomedicine.

Next coming to the classification of these piezoelectric materials, these piezoelectric materials broadly are categorized into inorganic piezoelectric materials and organic piezoelectric materials.

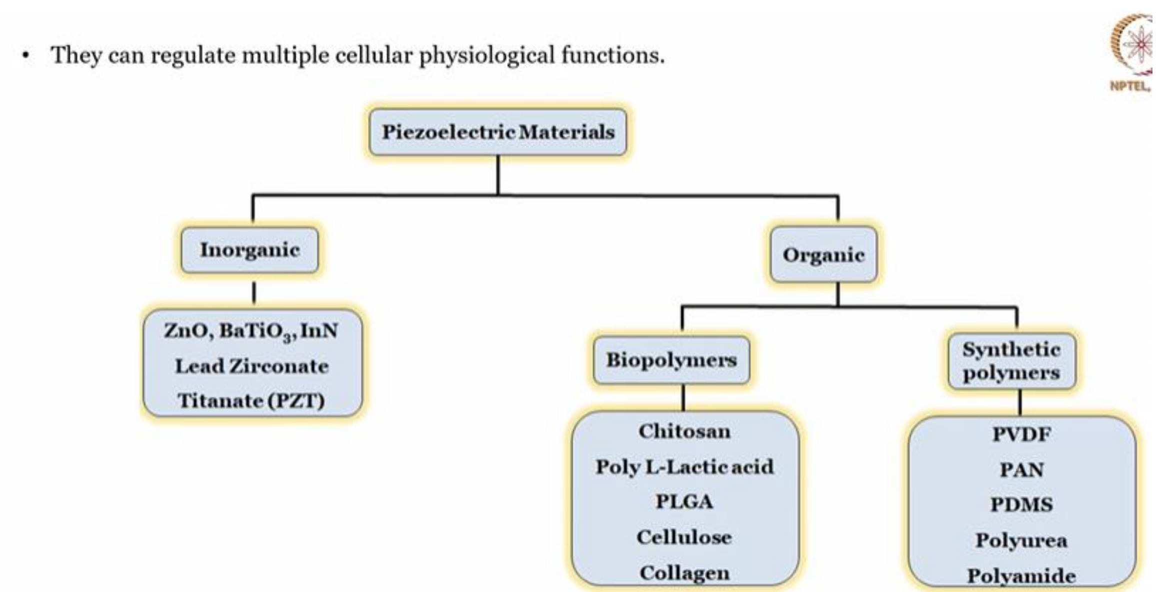


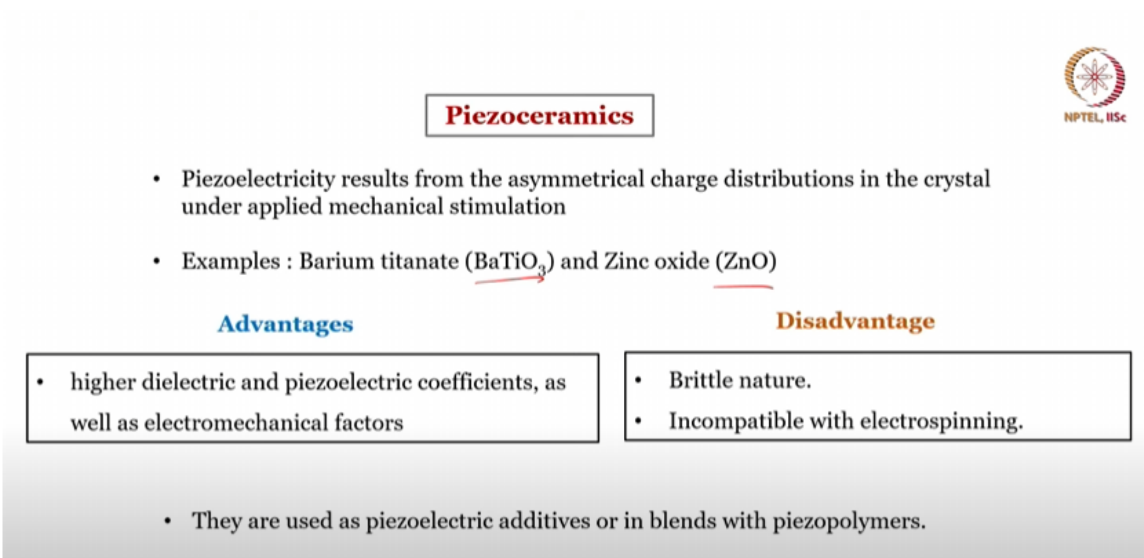
Figure 2: Classification of piezoelectric materials.

If we come to the inorganic piezoelectric materials, in inorganic piezoelectric materials as the name itself says these are derived from inorganic materials. such as ions of sodium, potassium etc. So, those inorganic counterparts will be present in these inorganic piezoelectric materials and the best example we can quote here is zinc oxide, barium titanate, indium nitride, lead zirconate titanate, gallium nitride etc..

Next if we come to the organic piezoelectric materials. So, these organic piezoelectric materials are nothing but the materials that are composed of carbon and hydrogen. So, these organic piezoelectric materials further are classified into two classes bio piezoelectric polymers and synthetic piezoelectric polymers.

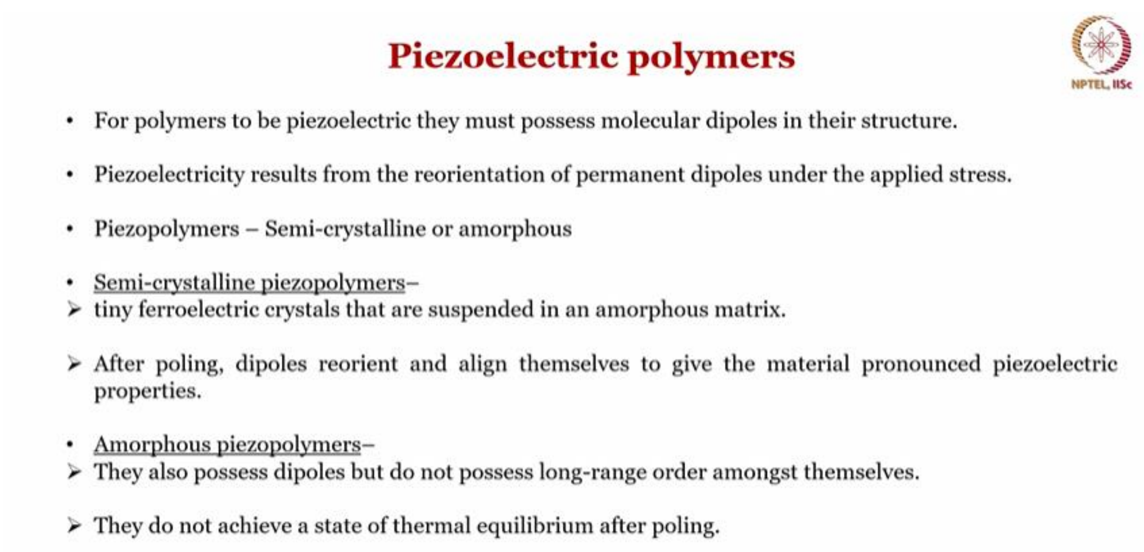
So, these bio piezoelectric polymers, are those piezoelectric materials which are from biological origin. And example for such biopolymers are chitosan, PLGA, cellulose, polylactic acid, collagen, etc. Coming to the synthetic polymers, in case of synthetic piezoelectric polymers, so these are the polymers which are prepared or produced within labs, and can be synthesized. So, that is why the name synthetic polymers and these synthetic polymers' examples are PVDF, polyacetonitrile, PDMS, polyurea and polyamide. So, both inorganic piezoelectric materials and organic piezoelectric material have good piezoelectric property which can be widely utilized in biomedical applications.

So, next coming to the inorganic piezoelectric materials which are also said to be the piezo ceramics. In case of these materials, the piezoelectricity it is generated from the asymmetrical charge distribution within the crystal under applied stress. So, when there is a asymmetrical charge distribution takes place, there will be a polarization of the material that takes place. So, when this polarization takes place, there will be a generation of piezoelectricity.



So, example for piezo ceramics are barium titanate, zinc oxide, gallium nitrate etc. And coming to the advantages of these piezo ceramics. So, these piezo ceramic materials have higher dielectric and piezoelectric coefficients and as well as electromechanical factors. So, high dielectric as well as piezoelectric coefficient help in the successive polarization of the material leading to the enhanced piezoelectric property. But these materials also have some disadvantages such as the nature of the material it is highly brittle. So, the brittle nature of the material poses complications during the processing. And also this electrospinning which is a widely used and well known technique in order to enhance the piezoelectric property of the material. In case of this electrospinning, due to this brittle nature of the material, it makes the piezo ceramics incompatible for electrospinning process. Because during electrospinning, the material is subjected for high mechanical stress and under that conditions these materials they cannot withstand the stress and thereby there will be a destruction of crystal structure leading to the destruction of piezoelectric property. So, that is why these piezo ceramic materials are used as additives or as blends along with the piezo-polymers during applications, because making blends or using them as additives helps in improving the mechanical property of the final material.

Next coming to the piezoelectric polymers. So, these piezoelectric polymers as the name itself says are the polymeric materials. Polymers are nothing but the macromolecules with a giant structure which are composed of large number of monomeric units that are connected to each other. So, in order to show their piezoelectric property, these piezoelectric polymers must and should possess molecular dipoles in the structural arrangement.



So, molecular dipoles are nothing but any groups that can provide charge on the material such as hydroxyl group, NH_2 group or carbonyl group. or COO group or any ester linkage. So, this piezoelectricity in case of these material, is mainly generated by the reorientation and alignment of these molecular dipoles under the applied stress. These piezopolymers can be either semi crystalline or amorphous in nature. So, semi crystalline nature of piezopolymers means that they will contain a mixture of tiny ferroelectric crystals that are dispersed within the amorphous polymer matrix. The best example for semi crystalline polymer is PVDF. Apart from that, these semi crystalline polymers are subjected for a process called poling, in order to enhance its piezoelectric power. So, these dipoles present in the material they undergo reorientation and alignment in such a way that they are going to give enhanced or increased piezoelectric power to the material during poling.

Next coming to the amorphous piezopolymers. In case of amorphous piezopolymers, they also possess dipoles in their structure, but they will not be having the long range order of arrangement. So, that is why, when these materials are subjected for poling process, they will not attain a state of thermal equilibrium due to which these amorphous piezopolymers find less application in any biomedical devices.

Next coming to the piezopolymers that is the crystalline nature. So, for any polymer in order to exhibit piezoelectricity must and should possess crystalline nature. So, crystalline nature helps in orientation as well as complete polarization of the material to improve the piezoelectric power. So, this crystallinity of any polymeric material or in general any piezomaterial, can be enhanced by a process of poling. So, poling means, a process wherein there will be an enhancement of piezoelectric nature of the material by subjecting the material to a high temperature and high electric field. Under this condition, there will be a reorientation as well as alignment of the polar charge groups, leading to ordered arrangement that finally leads to the improved piezoelectric effect.

- Crystallinity of the material improves piezoelectric behavior.
- Poling process – enhances crystalline nature rendering high piezoelectricity.
- In poling, a high temperature or high electric field is applied.
- Poling – 2 types:
  a) Contact poling: Material is sandwiched between two electrodes.

  b) Corona poling: Electrode is connected to one side of the material.

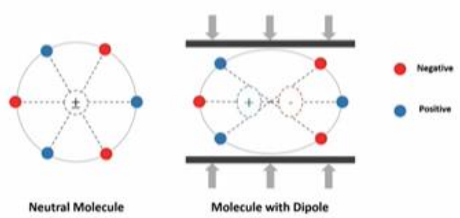


Figure 3: Diagrammatic illustration of polarization of the molecule by compressive forces.

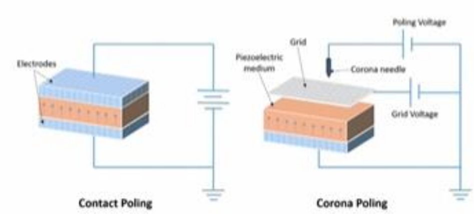


Figure 4: Contact poling and Corona poling.

And here in figure 3, you can see the case of neutral molecules wherein, the charges are arranged randomly. And whenever this neutral molecule is subjected for some compressive force or any stress, there will be an alignment and reorientation of the charges, that takes place, which leads to the piezoelectric nature of the material. So in case of this polling process, we can see two different types of polling. One is contact polling and another one is corona polling. So contact polling means here in figure 4, I have given that in contact polling, the bulk piezoelectric material is sandwiched between the two electrodes and thereby we are going to apply the current on the material.

So, whenever we apply the current, there will be an orientation as well as alignment of the crystal structure that takes place, leading to the piezoelectricity. And in case of this contact poling, the cooling of the material will be done in sandwiched condition itself, because we need to preserve the aligned crystals as it is, in order to maintain the piezoelectricity.

Coming to the corona polling. In case of corona polling, we can see the bulk piezoelectric material is coated on one side with the electrode material and other side will be free. Under this condition, we are going to apply current on the material which helps in the reorientation and alignment of charges and thereby piezoelectricity.

So, next coming to the advantages of these piezoelectric polymers.

Advantages of piezoelectric polymers:

- Have suitable flexibility, lightweight, and mechanical properties.
- They exhibit high strength and high impact resistance.
- Have high voltage sensitivity and low acoustic and mechanical impedance.
- High dielectric breakdown and high operating field strength.
- Offer the ability to pattern electrodes on the film surface.
- Low piezoelectric strain constant (d31) but higher piezoelectric stress constants (g31).
- Devices made of piezoelectric polymers are less expensive.
- Polymer-based devices do not require advanced microfabrication facilities.

So, as these piezoelectric polymers are basically polymers, they combine the advantages of piezoelectric effect as well as polymer structure. So, that is why, they have very good flexibility, lightweight, mechanical properties along with good strength. The strength of the material depending on the polymer will be very good and also they show high impact resistance. These materials are highly sensitive to voltage and also show low acoustic as well as mechanical impedance characters. These materials, are able to form films. So, on the films we will be able to pattern different types of electrodes by using different techniques, patterning techniques such as lithography and all.

So, these materials also show low piezoelectric strain constant, but the piezoelectric stress constant of the materials will be very high, which is one major advantage of this material. Apart from that, the devices that are produced by these materials, will be less expensive because the material that is used, which is the piezopolymer, will be fabricated in a cost effective way with easy processing techniques. And then the polymer based devices do not require any micro fabrication facilities such as micro machining in order to fabricate them. So, that is why the cost of these polymer based devices will be reduced.

So, next let us study about important piezoelectric polymers that are majorly used in biomedical applications. So, coming to the first polymer that is PVDF. PVDF is nothing but polyvinylidene difluoride or polyvinylidene fluoride. This PVDF was first discovered by H. Kawai and this is the first polymeric material studied with piezoelectricity. So this PVDF it is a semi-crystalline material and it has good dielectric properties also. This material it is highly biocompatible but not biodegradable. The material shows 5 major polymorphic forms.

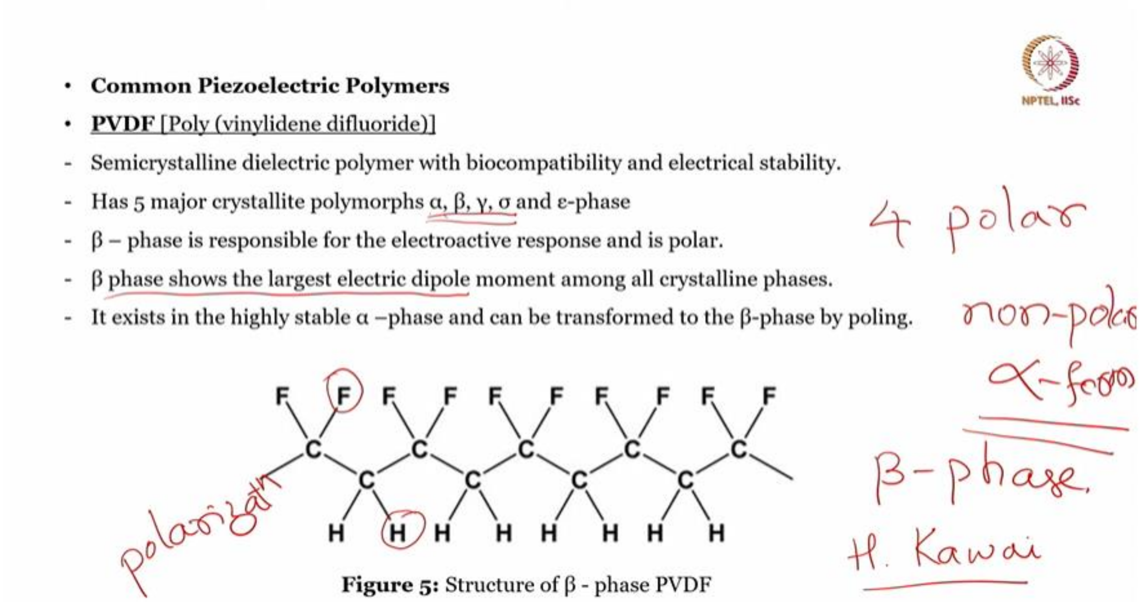


Figure 5: Structure of β - phase PVDF

Those forms are nothing but α form, β form, γ form, σ as well as ε form or phase. Among these 5 forms, the 4 forms are polar in nature and only one form of the material that is non-polar is the α form. So, this α form is a non-polar form and remaining are polar forms. But basically this material it exists in α form. Generally it exists in α form, but this α form can be converted or transformed to the highly piezoelectric form of this PVDF that is β form or β phase. So, here in the structure you can see the β phase of the PVDF wherein the arrangement of hydrogen atoms as well as fluoride atoms are in an orderly manner. All the fluoride atoms are arranged on one side of the carbon and the hydrogen atoms are arranged on another side of the carbon. So, due to the separation of these different functional groups properly throughout the polymer chain, the material undergoes effective polarization when it is subjected to any kind of stress. So, due to that reason, the material shows good piezoelectric properties. And among these 5 forms the β phase of the material has largest electric dipole and that is why it is the most widely used form in case of biomedical applications.

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- The piezoelectric nature of PVDF can be enhanced by electrospinning technique.
- PVDF has a higher piezoelectric coefficient than other known polymers.
- PVDF has a piezoelectric coefficient (d_{33}) of 13 to 28 pC/N and electromechanical coefficient, $k_{33} = 0.27$.
- The flexible PVDF and its copolymers exhibit excellent piezoelectric, pyroelectric, ferroelectric, and dielectric properties
- PVDF-based materials are biocompatible but **non-biodegradable**.
- Good flexibility, toughness, chemical resistance, and biocompatibility.
- Many techniques - stretching, polarization under high electrical field, thermal annealing, and filler incorporation - increase β-phase content.
- Copolymer of PVDF with trifluoroethylene (TrFE) – shows a higher level of crystallinity than pure PVDF (d_{33} = 24–38 pC N^{-1}) and electromechanical coefficient, $k_{33} = 0.37$.
- Applications – in regenerative medicine in bone, neural, cardiac tissue engineering, and permanent bioprosthetic implant for post-myocardium infarction treatments.

So as always, PVDF exists in the form of α form which is not piezoelectric. So, the piezoelectric power of this α form or the PVDF can be increased or enhanced by a process called electrospinning. So, in this electrospinning process, the solution of the polymer is prepared and the solution is subjected to high mechanical stress under which it will form fibric structure of the material and thereby the alignment of the crystals of this PVDF converts from α to β form and thereby it shows piezoelectricity. this PVDF has high piezoelectric coefficient compared to any other polymers known. And it shows the piezoelectricity in the range of 13 to 28 and this piezoelectric coefficient of the material depends on the content of β phase that is present in the PVDF. The enhancement of piezoelectricity of this material, can be brought about by using various techniques such as stretching of the material, polarization of the material under electric field and thermal annealing as well as filler incorporation. So, any of these techniques successively increase the β phase content of the material and thereby increase in piezoelectricity. So, due to these reasons, PVDF has applications in regenerative medicine in bone. So, in case of regenerative medicine in bone, neural as well as cardiac tissue engineering, it is widely used as a patch that helps in regeneration of the damaged tissues.

So next coming to the second polymer that is PLA (polylactic acid). This polylactic acid it is a homopolymer of lactic acid. The lactic acid units are linked to one another to form this polylactic acid and this material is a semi crystalline material, and is a synthetic material. So, it is synthesized by the fermentation of sugar present in any of the vegetables such as potatoes, corn, molasses or anything.

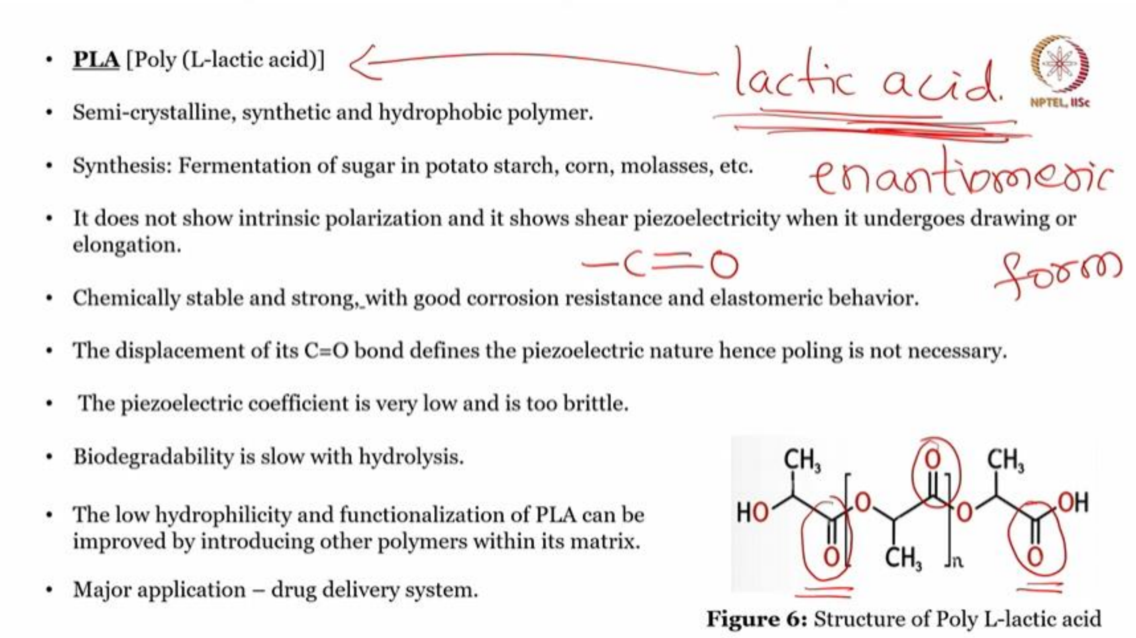


Figure 6: Structure of Poly L-lactic acid

So, that when it undergoes fermentation process, it leads to the generation of lactic acid and thereby polylactic acid. So, this polylactic acid, is present in different enantiomeric forms. depending on the monomeric unit. So, based on that, the polylactic acid will have its enantiomeric forms and this monomer that is lactic acid, will exist in three different forms.

One is called as (+) lactic acid or D lactic acid and another one is called L (-) lactic acid. and the last one is nothing but the racemic mixture that is DL (±) lactic acid. So, all the 3 forms of this polylactic acid is available and the majorly used lactic acid, in case of biomedicine is the poly L lactic acid form of the material. So, this poly L lactic acid shows intrinsic polarization property and that is why we need not to process this material by any other techniques such as elongation or compression or anything in order to improve its piezoelectric behavior. And in case of this polylactic acid, the piezoelectricity is a result of displacement of the carbonyl group that is present in the polymeric chain.

Here in the figure 6, you can see the presence of carbonyl groups throughout the chain of polylactic acid. So whenever the displacement of these carbonyl groups in the material takes place, that leads to the generation of piezoelectricity. A major disadvantage of this polylactic acid is its biodegradability. During biodegradation, this polylactic acid undergoes degradation by hydrolysis process and the hydrolytic product that is generated are majorly lactic acid. Whenever PLA undergoes hydrolysis, it produces lactic acid and this is acidic in nature, due to which it poses some serious health hazards to the living beings. Apart from that, this polylactic acid is highly brittle in nature. The brittle nature of polylactic acid makes it mechanically weak. The mechanical properties of the material are also very poor and due to this brittle nature of the material, it will have hydrophobic character. Due to this hydrophobic character, it cannot be properly attached to the cell surface or cell membrane within the cell. Due to that reason, it has found less application in tissue engineering fields and a major application of this material is found in drug delivery systems.

So, the next polymer is chitosan. Chitosan is a polymer, from animal origin. Chitin that is present in the exoskeleton of the any insects, when it undergoes deacetylation, leads to the generation of chitosan. So, this chitosan has a non centrosymmetric structure due to which it shows piezoelectricity. So, in the structure here, you can see the presence of amino as well as hydroxyl group in the material.

- **Chitosan**
- Biopolymer with non-centrosymmetric structure.
- Partial deacetylation of chitin gives chitosan.
- Has a piezoelectric coefficient of 0.2 to 1.5 pC/N.
- Structural similarity with glycosaminoglycans.

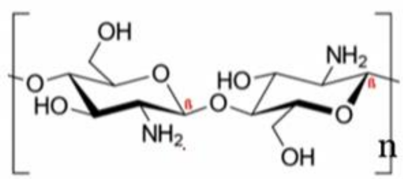


Figure 7: Structure of Chitosan

- It is hydrophilic and biodegradable with poor mechanical properties.
- Electrospun fibers - cardiac regeneration in combination with PLA – improved hydrophilic nature and promoted cardiac cell adherence with improvement in cell elongation and tensile strength.

So, this amine group as well as hydroxyl group are going to give polarity to the molecule. So, that is why, when it is subjected to stress, the polarization of the material takes place and thereby piezoelectricity of the material can be observed. So, this chitosan has structural similarities with glycosaminoglycans. These glycosaminoglycans, are the components that are found in cells. Usually the membrane of any cell contains one or the other type of glycosaminoglycans as the receptors for many of the ligands to attach.

So, as this material has structural similarity to this glycosaminoglycans, it confirms the biocompatible nature of this material. Apart from this, chitosan is highly hydrophilic because the groups that are present in the material here OH or the NH_2 groups, which are highly polar in nature and are able to form hydrogen bonding with the surrounding environment easily. So, that is why it increases the hydrophilic behavior of the material and apart from that, the material is biodegradable also. And one major disadvantage of this material is its poor mechanical property. But this mechanical property of the material can be increased by forming composites of this material with any other known polymers. So, one research group has studied the combination of this chitosan with PLA for cardiac regeneration applications, wherein they have observed that the addition of chitosan to the PLA matrix, has helped in improving the hydrophilic character of the final scaffold along with that it also promoted the cardiac cell adherence that improves the cell elongation as well as tensile strength.

Next polymer is collagen. So, collagen is of an animal origin. It is a major polymer that is observed in case of bones, ligaments, tendons as well as cartilage. So, this collagen is a natural piezoelectric polymer, and the structure of the collagen as you see here in the figure has a triple helical structure, which means that it consists of 3 polymeric chains that are twisted around each other to form the structure. And in case of each chain of this polymer, it consists of number of amino acids that are linked through peptide bonds to form the polymeric chain. In this collagen, the majorly found four amino acids are glycine, alanine, proline as well as hydroxyproline. So, among these four, the glycine as well as hydroxyproline are the two amino acids which are responsible for the piezoelectric behaviour of this collagen material. So, here the structure of glycine as well as hydroxyproline is given in figure 8.

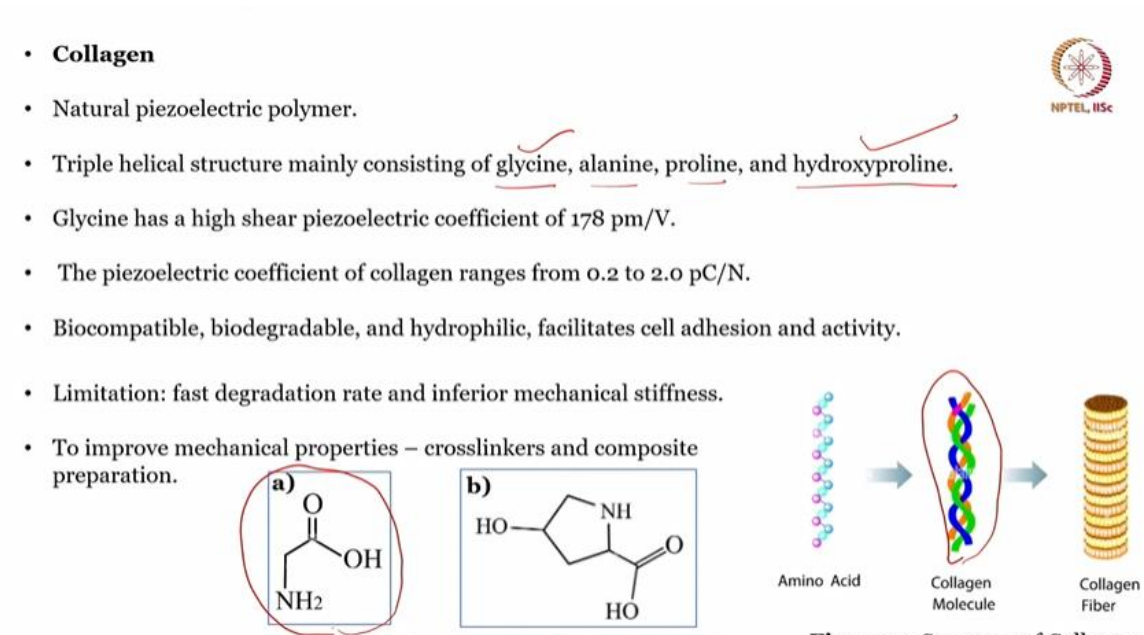


Figure 8: Structure of a) glycine and b) hydroxyproline

Figure 9: Structure of Collagen

So, based on the arrangement of this glycine structure within the polymeric chain, the piezoelectric property is going to vary. And this glycine is the main amino acid which has a shear piezoelectric coefficient of around 178 pC/N and hydroxyproline is having the shear piezoelectric coefficient of around 4. So, due to this reason, the collagen becomes intrinsically piezoelectric. And apart from this, collagen being of biological origin, is a highly biocompatible material and it undergoes biodegradation also. Along with that, it possesses various amino acids in its polymeric structure which makes the polymer hydrophilic in nature and due to which the addition of collagen based scaffold to the cell will be very easy.

The major limitation of this collagen for use in biomedical field is that this material undergoes very fast degradation. Being of biological origin, the degradation of the material is very fast. Apart from that, the mechanical property of this material is also very low. So, that is why so many researchers have tried to improve the mechanical property of the material by using different cross linking agents and also by making different composites of collagen with various other polymers. But during the usage of cross linking agents such as glutaraldehyde, finally it is going to show some poisonous effect on the cells where it is used. So that is also one major drawback. Even though we use cross linkers such as glutaraldehyde, we need to consider the hazardous nature of those cross linkers also.

So another important piezoelectric polymer that is studied is poly 3-hydroxybutyrate 3-hydroxyvalerate in short it is called as PHBV. So this PHBV belongs to a class of polyhydroxyalkanoates where it will have esteric functional group as you can see here. So, ester functional groups are present in the material. So, that is why it belongs to a class of polyalkanoate and this polyalkanoate is nothing but a polyester material synthesized from a bacteria under excessive carbon and nitrogen atmosphere.

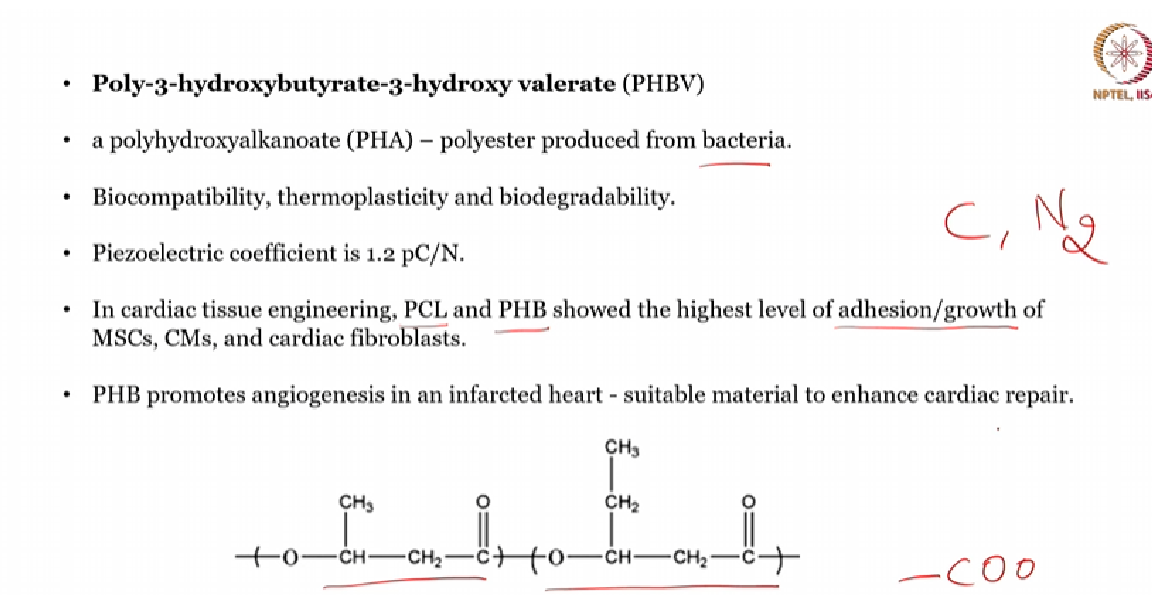
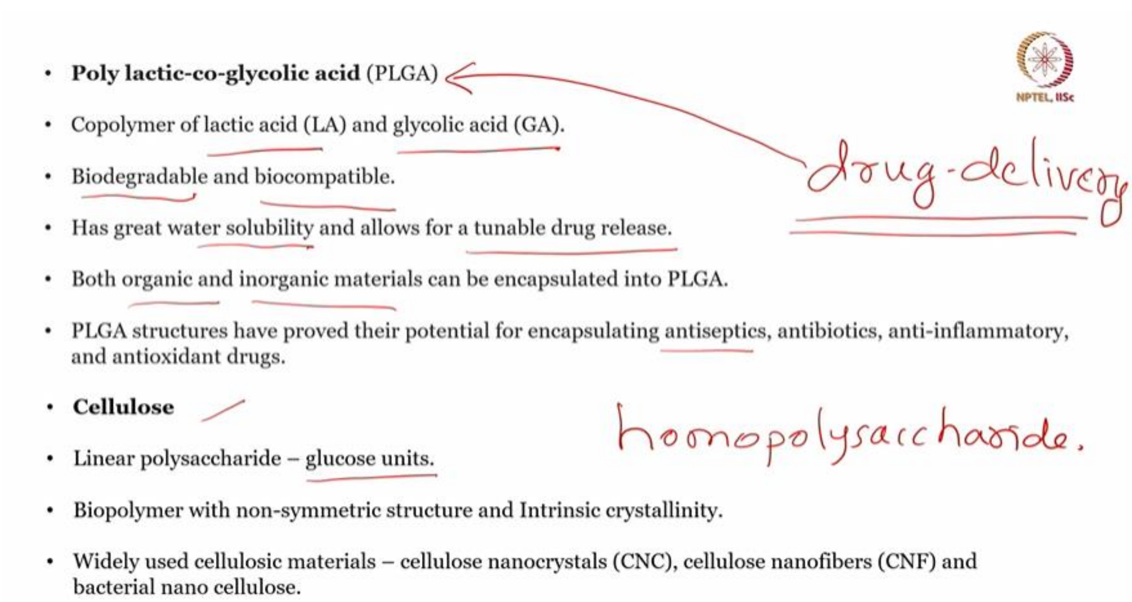


Figure 10: Structure of PHBV

So, this PHBV it is also one biocompatible polymer that shows biodegradability. Along with that, it has thermoplastic behavior. Thermoplastic behavior means this material when subjected for heating, shows softening and after that when the material is subjected for cooling, it gets hardened. So apart from that, this PHBV has found application in case of cardiac tissue engineering wherein the PHBV is used in combination with the polycapralactone PCL. So when the combination or the composite of PCL with PHBV is applied in cardiac tissue engineering, it has shown improvement in adhesion or the growth of myocardial cells as well as cardiac fibroblasts. Apart from that, PHBV is also known to promote angiogenesis that means the synthesis or generation of new cells. So, that is why, it has come out as a suitable material in order to enhance the cardiac repair.

So this PLGA has found major applications in drug delivery systems. The known drug delivery systems that are reported till today are usually based on this PLGA material. PLGA it is a copolymer made up of lactic acid and glycolic acid monomeric units which are joined together to form this polymer and this material being biological origin it is biodegradable as well as biocompatible. This material contains two monomeric units that are lactic acid and glycolic acid, and it is highly soluble in water because of these two monomeric units, which have the functional groups that are polar in nature.



They are capable of forming hydrogen bond with water and hence it shows great solubility in water and due to which, it has a tunable drug release characteristics. And apart from that, in case of this PLGA, within the PLGA matrix, we can encapsulate or we can add so many organic as well as inorganic materials of interest which are used as drugs to deliver it into the target area. Till now in research, so many materials such as antiseptics, antibiotics or antioxidant drugs or anti-cancerous drugs are encapsulated within this PLGA and they have been delivered to the target site successfully.

Next coming to the another important polymer, that is cellulose. So, the cellulose is a homopolysaccharide which is having linear arrangement of monomeric units. So, this homopolysaccharide consists of glucose units that are linked to one another to form this polymeric chain that is cellulose. It is a polymer with non-symmetric structure and apart from that, in case of this material, it shows intrinsic crystallinity. That means here the orderly arrangement of monomeric units in the polymeric chain helps in showing the crystalline nature or it gives the crystallinity to the final material. So, this cellulose is widely used in three different forms that is cellulose nanocrystals, cellulose nanofibers as well as bacterial nanocellulose. So, this cellulose has good mechanical behavior, the tensile strength of the cellulose is very good. So, due to that reason, cellulose also finds its application in biomedicine.

That is all for today's lecture. If you have any doubts feel free to contact us.