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Module - 8 Polymer Lecture - 2 Polymers: Polyolefins Polyethylene, Polypropylene and Polystyrene

We are discussing the organic chemical technology course, module 08 and that is about polymer elastomer and synthetic, synthetic fiber that is the we are having the 8 lecture in this. Already I discussed in lecture 01 I talk about the general introduction to the polymer elastomer and synthetic fiber, what are the various step of the polymer elastomer synthetic fiber. And how the what are the driving force of the development of these three important class of the polymer, that is the plastic elastomer and synthetic fiber.

And in that also we discussed the various type of the reaction that is taken in the place in the manufacture of the all the polymers, within the elastomer, synthetic fiber all the polymer as such. So, the and the different type of the reaction different type of the process that you are because those process are also being used in the various, whether you are manufacturing the poly olefins are others polymers.

And so the this lecture that will be about the polyolefin's, polyethylene and polypropylene and polystyrene because these are the three important polymers specially the ethylene and the propylene that has come in the large number of the a large increase in the capacity. That is in the with the coming of the petrochemicals or the cracker plants naphtha cracker and the gas cracker, and the with the availability of the ethylene, and the propylene. And the similarly, in case of the polystyrene they have availability of the benzene for making the ethyl benzene and ethyl benzene to styrene.

Coverage Of Lecture

- Poleolefins
- Polyethylene and uses of Polyethylene
- · Catalyst For Polyolefin
- Polyolefins By Metallocene Catalyst
- Important Characteristics of Metallocene Catalysts and Copolymers
- Polyethylene and Polyethylene Process Technology
- Polypropylene and Polypropylene Manufacturing
 Process
- Polystyrene

So, this will be the coverage of the lecture introduction general about the polyolefins and then you will be discussing about the polyethylene. And polypropylene catalyst, and development for the various step of the catalyst, we are using in case of the polyolefin. So, metallocene catalyst they have been actually the change in the whole pattern of the making of the polymers. In the polypropylene what are the various step of the polypropylene that you are making that will discuss. Process technology for manufacturing of these two in detail will be discussing, and then the polystyrene so this will be the broad coverage of the lecture.

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Polyolefins

Polyolefins are high polymers produced by polymerisation of olefins. Polyethylene (LDPE, HDPE, LLDPE) and polypropylene (PP) are main Polyolefins produced.

So, polyolefin's are high polymer produced by polymerization of olefin, polyethylene the various as I told you the various grade of the polyethylenes are L D P E low density, high density. Linear low density polyethylene and the polypropylene also in the polypropylene different grade of the polypropylenes are there. So, these are the main polyolefins that we are producing.

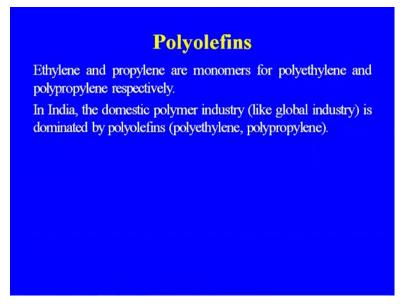
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Polyolefins

Polyolefins such as polyethylene (PE) and polypropylene (PP) are commodity plastics found in applications varying from house hold items such as grocery bags, containers, carpets, toys and appliances, to high tech products such as engineering plastics, industrial pipes, automotive parts, medial appliances and even prosthetic implants.

Polyolefin's such as polyethylene and polypropylene are commodity plastic found in application in vary from house hold items such as, grocery bags, containers, carpets, toys, appliances to high technical product such as engineering plastic, industrial pipes, automotive parts, medical appliances such like in case of the polypropylene. That is finding large application in the medical appliances and even the prosthetic in plant. Because now the we are having now we are talking about the artificial part of the body. So, from where, so we are using different type of the polymers there, even in case of the a large variety complex are also available.

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So, ethylene and propylene are the monomers for the polyethylene and the poly and the polypropylene because you see the these are the two. As I told you the starting also the ethylene and the propylene there availability from the petrochemical complexes, that has played an important role in the development of these two major product.

In India the domestic polymer industry is dominated by polyolefin's main the polyethylene and the propylene. And you see the in India the so far the polyolefin are concern reliance, haldia and the Gale these are the major and now the I O C that is also coming, and the O N G C after coming of the O N G C they will also a major player in case of the, but at the this stage the reliance then haldia and the Gale these are the three major. But still the major shares is of the Reliance so for the polyethylene and polypropylene is concerned.

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Polyolefins

Polyethylene is one of the most widely used thermoplastic and its ever increasing demand is due to availability of monomer ethylene from naphtha and Gas cracker plant.

First polyethylene plant in India was based on ethylene from molasses.

Polyethylene is the one of the most widely used thermoplastic and its even increasing demand is due to availability of monomer ethylene, which I told you the from the naphtha and the gas cracker. First polyethylene plant that was based on the ethylene from molasses that was the actually, they started the small polyethylene plant with the based on the ethylene from the molasses. And then it was the after coming of the gas small cracker plant naphtha cracker plant by union carbide in Bombay.

So therefore the smaller plant capacity that was, but after that after coming of the I P C L now reliance industry and then the reliance industry. And then the reliance hazira project in k l for. So, lot of the production path changes in the production that has communication of the polyethylene as well as the polypropelene.

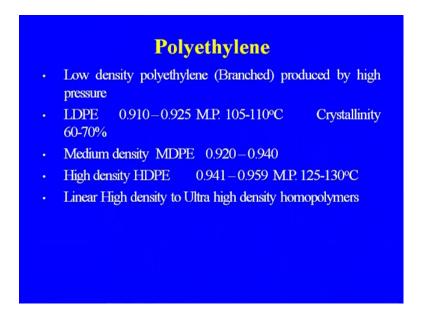
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Polyolefins

Some of the other deriving force for fast growth and use of polyethylene are ease of processing the polymer, its relative cost, resistance to chemicals and its flexibility [Hatch & Matar, 1979].

Some of the driving forces other deriving forces is the fast growth of the use of polyethylene, or ease of the processing the polymers that is the relative cost they resistance to chemical and its flexibility. These are the some of the major deriving force for the adaptability of the polyethylene. So, as I told you we are making the different grade of the polyethylene. So, low density polyethylene branch produce by high pressure.

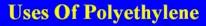
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So, L D P E medium density depending upon the density this also 0.940. So, 0.920, 0.940, 0.94. So depending upon the density you can differentiate whether it is the and even the

crystallinity that is also changing L P D E melting point. Slight difference in the melting point is also there and the linear high density to ultra high density polymer that we are also making in case of the... So these are the abroad grade of the polyethylene that you are making, this is the some of the your application your findings in case of the polyethylene packaging industry...

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Woven sacks; raschel bags for fruits & vegetables; containers for packaging edible oil, processed food, FMCG, lubricants, detergents, chemicals, pesticides; industrial crates & containers; carrier bags; houseware; ropes & twines; pipes for water supply, irrigation; process industry & telecom

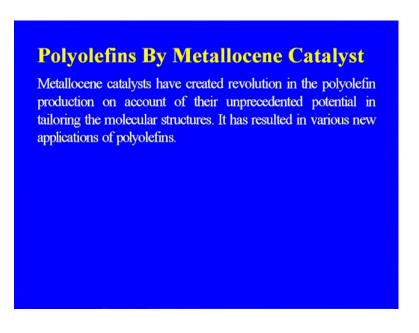


also we are having the packaging many of the convictional glass that has been replaced with the it may be the polyethylene it may be the p e t, in case of the mineral water. So, all those thing that is the for the containers for packaging edible oil, processed food lubricants detergents, chemical, pesticide, industrial crates and the containers carrier bags house wares, ropes and twines pipes of water supply everywhere they are using in some other either although the p v c is more. These are the some of the so far the piping is concern I was telling about the p v c, more p v c pipes in the irrigation and the house hold and is there. (Refer Slide Time: 08:37)

Туре	State	Typical examples
Ziegler/	Heterogeneous	TiCl ₃ , TiCl ₄ /MgCl ₂
Ziegler-Natta	Heterogeneous	$VCl_2, VOCl_3$
Phillips(chrome)	Heterogeneous	CrO ₃ / SiO ₂
Metallocene	Homogeneous	Cp ₂ ZrCl ₂
	Heterogeneous	Cp ₂ ZrCl ₂ /MgCl ₂
Late transition metalabsed	Homogeneous	Ni, Pd, Co, Fe, with diimine, and other ligands
Source: Kapur et	al. 2008	

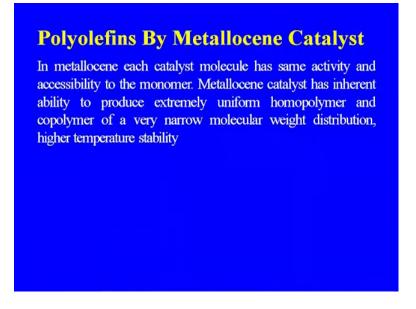
So, these are the some of the major catalyst development in the in case of the polyolefin Ziegler, Ziegler Natta catalyst, Phillips chrome, metallocene that has come in big way in case of the manufacture of the polypropylene.

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Polyolefins by Metallocene catalyst Metallocene catalyst have created revolution in the Polyolefin production, on account of their unprecedented potential in tailoring the molecular structure. It has resulted in various new application of the polyolefin, this is the actually the now the processes using these catalyst for polypropylene they have lot of changes in the quality of the product is there.

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In Metallocene catalyst, each catalyst molecule has same activity and accessibility to the monomer, which first not there in other type of the catalyst. So that is very important Metallocene catalyst has inherent ability to produce extremely uniform home homopolymer and co-polymer of a very narrow molecular weight distribution higher temp stability. Very narrow molecular distribution means, more uniformity is there so this is the advantage why the metals and catalyst they have enter in the manufacturing of the and the why the, why it availability of the Metallocene catalyst is there.

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Important Characteristics
Very high activity towards mono-, co- and terpolymerisation with very high turnover time.
Produce very high molecular weight polymers with extremely narrow MWD.
Very sensitive to hydrogen and only trace amount is required to control molecular weights.
Highly stereospecific in nature.

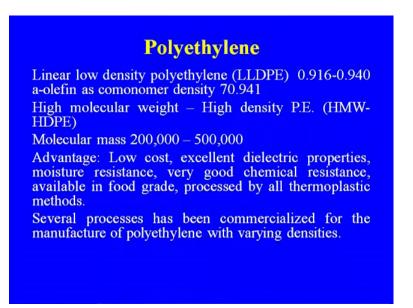
This is the just comparison, why the, what are the advantage important characteristics activity and its very high activity towards mono co and the ter-polymerisation with the very high turnover time. Then the produce very high molecular weight, very sensitive to the hydrogen and only trace amount is required to control molecular. Highly stereospecific in nature, comonomer is highly random and the homogenous.

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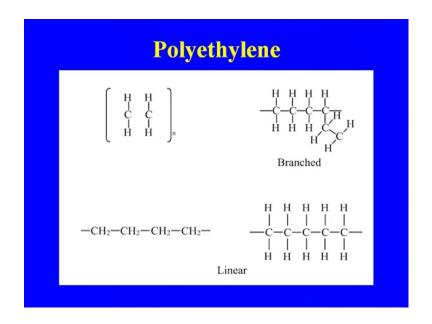
Features	Important Characteristics
Incorporation of Polar monomers	Can incorporate polar monomers.
Structure of Polymers	Provide polymers which are highly linear to.
Heat seal temperature	Polymer exhibit low heal temperature.
Haze	Polymer with low haze.
Hexane Extractable	Low.
Mechanical properties	High.
· ·	Can produce tailor made product.

Can incorporate polar monomers, provide polymers which are highly linear polymers exhibit low heat temp. And then the polymers with low haze low, high the hexane extractable mechanical properties, tailoring of the products can produce tailor made product. So, these are the some of the characteristics of the metallocene catalyst and the copolymers, and why we are using more now the metallocene character based process are there. Now, let us discuss about the polyethylene. As I discuss these are the some of the actually the broad classification already, we discussed about the low density high density and the accordingly the process technology that has been also developed.

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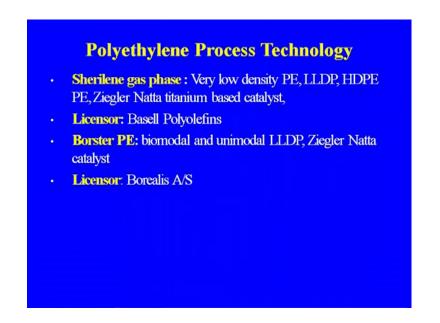


This is the molecular mass advantage, low cost excellent dielectric properties moisture resistance, very good chemical resistance, availability in the food grade, process by all thermoplastic methods. Several processes has been commercialized for the manufacture of polyethylene with varying density.



This is how the branch and the linear polyethylene look like, polyethylene process actually. As I told you there are various process licensor and different type of the process that has not develop for producing wide variety of the polyethylene that is one of process.

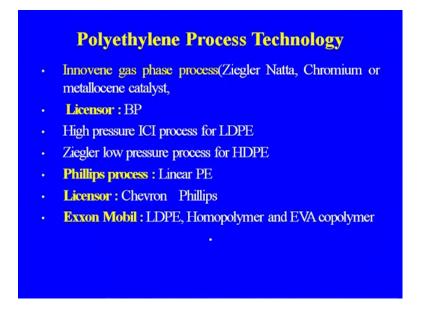
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Sherilene gas phase process very low density polyethylene. So that is L L D P, V L D P they are also called this process V L D P, L L D P high density polyethylene and then the Ziegler Natta, titanium based catalyst that we are using. And basell is the your process licensor

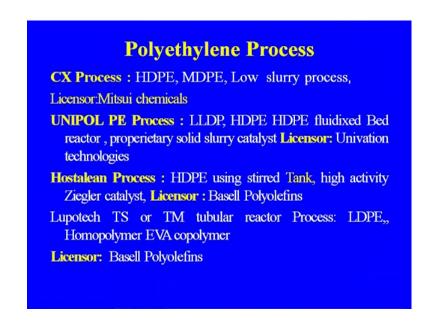
borster p e biomodal and unimodal L L D P Ziegler Natta catalyst. And licensor the borealis A S.

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Innovene gas phase that is Ziegler Natta catalyst, that we are using chromium or the Metallocene catalyst that can be used licensor BP. High pressure I C I process for L D P E Ziegler low process for H D P E, Philips process linear polyethylene licensor chevron Philips, exxon mobil, L D P E home homopolymer and the ethyl acetate copolymer.

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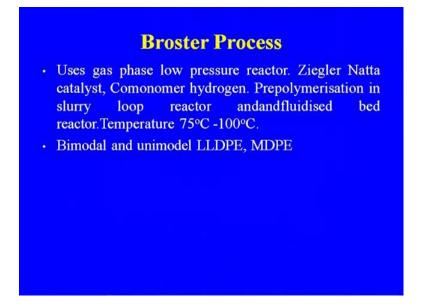
Other process licensor C X process for H D P E, M D PE low slurry process licensor is the mitsui chemicals. Unipol process L L D P, H D P E fluidized bed reactor as we are using in this process. Then the hostalean process H D P E using stirred tank, high activity ziegler catalyst we are using here. Licensor basell polyolefins then the lupotech T S or the T M modular reactor process, this is the L D P E homopolymer EVA copolymer licensor is the your basell polyolefins. So, these are the some of the commercial process that is available for making of the different grade of the polyethylene.

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- Innovene Process
- Polymerisation in Fluidised bed reactor using Ziegler
 Natta catalyst or Chromium catalyst
- Temperature 75°C -110°C
- LDPE,HDPE

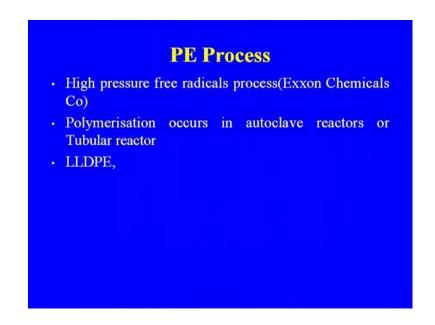
This is the again innovene process polymerization in fluidized bed reactor using Ziegler Natta catalyst. This is the temperature condition and this is the product that you are getting.

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Broster process uses slightly more detail about that process that was not there only I gave the various process. So, here in case of the broster process usage gas phase low pressure reactor, Ziegler Natta catalyst comonomer hydrogen pre-polymerisation in the slurry loop reactor and a fluidized bed reactor temperature 75 to 100 degree centigrade. Bimodal and unimodal L L D P E and the medium density polyethylene.

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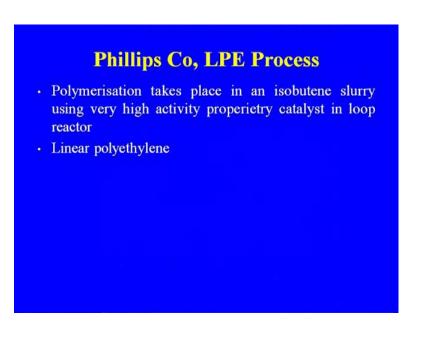
High pressure free radicals process by exxon chemicals. Polymerization occurs in autoclave reactors or the tubular reactor and the L L D P E linear low density polyethylene that you are making by this process.

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Speriline gas phaseProcess (Montell Technology
Polymeristion in Gas phase reactor using Ziglernatta catalyst
LLDPE, HDPE

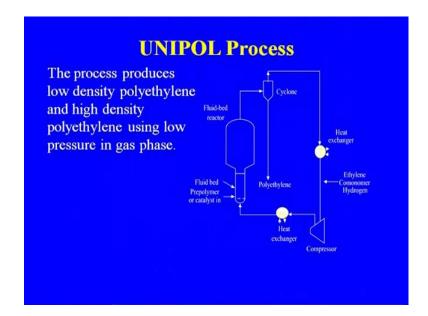
Speriline gas phase process, Montell technology that we are having the polymerization in gas phase reactor using the Ziegler Natta catalyst. Here the linear low density polyethylene or the high density polyethylene that is the product that we are getting.

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Philips low polyethylene low density polyethylene process polymerization take not linear polyethylene process. The polymerization takes place in as isobutene slurry using very high activity properierty catalyst in loop reactor. So, this is the linear polyethylene.

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So, unipol process the process produces low density polyethylene and high density polyethylene using low pressure in the gas phase. And this is the fluidized bed reactor in the fluidized bed reactor after the polymerization is completed, then it will go to the cyclone the separation of the catalyst that will take and the polyethylene, that will be getting from here. And then it is with the recycle unreacted part that will be gas that will be recycle here. Here it will be separation of the polyethylene that will be there.

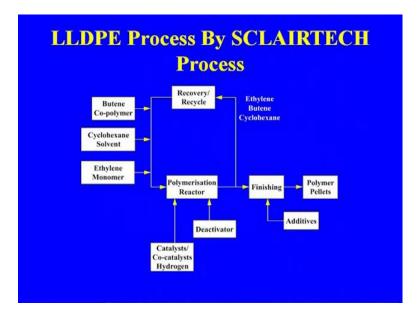
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Dupont Sclairtech Process

- A broad range of polyethylene with density varying from 0.919 to 0.9605 g/cm²with varying melt indexcan be made by this process. The process can be divided into three major areas
- Reaction area
- Recycle /recovery Area,
- · Extrusion and Finishing
- Dowtherm Vaporizer

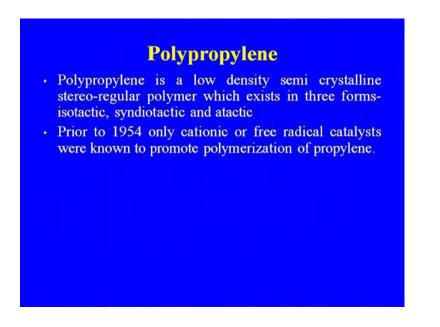
And dupont sclairtech process is a broad range of the polyethylene with a density varying from 0.919 to 0.9605 varying melt indexcan can be produce. Various melt indexcan that is the actually the this is the one of the new process or the modified process where the high varying melt indexcan can be made by this process. The process can be divided into three major area reaction area, recycle recovery area, extrusion and finishing and dowtherm vaporizer these are the some of the units various steps are there.

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This is the why sclairtech process that is the butene here we are using the copolymers cyclohexane solvent and ethylene monomer, that is going to the polymerization reactor. And then the ethylene butene cyclohexane again that is the recycle and then the finishing after the catalyst and here the co-catalyst deactivator, additive and the polymer pellets that you are getting in this process. Now, let us these this was the various processes that is available for making of the polyethylene. Now we will be discussing about the polypropylene.

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Polypropylene is a low density semi crystalline stereo regular polymer, which exists in three forms isotactic, syndiotactic and the atactic. So, these are the three forms of the polypropylene that prior to 1954 only cationic or the free radical catalysts were known to promote the polymerization of the propylene.

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This is the actually if you see the, this is the courtesy of the reliance industry this is the because they are the main major manufacture of the polypropylene. And so the you see the as I told you the in case of the hospital and there the conventional in the syringes and the bottles glass was, that has completely replaced the replaced by polypropylene syringes. That is the 1.5 billion use now we are with the coming of the polypropylene at a very cheaper rate, now it is the disposable syringes million of mask that we are using caps uses in the hospitals.

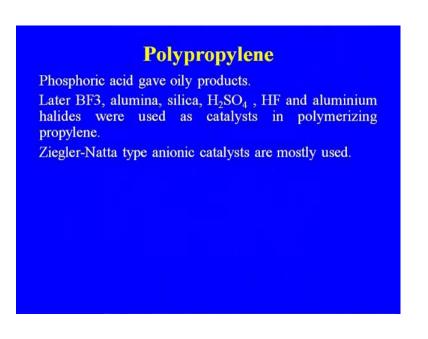
These are all actually the polypropylene fibers are also that is being used divers are the rise in the senior citizen population, health awareness and enhance more disposable, India and the medical destination polypropylene usage 30 kilo tons per annum. So good growth in the health care industry and these are the some of the this the syringe and the bottles glucose bottles earlier that is to be the glass. So, you see the even the this day mask another thing that is also we are using the...

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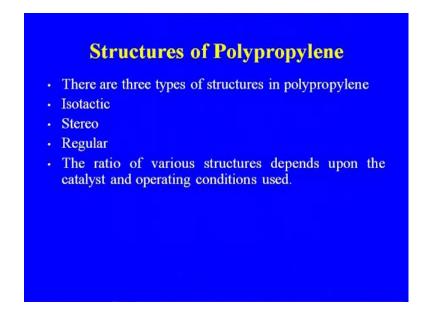
Similarly you see the other application of the rigid packing, this is also one of the here the driver growth driver for the polypropylene are the increase consumption, and the growth India organize retail good processing, horticulture dairy sector, increasing health safety concern disposable single serve packaging formats. So, polypropylene that is 250 kilo tons new application are also there glass replacement, multiwall containers are the growth drivers. So, these are the some of the containers made of the polypropylene.

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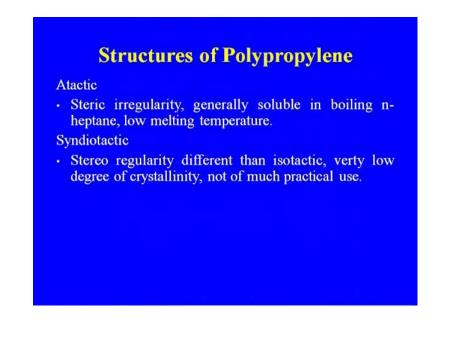
Phosphoric acid because that was the earlier in the catalyst phosphoric problem. The phosphoric acid gave oily products later BF 3, alumina silica H2So4, hydrofluoric acid aluminum halides were used as catalyst in polymerizing polypropylene, polymerizing the propylene. But the Ziegler Natta catalyst that was the mostly widely used catalyst.

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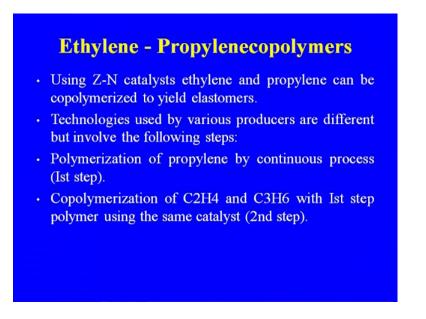
There are structure in the polypropylene the ratio of the various structure depends upon the catalyst, and the operating condition used. So, already I told you the isotactic or stereo or the regular and the different type of the actually the configuration are there.

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The atactic there is another the second and the third is the syndiotactic.

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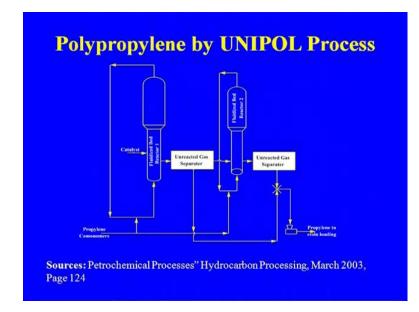
Ethylene propylene co polymers are also there using Ziegler Natta catalyst ethylene and propylene can be copolymerized to yield elastomers. Technologies used by various produces are different, but involve the following steps. Polymerization of polypropylene by continuous process, copolymerization of ethylene and the propylene with the first polymers using the same catalyst in the second step.

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Polypropy	lene Process
Propylene ——— Catalyst ———	Polymerization
	Resin degassing
	Pelletizing
	Product

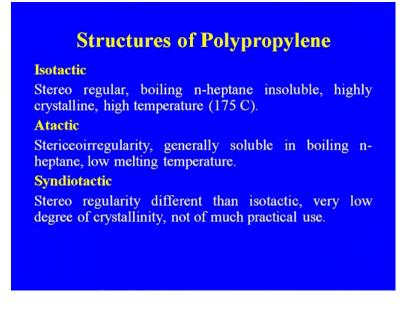
So, this is the polypropylene process that we are using the propylene that is going to the polymerization, then the resin degassing pelletizing and then the products. So, this is the simplest actually the one of the process, where you are using the that you can made how the we are making the polypropylene pallets.

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This is the unipol process where we are using the your fluidize reactor propylene, that is going to the polymerization reactor. And then the here we are having the reactor one and reactor two, defencing reactor and then finally, the polypropylene resin that we are getting in the final stage. So, this is the process unipol process where we are using the fluidized bed reactor, this was I was telling about the why the three structure they are very important in case of the polypropylene.

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That is the isotactic stereo regular boiling n-heptane insoluble highly crystalline high temperature. The atactic stereo irregularity generally soluble in boiling n-heptane low melting temp. Here in case of the syndiotactic that is stereo regularity different that isotactic very low degree of crystallinity not much in the practical use.

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Process licensor	Summary of process	
e process	Produced by bulk Polymerisationin loop reactor followed by final gas phase a fluidised bed reactor(temp. 80-90°C and 25-35 bar.	
Spheripol Process Montell technology	Homopolymer and Random copolymer polymeristion takes place in liquid propylene in a loop reactor. Heterophasic impact compolymerisation is done by adding a gas phase reactor.	

These are the summary of the processes in case of the polypropylene, that is available that the borstar polypropylene process licensor borealis, and the produced by bulk polymerisation loop reactor followed by the final gas phase reactor. So two step process that is the spheripol

process montell technology, homopolymer and random copolymer polymerisation takes place in liquid propylene in a loop reactor. Heterophasic impact co polymerisation is done by adding a gas in the gas phase reactor.

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Process and licensor	Summary of process
Novolen Process	Polymerization is conducted in one
Krupp Uhde GmbH	or two gas phase reactors connected in series.
Union carbide gas phase	A wide range of polypropylene is
UNIPOL PP process	made in a gas phase, fluidised bed reactor using proprietary catalyst
Sperizone Process	Sperizone Process is new proprietary
Technology owner:	gaseous technology based on a
Basellpolyolefins	multizone circulating concept reactor

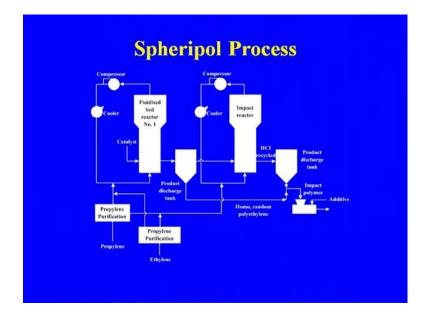
Then the novolen process that the polymerisation is conducted in one or two gas phase reactors connected in series. Union carbide gas that gas phase unipol process a wide range of polypropylene is made in gas phase fluidized bed reactor, using proprietary catalyst. Then the sperizone process technology that is new proprietary gaseous technology based on the multizone circulating system that is there.

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Polypropylene : Spheripol Process

This process can produce a broad range of propylene polymers including homopolymer PP, random copolymers and terpolymers, heterophasic impact, speciality impact as well as high stiffness copolymers. In this process, homopolymer and copolymer polymerisation takes place in liquid propylene within loop reactor. Heterophasic impact copolymerisation is achieved by adding a gas phase reactor.

This process spheripol process this process can produce a broad range of propylene polymers including the homopolymer, polypropylene random copolymer terpolymer. Teropolymer means the two this monomer additional monomer that may be there. Heterophasic impact specialty impact as well as high stiffness copolymer, in this process homopolymer and the copolymer polymerization takes place in liquid propylene with loop reactor. Heterophasic impact copolymerization is achieved by adding as gas phase reactor.



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This is the process which you are having the two stages a reactor here, the finishing the for this is called the impact reactor. And the finally, we will be getting the your polypropylene then the process. Now let us this was about the polypropylene manufacture and as I told you the polypropylene that was the actually, the automobile sector, that has come in a big way and the huge amount of the polypropylene that we are using in the automobile sector where the we are making the pumper other material of the polypropylene. That is after certainly after the processing that polypropylene that we are using. So, another important this polystyrene is a important thermoplastic when styrene is copolymers different type of the combination of the styrene with the acrylonitrile butadiene is there.

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Polystyrene

Polystyrene is an important thermoplastic.

When styrene is copolymerized with acrylonitrile, the polymer Styrene Acrylonitrile (SAN). Resin has a higher tensile strength than polystyrene.

Acrylonitrile butadiene styrene (ABS) polymer has special mechanical properties and find application as engineering plastics.

Styrene is produced by dehydrogenation of ethyl benzene which is made by alkylation of benzene.

So, when styrene is copolymerized with the acrylonitrile the polymer is styrene acrylonitrile san resin has a higher tensile strength, then the polystyrene. Next is the acrylonitrile because in case of the combination of the polystyrene acrylonitrile butadiene styrene polymer has special mechanical properties, and find application as the engineering plastic. Styrene as I discussed in the while discussing the petrochemicals, we discuss the manufacture of styrene that was the from the ethyl benzene dehydrogenation of the ethyl benzene, which is made by the alkylation of the benzene.

So, the benzene and the ethylene that was the two major raw for the styrene and so with the development at the petrochemical industry. Now, we have been able to make the polystyrene at the cheaper rate and polystyrene that is fine wide application in the industry.

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Polystyrenes

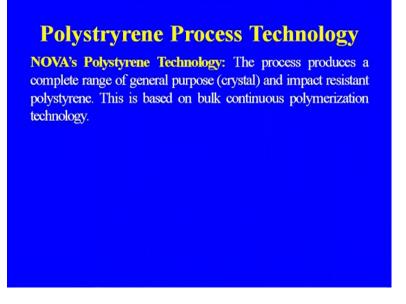
Styrene co-polymerised with acryloonitrile resulting in SAN polymer is characterized with high tensile strength than polystyrene. Another important styrene copolymer is Acrylonitrile Butadiene

styrene (ABS) plastic find use in engineering plastic and is characterized with special mechanical properties.

So styrene co polymerized with the acrylonitrile resulting in the acrylonitrile resulting the san polymers is characterized with the high tensile strength then the polystyrene. So, this is the reason because this special, specialized plastic we are using this styrene acrylonitrile plastic that we are using. Another important styrene co copolymer that which I told that the acrylonitrile butadiene ABS plastic which is find use in the engineering plastic, and is characterized with the special mechanical properties. Even you are having the polymer metal composite also.

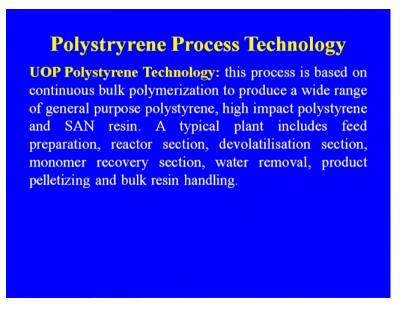
So, ABS they are also being used in case of the your some of the composite in the automobile sector also. That is the important in case of the when we are acrylonitrile and butadienes are also there when we are polymerizing the styrene acrylonitrile butadiene.

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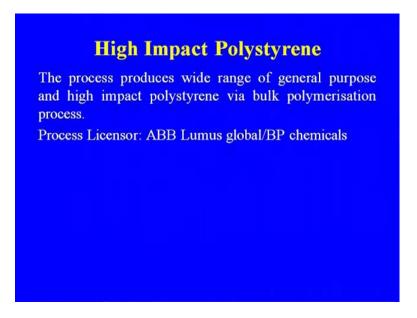
We are discussing the various polystyrene process technologies and one of the processes is nova's polystyrene process, polystyrene technology. The process produces a complete range of general purpose crystal and the impact resistant polystyrene, this is based on the bulk continuous polymerization technique.

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This is the polystyrene process technology by UOP, this process is based on continuous bulk polymerization to produce a wide range of general purpose, polystyrene because we are having the different gate of the one is the general purposed polystyrene and at the high impact polystyrene and the expendable also. But here we are making this two type of the general purpose and the high impact polystyrene and styrene niclo nitrate resin. A typical plant included feed preparation reactor section, devolatilisation section, monomer recovery section, water removal product pelletizing, and the bulk resin handling. Another quality of the your this polystyrene that is the high impact polystyrene. So, high impact polystyrene process, this is the process licensor is heaviest global BP, chemical.

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The process produces wide range of general purpose and high impact polystyrene via bulk polymerization process. So, another great of the polystyrene that is the expandable polystyrene EPS which called it the EPS expandable polystyrene. So, this is the process technology where BP, chemical NABABB lumus global, here in this process you are making the expandable polystyrene.

Polystryrene Expandable

BP Chemicals /ABB Lumus Global Technology

The process produces regular and Flame retardant grade EPS. It is batch suspension proces followed by continupus dewatering, drying, and size classification Process licensor: ABB Lumus global/BP chemicals

The process produces regular and the flame retardant grade EPS it is batch suspension process followed by continuous dewatering, drying and size classification. So, this was the about the various grade of the polystyrene, we discuss in this lecture about the polyolefin, polyethylene and the polypropylene, and the various process technology. And as I told you the major driver the for this development of the polymer industry, that has been the availability of the raw material especial ethylene, propylene, benzene from the petrochemical complexes.

And so far the in the near future polyolefin they are going to be play a very important role, and with the coming of the metals and the catalyst definitely the polypropylene that will be use for more specialize purpose also. In the next lecture, will be lecture three will be discussing about the polyvinyl chloride and some other polymers also, which are finding wide application.

Same thing has been in case of the polyvinyl chloride also where the petrochemical complex specially, the naphtha cracker they have played an important role in the manufacture of the polyvinyl chloride. And the cost reduction because they are p v c as I told you the while in beginning also that was the acetylene root from the acetylene to that was produce from the calcium carbide. So, in the next lecture we discussing about the p v c.