Lec 32: Polymer Industry.

Welcome to the MOOCs course organic chemical technology, the title of today's lecture is polymer industry. In this particular chapter, we will be discussing about the production of different types of polymers, right? So, actually polymers or polymerization, polymer science and technology, polymer science and engineering, different types of courses are there, indeed different types of disciplines are also there. So, covering all the aspects of the polymers and associated things would not be possible in this particular single chapter.

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* polymer technology
- production of different polymers
* Introduction *
* No details reaction mechanism kinetics, etc

PF
PP
ABS
PS

So, we will be restricting our discussion to the technological aspects because the course is on the organic chemical technology that is on the production of different types of organic chemicals production we are discussing. So, in the case of polymer industry also, we will be discussing about the polymer technological details, something like production of different types of polymers, right? So, that is what we are going to primarily discuss in this particular chapter, right? However, directly going into the details of production of certain type of chemical is not feasible unless until we have some kind of introduction about such kind of chemicals. Even for the known chemicals like soaps, detergents, etc., what we have done? We have done some kind of introduction and then properties, chemical reaction, etc., those kinds of things we have discussed. But here in the case of polymer industry chapter, we will be having an introduction chapter primarily on something like basics of polymers, types of polymers and different types of reactions associated with the polymer engineering, etc. Those things we are going to discuss.

However, we are not going into the details of reaction mechanisms, mechanisms we are not going to discuss, kinetics, etc., we are not going to discuss. We primarily restrict ourselves to the very basic nature of polymer, what is a polymer, how a given polymer type of material is produced and then what is the range of molecular weight in general and then how these polymers are being classified, etc., those kind of details we discuss and then we get into the production of different types of polymers in this particular chapter, okay? Today's lecture will be primarily concentrating on the introduction part associated with the technological aspects of the polymers and then we discuss the production of polyethylene and then polypropylene. In the subsequent lecture of this chapter, we will be discussing on production of other types of polymers like ABS, polystyrene, phenol form, molyhydrazine, etc., those things we will be discussing in the next lecture.

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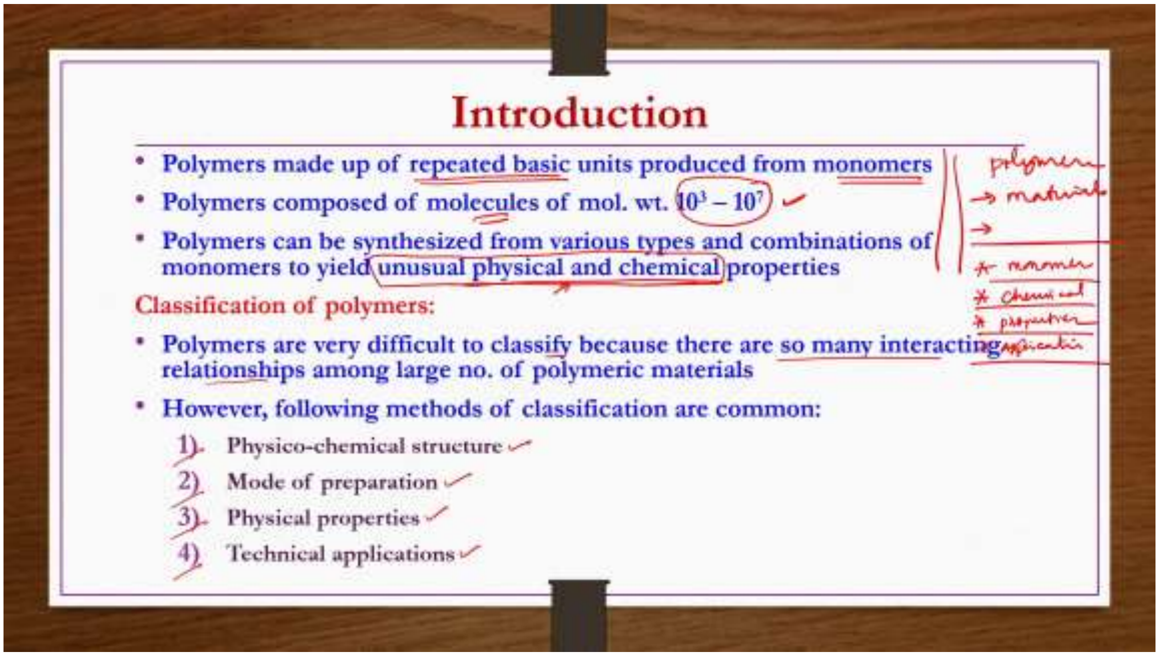

Introduction

- Polymers made up of repeated basic units produced from monomers
- Polymers composed of molecules of mol. wt. $10^3 - 10^7$ ✓
- Polymers can be synthesized from various types and combinations of monomers to yield unusual physical and chemical properties

Classification of polymers:

- Polymers are very difficult to classify because there are so many interacting relationships among large no. of polymeric materials
- However, following methods of classification are common:
  1) Physico-chemical structure ✓
  2) Mode of preparation ✓
  3) Physical properties ✓
  4) Technical applications ✓

polymers

→ materials

→

* monomers

* chemical

* properties

applications

So, let us start with the introduction of polymers. Polymers are usually made up of repeated basic units produced from monomers. Actually, basically you have a monomer, let us say what you have? You have ethylene. So, this ethylene monomer you are having, so when it undergoes polymerization under specified temperature, pressure conditions and then under specific catalyst, this double bond would be broken up and then you would be having CH_2-CH_2 like this kind of structure, right? So, n number of ethylene molecules would be polymerized to form like $(CH_2\text{-}CH_2)_n$, this kind of structure.

So, then this is a monomer and this is a polymer and then such polymer is having n number of repeating units of CH_2-CH_2, right? So, such kind of n number of units being repeated and then combined together to form a bigger molecule of a high molecular weight, okay? So, that is what in general in any of the polymers takes place. This is one simple reaction.

There are some other kind of polymerization processes. Let us say you take phenol and then react with the formaldehyde. So, then you can have a kind of phenol formaldehyde kind of reactions where water kind of molecules are also being removed or in some cases, some other examples like smaller molecules like ammonia, etc., formaldehyde, etc. are also being released. So, such kind of reactions are known as the polymer condensation reactions and then whereas these polyethylene kind of reactions are known as the addition polymer reactions where new molecules or no other molecules are being separated out. Only the addition stepwise or the rapid wise whatever possible way they are being added up and then bigger molecules are forming. So, other kind of polymerization, when the polymerization taking place between 2 different types of monomers, water or ammonia or formaldehyde, these kind of molecules are being released.

Polymers composed of molecules of molecular weight order of 10^3 to 10^7, such high molecular weight polymers are being produced from a simple monomer having very low molecular weight. Let us say ethylene how much you have. So $CH_2=CH_2$. So here the molecular weight of ethylene is nothing but you know 12 plus 2 plus 12 plus 2 simply you know 28. This much only is molecular weight, but when it is polymerized, it may be producing a higher molecules of having a molecular weight order of 10^3 to 10^4 or even higher also, okay? Polymers composed of molecules of a molecular weight order of 10^3 to 10^7.

Polymers can be synthesized from various types and combinations of monomers to yield unusual physical and chemical properties. This is the most important aspect of any of the polymer that is being produced. Why are we producing these polymers actually, right? So, they are producing some kind of materials which are competitive with the existing material something like wood and metal. In place of the metal you can use such kind of polymers. In place of wood you can use some kind of polymers.

So that is the purpose. So then, but these are being produced from simple chemicals like you know polyethylene if you take, monomer is ethylene, very simple. Their physical properties of ethylene and polyethylene if you compare, huge difference is there. So unusual physical and chemical properties these polymers would be gaining because of the polymerization of a simple monomers, right? So that is one of the important and then why should we do that one? So, in order to make materials which are competitive with the existing materials like wood or metal, etc. Or we can even develop some kind of polymers which are you know all together having very unique properties which may not be having any of the existing natural materials.

That is also one of the purpose, okay? Now classification of polymers. So, polymers classification is very very difficult, why? Because you know now one is the important factor is the what type of monomer it is, are you using to get the polymer, whether it is mono functional, bi functional, tri functional, poly functional and then what type of reaction, chemical reaction it is going. Based on that one again you can have different types of polymers and then based on the physical properties, physical properties, strength, etc. Resistance, thermal, mechanical, chemical resistance, etc. These kind of you know properties if you consider then you can have a different types of classification and then also sometimes of technical applications.

Based on the technical applications also you can have something like in films forming polymers, fibers forming polymers, like adhesives forming polymers, like different types of polymers are possible, right? And then some of these things you know when you take these properties, so most of the polymers when you are doing the grouping a kind of interactions are there amongst these properties. So then because of that one simple straightforward classification of polymers is not possible, okay? Polymers are very difficult to classify because there are so many interacting relationships among large number of polymeric materials. However, following methods of classifications are very common. Based on the physicochemical structure you can do some kind of classification, you can do some kind of classification based on mode of preparation, you can do some kind of classification based on the physical properties, you can do some kind of classification based on the technical applications, right? So, what we do? We see some details of you know different types of polymers are possible under each of these kind of categories we discuss and then we get into the production of different types of polymers.

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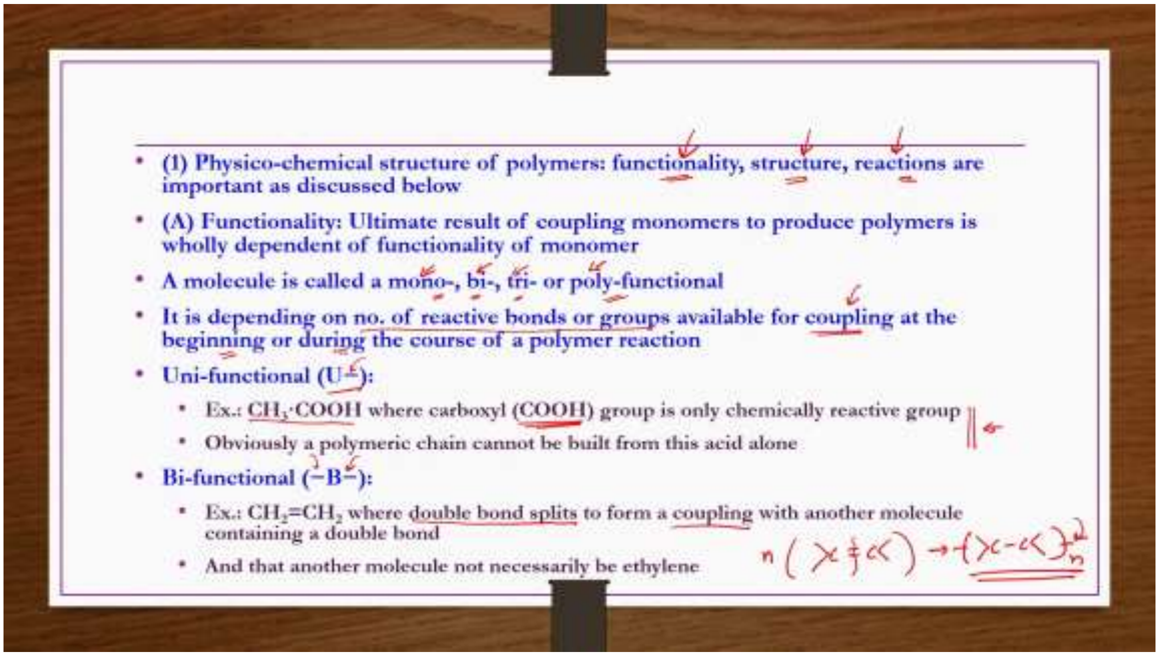

- (1) Physico-chemical structure of polymers: functionality, structure, reactions are important as discussed below
- (A) Functionality: Ultimate result of coupling monomers to produce polymers is wholly dependent of functionality of monomer
- A molecule is called a mono-, bi-, tri- or poly-functional
- It is depending on no. of reactive bonds or groups available for coupling at the beginning or during the course of a polymer reaction
- Uni-functional (U–):
  - Ex.: $CH_3{\cdot}COOH$ where carboxyl (COOH) group is only chemically reactive group
  - Obviously a polymeric chain cannot be built from this acid alone
- Bi-functional (–B–):
  - Ex.: $CH_2{=}CH_2$ where double bond splits to form a coupling with another molecule containing a double bond
  - And that another molecule not necessarily be ethylene

$n\left(\rangle\!=\!\langle\right) \rightarrow \left(\rangle\!-\!\langle\right)_n$

So, let us start with the polymers classification based on the physicochemical structure of polymers, right? Under the physicochemical structure of polymers what are the important things to be understood? First one is the functionality of the monomer because this is the most important one and then this is the one ultimately deciding the structure of the polymer.

So, functionality of monomer is one important thing and then structure, what kind of structure of the polymer are you getting? Linear polymer or branched polymer or cross-linked polymer such kind of structure is the other thing and then reactions, how or what kind of reactions are undergoing whether it is addition reaction or condensation reaction, what kind of reactions are undergoing so that you are getting required polymer. So, these are the important thing to understand from the physicochemical structure of polymers category to make classification of the polymers. So, what we do? We start discussing some details about each of these things before going to the second category. So, let us start with functionality. Ultimate result of coupling monomers to produce polymers is wholly dependent on functionality of the monomer.

For example, a molecule can be called as monofunctional, bifunctional, trifunctional or polyfunctional depending on the chemical or reactive bond that particular molecule may be having. It is depending on number of reactive bonds or groups available for coupling. It is not just number of reactive bonds or groups, but they should be available for what for the purpose of coupling in the polymer a kind of coupling joining of several monomers taking place to produce a bigger molecule kind of thing that is what happening, what mechanism, what method it is falling that is a different thing, but basically that is what happening. So, if coupling is not taking place, so then that is that reactive functional group will not be forming any kind of polymer. So, whatever the bonds reactive bonds you have to see and then how many of them are there and then are they available for coupling at the either at the beginning of the polymer reaction or during the course of the polymer reaction.

Based on that one you decide whether a given monomer is monofunctional, bifunctional or trifunctional or polyfunctional you can decide accordingly. So, we start unifunctional or monofunctional which is indicated like U hyphen like this. So then here that means it is only one functional is there it is only one hyphen is shown here. For example, acetic acid if you take where carboxylic group whatever is there that is the only chemically reacting group, but obviously it cannot form a polymeric chain from this group alone. So that is the reason it is not possible to have a polymer from a monomer which is a monofunctional or a unifunctional.

So, a unifunctional or monofunctional monomer can be utilized as may be present as an impurity to form a bigger molecule or polymer where that basic polymer formation is taking place by some other bifunctional or trifunctional monomers. So that is what we are going to see anyway. So, let us say bifunctional monomer if you are having so now here so either side one hyphen is shown. So that means 2 functional groups are possible. So, for example, ethylene where double bonds splits to form a coupling with another molecule containing a double bond.

So, and that another molecule not necessarily be ethylene alone. So, let us say you have CH_2 like this n number of such molecules are joining together. So, this double bond breaking taking place and then you have CH_2 CH_2 like this n number of monomers are joining to form a bigger molecules. So, this joining when you are doing so if you are doing only with ethylene molecules, then it would be polyethylene. But if you join or do the coupling with some other molecules, so copolymer may take place.

So those things are known as the copolymer that is they form with not because of the single monomer but more than one monomer is present. So that is the reason such polymers formed from more than one monomer are known as the copolymers and such monomers are known as the comonomers.

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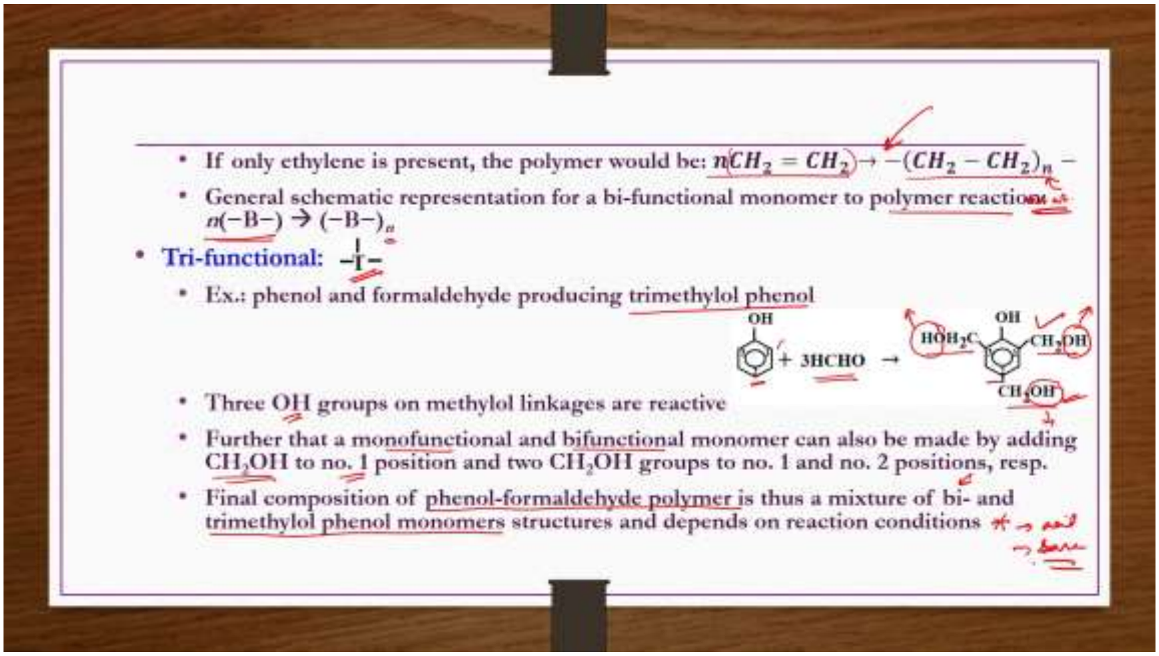

- If only ethylene is present, the polymer would be: $nCH_2 = CH_2 \rightarrow -(CH_2 - CH_2)_n -$
- General schematic representation for a bi-functional monomer to polymer reaction: $n(-B-) \rightarrow (-B-)_n$

- **Tri-functional:** $-\overset{|}{T}-$
  - Ex.: phenol and formaldehyde producing trimethylol phenol
  - Three OH groups on methylol linkages are reactive
  - Further that a monofunctional and bifunctional monomer can also be made by adding CH_2OH to no. 1 position and two CH_2OH groups to no. 1 and no. 2 positions, resp.
  - Final composition of phenol-formaldehyde polymer is thus a mixture of bi- and trimethylol phenol monomers structures and depends on reaction conditions

Let us say in this case if you take ethylene alone is present, then polymer would be $n(CH_2{=}CH_2)$ that is n moles of ethylene reacting together to form polyethylene having this structure common structure. This n is the number of repeated units that are being formed that it indicates depending on this n the molecular weight of the final polymer will depend or the final molecular weight of the polymer whatever you say that would be dependent on this n value how many repeating units are you having. General schematic representation for a bifunctional monomer to polymer reaction is nothing but n bifunctional B giving rise to bifunctional B monomer n times.

This is the general representation and whereas this representation is only for the ethylene. Let us say if you have trifunctional monomer, so it is represented like this. That means it is having 3 reactive groups which can be utilized or you know joined or coupled with some other you know monomer to form a bigger molecule that is the possibility. So, such kind of monomers are known as the trifunctional monomers. For example, phenol and formaldehyde if you react then what you get trimethylol phenol which is having structure like this.

Phenol reacting with 3 moles of the formaldehyde to give trimethylol phenol. So, 1-methylol, 2-methylol, 3-methylol. So trimethylol functional groups are attached to a phenol molecule. So, this OH of 1-methylol may be joining or coupling with the other monomer and then likewise this can also be joining with the other monomer and this can also be joining with the other monomer. That other monomer can be you know any of these 2 or any other monomer that is also possible.

So, if you have different types of trimethylol phenols like this joining together and then forming a bigger molecule then we call them phenol formaldehyde resins. Three OH groups on methylol linkages are reactive. Further that a monofunctional and a bifunctional monomer can also be made by adding a methylol group to number 1 position here that is this one and then 2 methylol groups to number 1 and number 2 positions respectively. So, like this so many of these trimethylol phenol monomers may be joining together and then forming a bigger molecules a cross-linked polymer like phenol formaldehyde resins may be forming. So, final composition of phenol formaldehyde polymer is thus a mixture of bi and trimethylol phenol monomer structures and depends on the reaction conditions because such kind of reactions can be done using acid catalyst as well as the base catalyst and then different temperature.

So, they would be discussed subsequently when we discussed about such kind of resins production in the next class.

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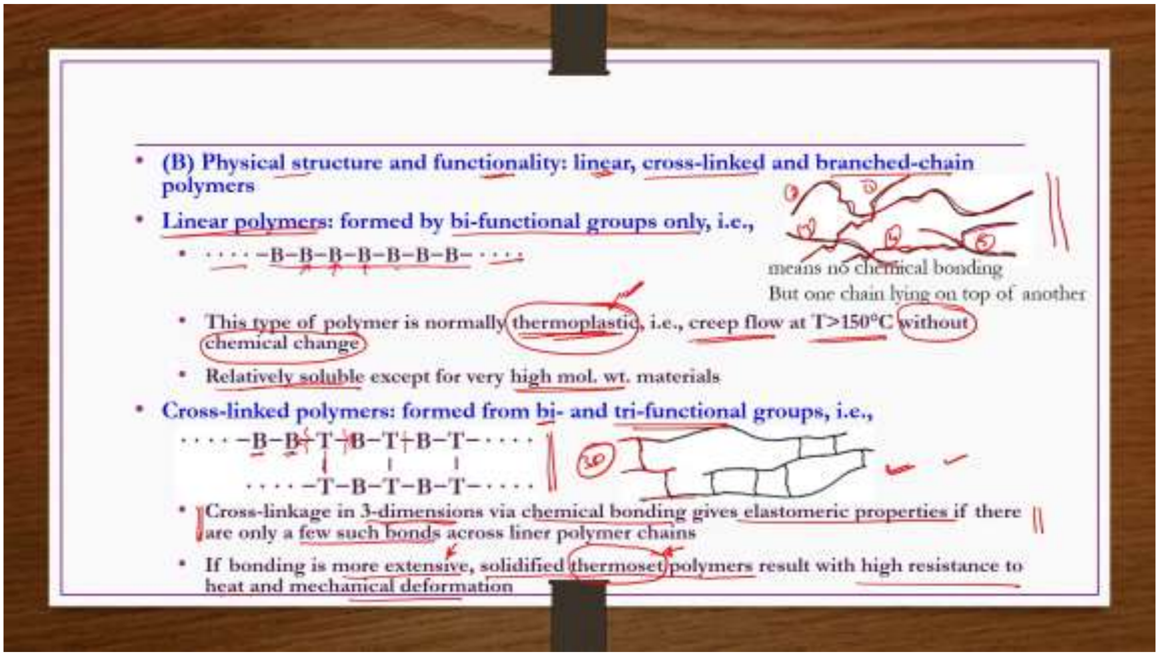

- **(B) Physical structure and functionality: linear, cross-linked and branched-chain polymers**
- **Linear polymers: formed by bi-functional groups only, i.e.,**
  - · · · · −B−B−B−B−B−B−B− · · · ·
  - This type of polymer is normally thermoplastic, i.e., creep flow at T>150°C without chemical change
  - Relatively soluble except for very high mol. wt. materials
- **Cross-linked polymers: formed from bi- and tri-functional groups, i.e.,**

$$\begin{array}{l} \cdots\cdots -B-B-T-B-T-B-T- \cdots\cdots \\ \qquad\qquad\quad | \qquad | \qquad | \\ \qquad \cdots\cdots -T-B-T-B-T- \cdots\cdots \end{array}$$

  - Cross-linkage in 3-dimensions via chemical bonding gives elastomeric properties if there are only a few such bonds across liner polymer chains
  - If bonding is more extensive, solidified thermoset polymers result with high resistance to heat and mechanical deformation

Now other category within the first category of physicochemical structure of the polymers. So, the other one is the physical structure and functionality. Now you already understand that a polymer can be formed if a monomer either is bifunctional or trifunctional if it is only mono functional it cannot form a polymer. So, either same types of bi functional or different types of bi functional can join together to form certain kind of polymers.

Some types of bi functionals may also be joining with different types of tri functionals and then also form different types of polymers. All those number of infinite numbers of possibilities are possible in general. Out of such kind of possibilities 100 possibilities more than 100 possibilities are already commercialized polymers that are available in the market. So, such polymers structure if you classify then we can have a linear polymer cross linked polymer and then branched chain polymers. So, we see what are they linear polymers formed by bi functional groups only that is if you have a bi functional group B.

So, n number of such B monomers joining together to form a linear polymer like this. One bi functional monomer is being coupled with the other bi functional monomer that is being coupled with the other one like this series continues you know as long as you allow the polymerization to take place under the feasible or you know possible temperature pressure and catalytic conditions, etc. These conditions or different aspects we are not going into those details because conditions are specific to the given type of polymer whereas these concepts we are discussing generalized one. So, this type of linear polymer whatever shown is normally thermoplastic. Thermoplastic in the sense that you can melt, re-melt again again some kind of plastic nature they will be having so you can re-melt again and again.

So when you melt beyond certain temperature let us say 150 degrees centigrade, etc. then they start creep flowing without any chemical change that also without any chemical change there would not be any chemical change but they would be you know under creep flowing conditions and then also you can heat them melt them and then you stop cool them and then again whenever you required you can reheat them re-melt them that is kind that kind of possibilities there in the thermoplastic you know polymers. So thermoplastic on heating which shows a kind of plastic melting kind of behavior. So those materials are known as the thermoplastic polymers here in this particular case. These are relatively soluble until and unless if the final produced material is having very high molecular weight order of 10^6, 10^7 molecular weight polymer you are producing though they are linear polymers then they may not be soluble in some kind of solvents.

Otherwise if you are producing low to intermediate molecular weight polymers like you know 1000, 1500 molecular weight such kind of range of you know molecular weight polymers then it is possible they may be relatively soluble. Pictorial representation is given like this. So now this is one type of you know representation. This is one type of a linear polymer. This is another type of a linear polymer which looks more straight.

So, this is not that straight. Linear in the sense it is not straight or you know this thing it is not branched or cross linked that is what it mean by. So, then it is one why it is one showing different types of this is one type, this is another type, this is another type like you know different types of you know representations of a linear polymers are shown. They are not reacting on to each other. They are just lying on top of the another one this representation. This representation does not show any chemical bonding.

It just showing that you know it is one chain or one linear chain polymer is lying on top of the another one. That kind of representation is shown. Five different types of linear polymer chains are shown here. Next one is the cross-linked polymers formed by bi and tri-functional monomers or groups only that is let us say you have a bi-functional monomer. So, one end of bi-functional monomer is being joined with the tri-functional monomer or tri-functional group.

So that is again joining with another bi-functional one and then that is again joining with another tri-functional one like this you know because now it is tri-functional. So, one is being connected to this B another one is coupled with this B. What about the third reactive group? The third reactive group now it is being connected with the another tri-functional like this. So now a kind of cross linking takes place. This kind of cross linking takes place and then you can get a very complicated rigid kind of solidified structures in general you can get.

Cross linking is taking place in general in three dimensions whereas the linear polymer formation is taking place only in the two dimensional. So now here also though it is possible in three dimensional we have shown in the two dimensional only. So that linkages via chemical bonding gives elastomeric properties if there are only a few such bonds across linear polymer chains and these are very much common in most of the elastomers that are common in the rubber industries. If bonding is more extensive more extensive that is more extensive cross linkage is taking place then solidified thermoset polymers would be forming which are having high resistance to heat and mechanical deformation. So, what do you mean by thermoset here? So, when you heat it they will be setting they will be setting into the more solidified you know clustered or you know much more solidified strong structure it may be forming and then when you stop heating it and then cool it and then you cannot reheat it.

If you reheat it, it will not be melted again as in the case of thermoplastic. Thermoplastic you can remelt again and again whereas thermoset once it is formed the structure cannot be destroyed. So, this is now one type of representation of cross-linked polymers. Let us say this bi-functional now tri-functional is connecting with the this bi-functional and then third reactive group of tri-functional is reacting with the other one here like this. So, this kind of cross linking may go in the third direction also though it is shown only two-dimensional representation.

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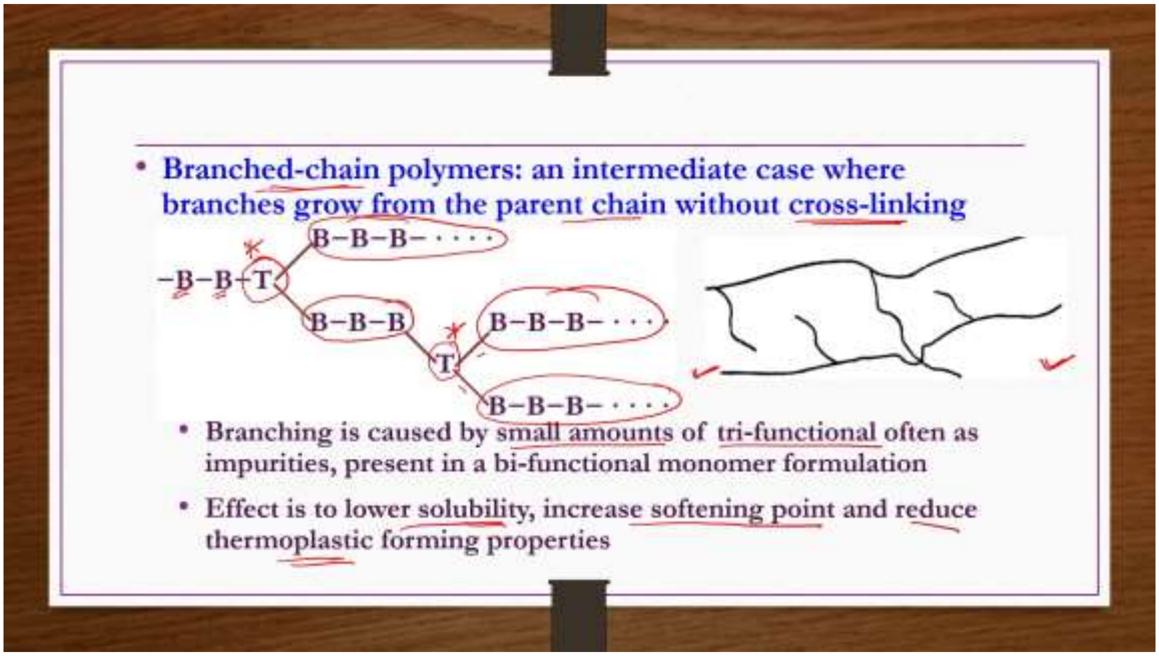

- Branched-chain polymers: an intermediate case where branches grow from the parent chain without cross-linking

  - Branching is caused by small amounts of tri-functional often as impurities, present in a bi-functional monomer formulation
  - Effect is to lower solubility, increase softening point and reduce thermoplastic forming properties

Third one is the branch chain polymers. It is an intermediate case where branches grow from the parent chain without cross linking. What does it mean by? Let us say you have a few bi-functional monomers and then there is a tri-functional monomer. So, from this tri-functional monomer one reactive group is forming a branch with different bi-functional monomers whereas the third reactive group of this tri-functional monomer would be forming a branch with you know bi-functional monomers. Now this bi-functional monomer again forming a linkage or coupling with the tri-functional monomer. So, remaining two reactive groups of tri-functional monomers are forming branches with the bi-functional monomers like this.

A kind of branching sister formation kind of branching is taking place. So, these things are known as the branched chain polymers. They are also chain form in general like linear but they are you know in a branches kind of thing. They are not like a straight linear chains like in the previous slide we have seen.

Branching is caused by small amounts of a tri-functionally. Now what you can see here tri-functional monomers are very few compared to the bi-functional monomer. So, we can see them as impurities that are present in bi-functional monomer to form branches. So that way we can see. Effect is to lower solubility. Why do we do this kind of branched chain polymer formation? If you wanted to lower the solubility, increase the softening point and reduce the thermoplastic forming properties, then you can do this one.

Let us say you wanted to produce a plastic material but you wanted to have a less plastic behavior, less plastic behavior and then more kind of solidified behavior. Then you can have this tri-functional monomer as impurities and then develop branched chain polymers like this. So, you do not want neither completely thermoplastic which you can obtain by the linear chain polymerization as shown in previous slide or you do not want completely thermosetting which you get by the crosslinking. If you want intermediate kind of thing, then you can have this branched chain polymer approach. So, this is one kind of representation of branched chain polymers. So, this is about based on the physicochemical structure of polymers, how we can do the classification.

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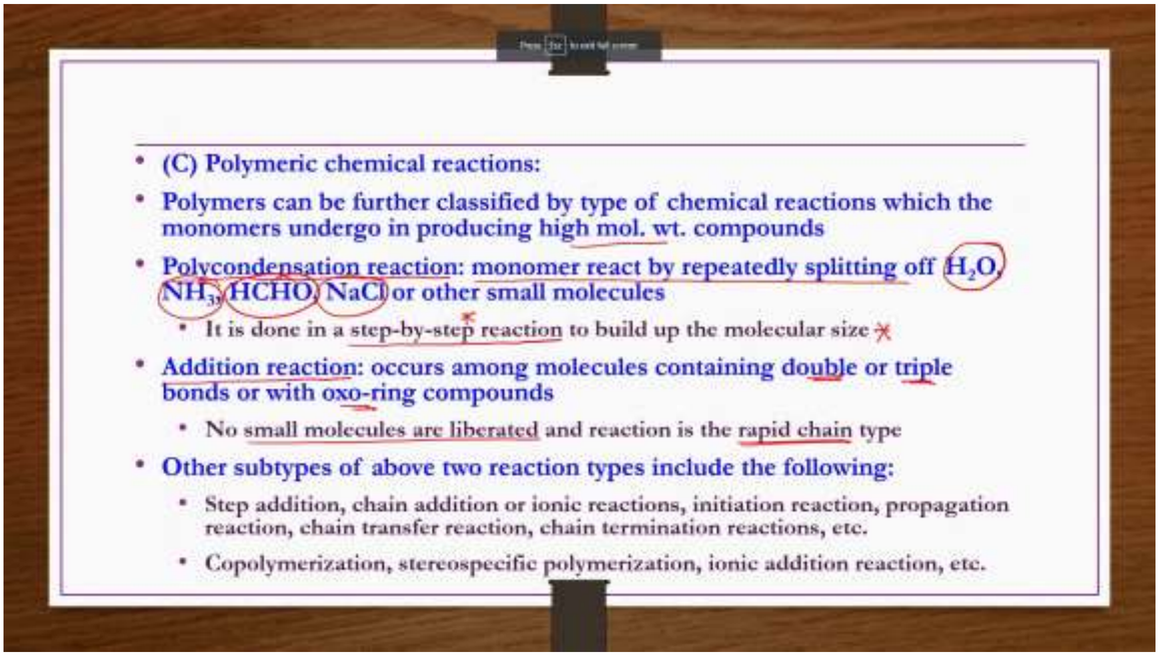

- (C) Polymeric chemical reactions:
- Polymers can be further classified by type of chemical reactions which the monomers undergo in producing high mol. wt. compounds
- Polycondensation reaction: monomer react by repeatedly splitting off H_2O, NH_3, HCHO, NaCl or other small molecules
  - It is done in a step-by-step reaction to build up the molecular size
- Addition reaction: occurs among molecules containing double or triple bonds or with oxo-ring compounds
  - No small molecules are liberated and reaction is the rapid chain type
- Other subtypes of above two reaction types include the following:
  - Step addition, chain addition or ionic reactions, initiation reaction, propagation reaction, chain transfer reaction, chain termination reactions, etc.
  - Copolymerization, stereospecific polymerization, ionic addition reaction, etc.

Now, we see the classification again under the category of physicochemical structure of polymers but based on the chemical reactions, what kind of chemical reactions are involved in order to produce a given polymer based on this classification is done. That is polymers can be further classified by type of chemical reactions which the monomers undergo in producing high molecular weight components. They include different types, one is the polycondensation reaction as I already mentioned. In this type of reaction, monomer react by repeatedly splitting of small molecules like water, ammonia, formaldehyde, sodium chloride, etc., or other small molecules. It is done in a step by step reaction to build up the molecular size. Step by step reactions are taking place in general. Whereas the other one addition reaction, here it occurs among molecules containing either double bond or triple bonds or with oxo ring compounds and then it occurs like in a rapid chain form. Rapid chain formation way it is occurring and then it does not liberate any small molecules. There are also other subtypes of above two reactions are possible which are listed below here.

So, this is how by considering the physicochemical structure of polymers, these 3 different ways you can categorize the polymers.

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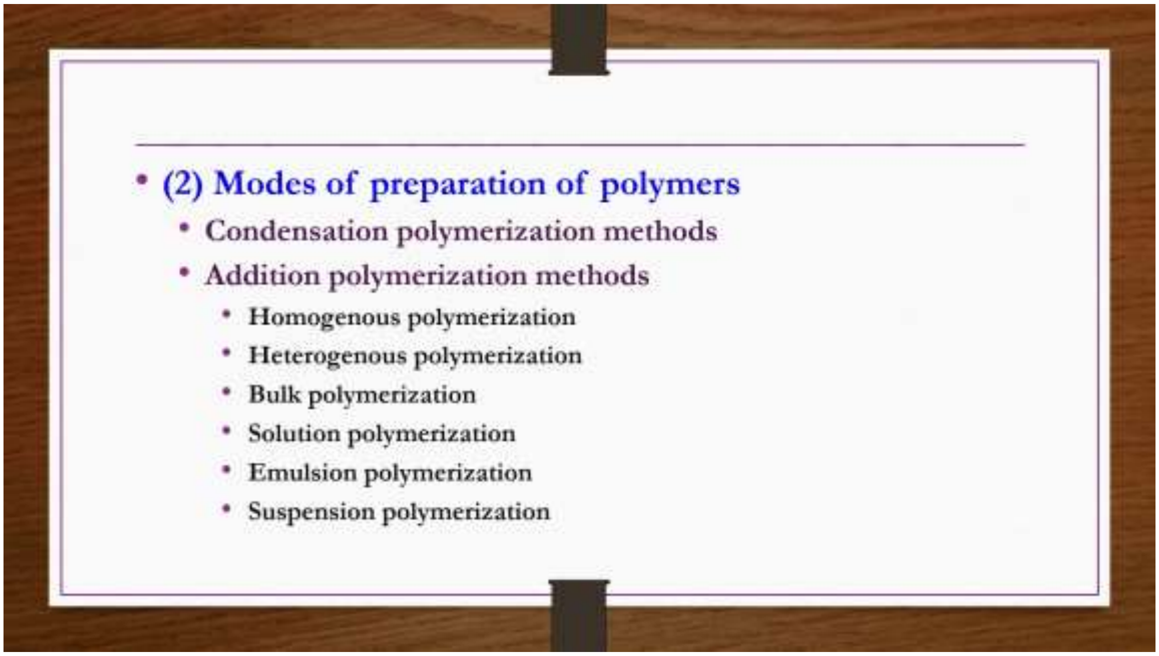

- (2) Modes of preparation of polymers
  - Condensation polymerization methods
  - Addition polymerization methods
    - Homogenous polymerization
    - Heterogenous polymerization
    - Bulk polymerization
    - Solution polymerization
    - Emulsion polymerization
    - Suspension polymerization

Now we go to the second category of classification or second way of classification of polymers that is based on the modes of preparation of polymers. How the polymer is being prepared based on that one, you can do a classification that is presented here. So, condensation polymerization method is one, other one is the addition polymerization method. So, there are also sub methods like homogeneous polymerization, heterogeneous polymerization, bulk polymerization, solution polymerization, emulsion polymerization, suspension polymerization, etc.

So, we are not going into the details of all of these things and their reaction mechanism, kinetics, etc., out of the scope of the course. So, we just listed them out here.

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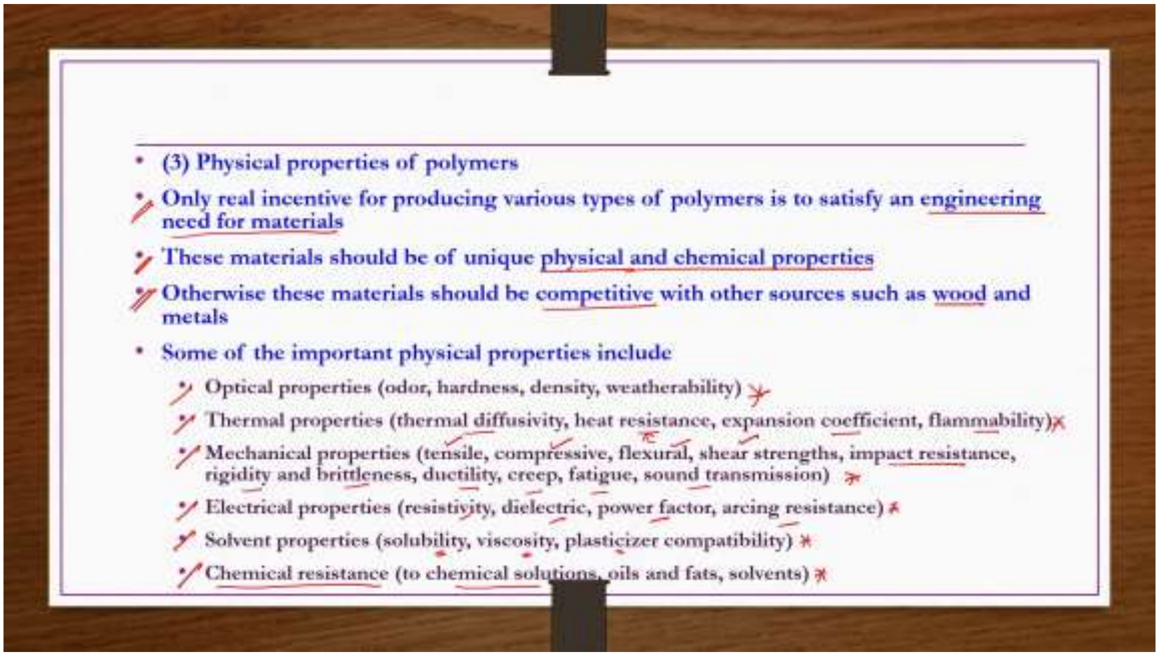

- (3) Physical properties of polymers
- Only real incentive for producing various types of polymers is to satisfy an engineering need for materials
- These materials should be of unique physical and chemical properties
- Otherwise these materials should be competitive with other sources such as wood and metals
- Some of the important physical properties include
  - Optical properties (odor, hardness, density, weatherability)
  - Thermal properties (thermal diffusivity, heat resistance, expansion coefficient, flammability)
  - Mechanical properties (tensile, compressive, flexural, shear strengths, impact resistance, rigidity and brittleness, ductility, creep, fatigue, sound transmission)
  - Electrical properties (resistivity, dielectric, power factor, arcing resistance)
  - Solvent properties (solubility, viscosity, plasticizer compatibility)
  - Chemical resistance (to chemical solutions, oils and fats, solvents)

Third way of classifying the polymers is based on the physical properties of the final polymeric material that you have produced.

Based on that one also you can do a classification. So only incentive for producing various types of polymers is to satisfy an engineering need for materials. Let us say for some kind of engineering application you want steel and then steel you are not able to get or you are getting at very high pressure, can you not develop a kind of polymer material which is having properties or which is having properties equivalent to the steel? So, if that is possible, so then why cannot we go for this polymerization that is one of the primary indeed most important real incentive for producing various types of polymers. So, these materials should be having unique physical and chemical properties. Otherwise, these materials should be competitive with other sources, natural sources like wood, metals, etc. So, with this purpose only actually polymers have been developed or the production of polymer has been taken place with this primary objective.

Primary objective is that it should supply you some kind of engineering need for the material. Second one is that this material should have a or these materials should have a very unique physical and chemical properties and then third one most important one is that these materials should be competitive with other sources like wood and metal. So rather using wood and metal you can use this kind of polymers and then fulfill the engineering needs. So, some of the important physical properties to discuss or consider when you prepare a polymer are provided here.

Optical properties like ordor, hardness, density, weatherability, etc. Then thermal properties very important one where you have thermal diffusivity, heat resistance, expansion coefficient, flammability should be considered. Sometimes you want inflammable, sometimes you want flammable, sometimes you want more heat resistance, sometimes you want more thermal expansion coefficient, less thermal diffusivity, etc. As per your requirement these properties should be considered. Then mechanical properties also you have to see under the mechanical properties of polymers you should see the tensile strength, compressive strength, flexural strength, shear strength also impact resistance, rigidity and brittleness, ductility, creep, fatigue, sound transmission all these properties you should consider. Electrical properties something like resistivity, dielectric, power factor, arcing, resistance, etc.

All those things you should consider when you develop a polymer material and then most importantly solvent properties. Solubility is also important, viscosity, plasticizer, compatibility with other material. These things are very essential to consider. Finally, chemical resistance, resistance to chemical solutions like oils and fats and solvents is very much essential. So, all these properties are essential, some are very much essential, some are less important depending on application to application.

But you should consider all these properties and then accordingly you should decide your applications or based on your applications you should consider the properties accordingly you should tune the production methods and then selection of the monomers, etc. All that you have to decide accordingly based on your applications.

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- Polymers classification by physical properties:
- Thermoplastic: linear or slightly branched molecules
  - Solvent soluble; can be repeatedly melted and useful for melt casting and spinning, injection molding and extrusion
  - Vinyls, cellulose derivatives, polyethylene, polypropylene, oxides and amines
- Thermosetting: cross-linked or heavily branched molecules
  - Largely solvent insoluble, good heat resistance, but cannot be melted after forming or crosslinking
  - Phenol-formaldehyde, urea-formaldehyde, silicones, protein-aldehydes, etc.
- Elastomers: resistance solids with high flexural strengths
  - Butadiene and derivatives, butadiene copolymers, ethylene-propylene stereospecific, isobutylene and derivatives, polyisoprenes, polyurethanes, silicones, thiokols, etc.
- Fibers: thread-forming solids with high tensile strength
  - Polyamides, polyesters, polyurethanes, polycarbamides, cellulose and its derivatives, polyvinyliding chloride, polyvinyl deri, protein derivatives, etc.

Polymers classification by physical properties if you see then we can have thermoplastic as already discussed which can be melted, re-melted again and again. These are formed by either linear or slightly branched molecules only having low to intermediate molecular weights. Other one is the thermosetting which obtained by cross linking or heavily branched molecules.

Other category is the elastomers where they should have resistance solids with high flexural strength, etc. Then fibers like you know thread forming solids with high tensile strength is the other category. So, based on the physical property if you wanted to classify the polymers, so these 4 types of polymers are possible. So, thermoplastics are usually solvent soluble especially if their molecular weight is low to intermediate. If the molecular weight is very high even though it is thermoplastic that cannot be you know soluble in solvents in general.

These can be repeatedly melted and useful for melt casting and spinning, injection molding and extrusion purpose these are used. Some examples are vinyls, cellulose derivatives, polyethylene, polypropylene, oxides and amines, etc. are counted as thermoplastics. Thermosetting largely solvent insoluble especially if the molecular weight is high. They have good heat resistance but cannot be melted or re-melted after forming or cross linking has already been taken place.

Once cross linking has taken place you cannot re-melt them that is what mean by thermosetting. Phenol formaldehyde, urea formaldehyde, silicones, protein aldehydes, etc., are some examples. Elastomers mostly used in the rubber industries like you know butadiene and derivatives or butadiene copolymers, ethylene, propylene, stereospecific polymers, isobutylene and derivatives, polyisoprenes, polyurethane, silicones, thiocols, etc., some example. Coming to the fibers thread forming solids with high tensile strength usually mostly used in textile industries like polyamides, polyesters, polyurethanes, polycarbamides, cellulose and its derivatives, polyvinyl chloride, polyvinylin chloride, polyvinyl derivatives, protein derivatives, etc. Some of these polymers are also natural also. Let us say cellulose and cellulose derivatives like dextrin, etc. which we have already discussed under the natural product industries, one of the chapter that we have already discussed.

So, some of them are you know natural polymers as well. These natural polymers are used as a base for the final product that we are going to develop in general, but not all cases, for some cases it is done like that.

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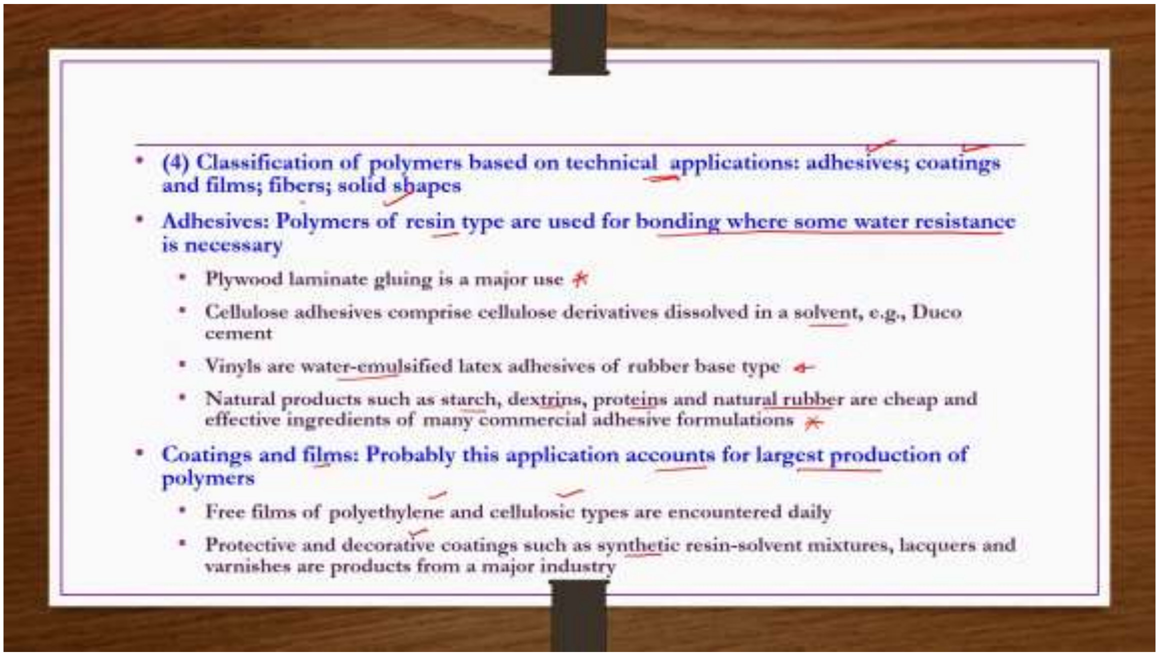

- **(4) Classification of polymers based on technical applications: adhesives; coatings and films; fibers; solid shapes**
- **Adhesives: Polymers of resin type are used for bonding where some water resistance is necessary**
  - Plywood laminate gluing is a major use
  - Cellulose adhesives comprise cellulose derivatives dissolved in a solvent, e.g., Duco cement
  - Vinyls are water-emulsified latex adhesives of rubber base type
  - Natural products such as starch, dextrins, proteins and natural rubber are cheap and effective ingredients of many commercial adhesive formulations
- **Coatings and films: Probably this application accounts for largest production of polymers**
  - Free films of polyethylene and cellulosic types are encountered daily
  - Protective and decorative coatings such as synthetic resin-solvent mixtures, lacquers and varnishes are products from a major industry

Fourth category or fourth method of classification of polymer is based on the technical application. So here we have adhesives, coatings and fins, fibers and solid shapes. So, this way if you see adhesives or polymers of resin type which are used for bonding where some water resistance is necessary.

Plywood laminate gluing is one of the major use of such kind of adhesives. Cellulose adhesives comprise cellulose derivatives dissolved in a solvent example, duco-cement, etc. Vinyls are water emulsified latex adhesives of rubber base type. Natural products such as starch, dextrins, proteins and natural rubber are cheap and effective ingredients of many commercial adhesive formulations. Then coatings and fins, probably this is the one application which accounts for largest production of polymers where free films of polyethylene, cellulosic types are encountered daily in society, household purpose, industrial purpose as well. Protective and decorative coatings such as synthetic resin, solvent mixtures, lacquers and varnishes are products from a major industry.

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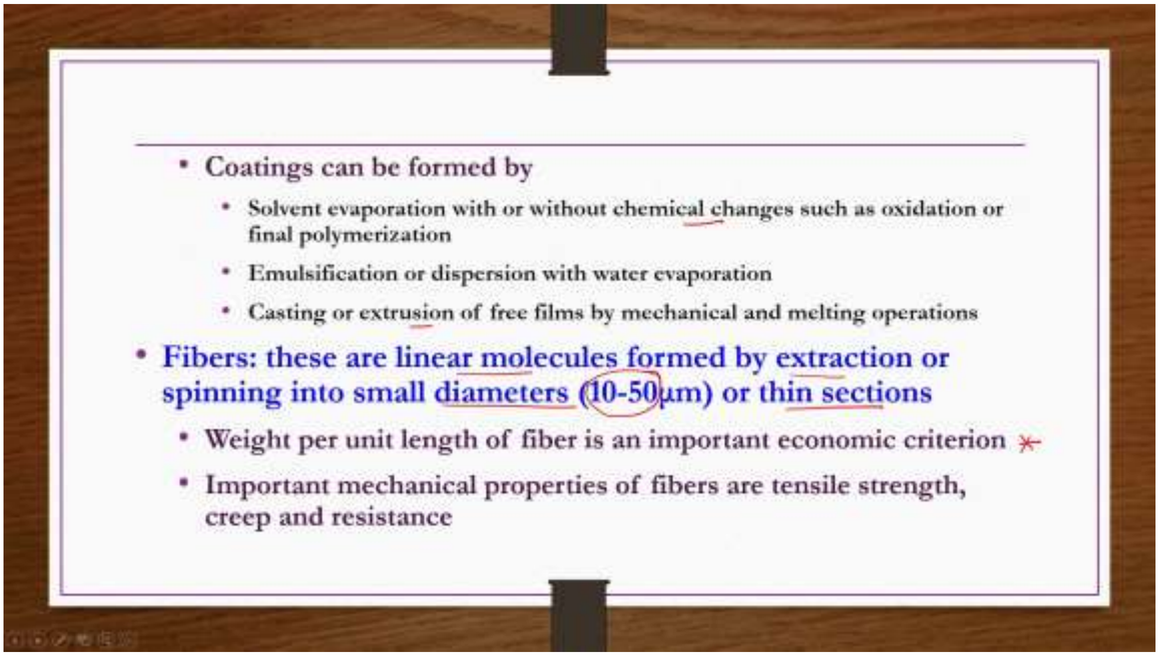

- Coatings can be formed by
  - Solvent evaporation with or without chemical changes such as oxidation or final polymerization
  - Emulsification or dispersion with water evaporation
  - Casting or extrusion of free films by mechanical and melting operations
- **Fibers: these are linear molecules formed by extraction or spinning into small diameters (10-50μm) or thin sections**
  - Weight per unit length of fiber is an important economic criterion *
  - Important mechanical properties of fibers are tensile strength, creep and resistance

Coatings can be formed by different ways. One is like you know when you do the painting, painting is what now it is basically you know you have a pigment and then it is uniformly dissolved, dispersed in a you know vehicle like oils or polymers, etc. So, when you apply these paints, you know slow oxidation takes place and then polymer coating will become drying. So, such kind of coating is also done. Likewise, different types of coatings are possible. Solvent evaporation with or without chemical changes such as oxidation or final polymerization is one of the way.

Other one is the emulsification or dispersion with water evaporation and then casting and or extrusion of free films by mechanical and melting operations is the other one. Coming to the fibers, these are linear molecules formed by extraction or spinning into small diameter having 10 to 50 microns or thin sections for that purpose these are used. Here in such kind of fibers, weight per unit length of fiber is an important economic criterion. Important mechanical properties of fibers are tensile strength, creep and resistance. These are primarily used in textile industries.

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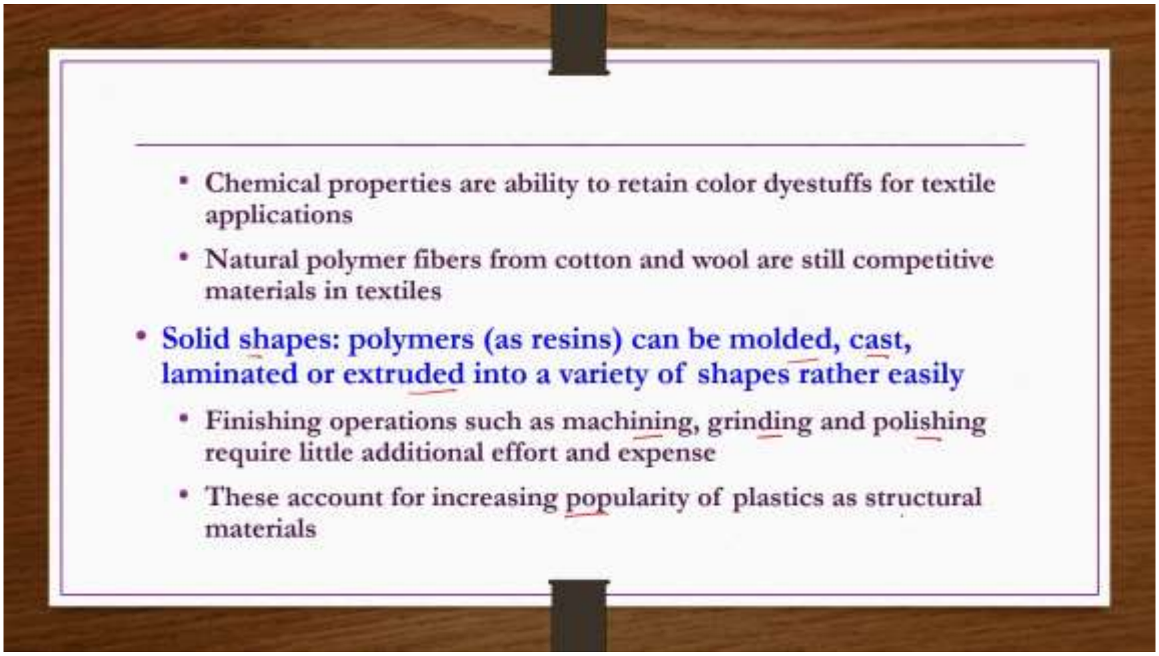

- Chemical properties are ability to retain color dyestuffs for textile applications
- Natural polymer fibers from cotton and wool are still competitive materials in textiles

- Solid shapes: polymers (as resins) can be molded, cast, laminated or extruded into a variety of shapes rather easily
  - Finishing operations such as machining, grinding and polishing require little additional effort and expense
  - These account for increasing popularity of plastics as structural materials

Chemical properties are ability to retain colored dyestuffs for textile applications if it is fiber type polymer. Natural polymer fibers from cotton and wool are still competitive materials in textile industries. Final type of material based on the technical application is the solid shapes. Polymers as resins can be molded, cast, laminated or extruded into a variety of shapes rather easily.

We see so many types of you know, chest, buckets, mugs, etc. in general in our daily life. All of them are made one or other type of polymers, they are converted into the final solid shapes. Finishing operations such as machining, grinding and polishing require little additional effort and expenses in general. These account for increasing popularity of plastics as structural materials. So that is all about a few basics introductory concepts of polymers and then different types of polymers or different types of classifications of polymers.

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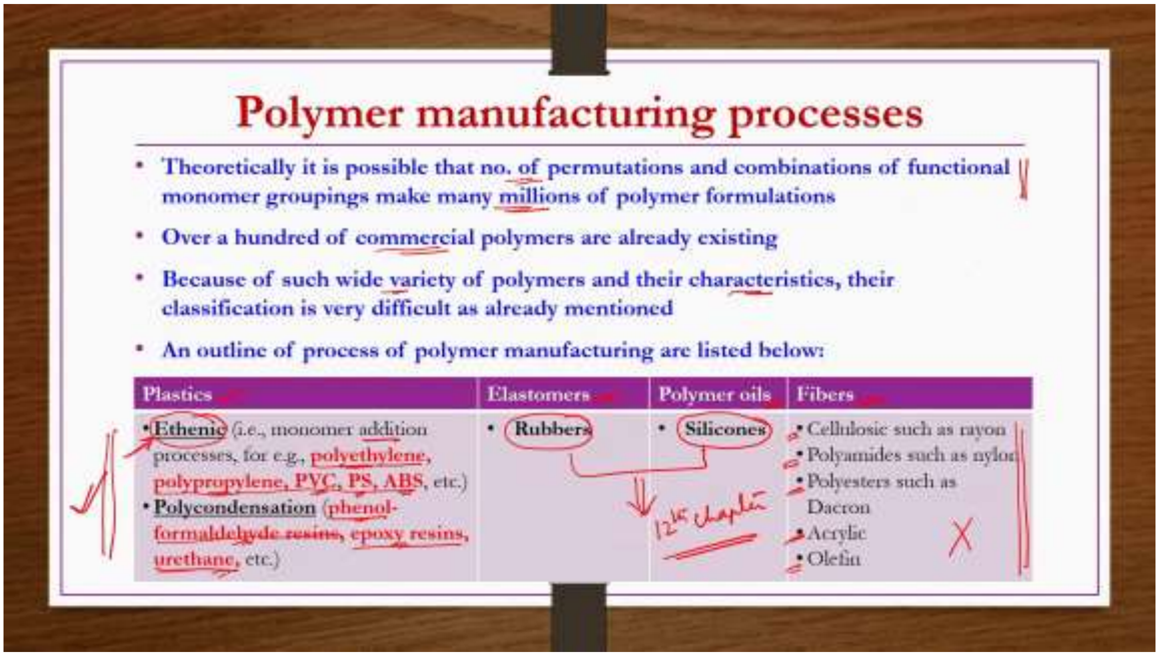

Polymer manufacturing processes

- Theoretically it is possible that no. of permutations and combinations of functional monomer groupings make many millions of polymer formulations
- Over a hundred of commercial polymers are already existing
- Because of such wide variety of polymers and their characteristics, their classification is very difficult as already mentioned
- An outline of process of polymer manufacturing are listed below:

Plastics	Elastomers	Polymer oils	Fibers
• Ethenic (i.e., monomer addition processes, for e.g., polyethylene, polypropylene, PVC, PS, ABS, etc.) • Polycondensation (phenol-formaldehyde resins, epoxy resins, urethane, etc.)	• Rubbers	• Silicones	• Cellulosic such as rayon • Polyamides such as nylo • Polyesters such as Dacron • Acrylic • Olefin

12th chapter

Now, we get into the polymer manufacturing processes. Theoretically, it is possible that number of permutations and combinations of functional monomer groupings make many millions of polymer formulation. Theoretically, it is possible that you know you have a n number of permutations and combinations of different types of bi and tri functional groupings, monomer groupings, etc. to have a millions of polymer formulations out of which over a 100 of commercial polymers are already existing in the market. Because of such wide variety of polymers and their characteristics, their classification is very difficult as we have already discussed. An outline of process of polymer manufacturing are listed below where we have plastics type polymers manufacturing, elastomers type polymers manufacturing and then polymer oils type polymers manufacturing and then fibres type polymers manufacturing.

Under the plastic we have 2 important types, one is the ethenic. Ethenic because of the ethylene type of reactions like you know double bonds, triple bonds are there, ethylene, propylene, etc. and then they are forming some kind of you know polymerization. So, such kind of a nature is there because of that one these things are known as the ethenic that is monomer addition processes. For example, polyethylene, polypropylene, polyvinyl chloride, polystyrene, this kind of acrylonitrile, butadiene, styrene, copolymers, etc. are all possible or grouped under the ethenic because they are obtained by the addition process. Whereas the other one is the polycondensation process where splitting of water, ammonia, formaldehyde, NaCl kind of small molecules is may be taking place. So, under this category we have phenol formaldehyde resins, epoxy resins, urethanes, etc. polyurethanes, etc. So, in this particular chapter, we are going to discuss the polymers or the production of these types of polymers which are highlighted in red font here. Some of them we are discussing in this lecture and then remaining of them we will be discussing in the next lectures.

Whereas the elastomers primarily we have rubbers and then polymer oils primarily we have silicones, their production we are going to discuss in the next chapter or the last chapter of the course. Whereas the fibers primarily they are related to the textile application. So, this we are not going to discuss in this particular course. So, we are going to discuss these production of these types of polymers in this chapter and then remaining these 2 types we are going to discuss in the last chapter that is 12th chapter which is obviously the next chapter of the course. So, we are going to discuss the production of these type of polymers however, we are not going to discuss fibers.

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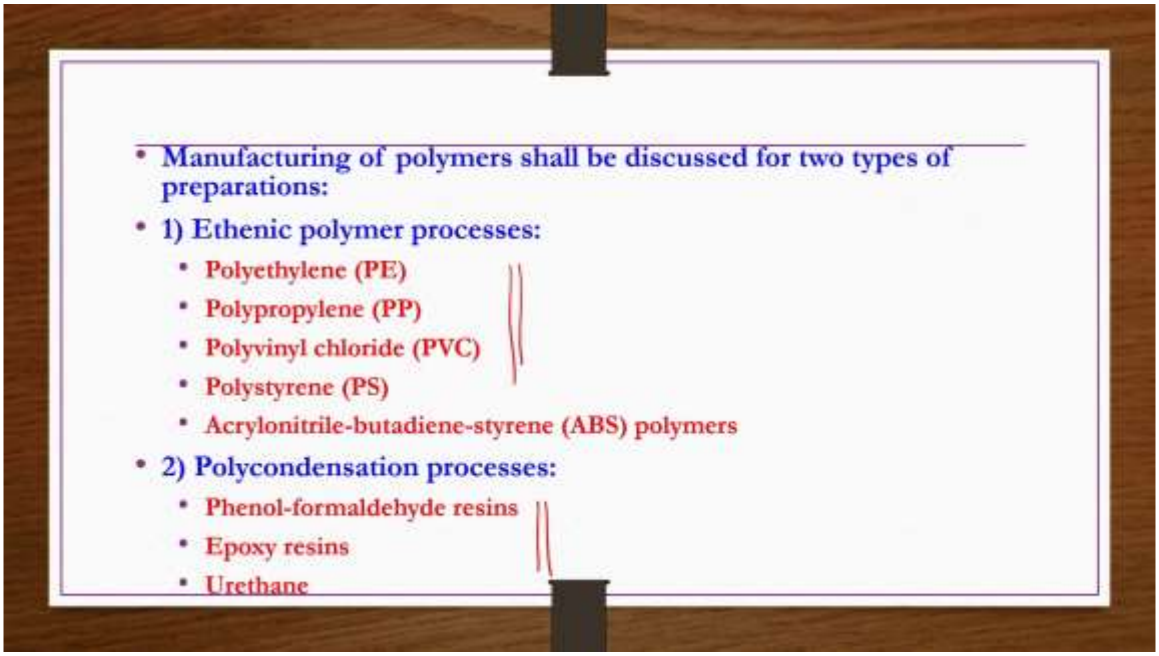

- Manufacturing of polymers shall be discussed for two types of preparations:
- 1) Ethenic polymer processes:
  - Polyethylene (PE)
  - Polypropylene (PP)
  - Polyvinyl chloride (PVC)
  - Polystyrene (PS)
  - Acrylonitrile-butadiene-styrene (ABS) polymers
- 2) Polycondensation processes:
  - Phenol-formaldehyde resins
  - Epoxy resins
  - Urethane

Manufacturing of polymer shall be discussed for 2 types of preparations include under the ethenic polymer processes few are there under the poly condensation process few are there. Under the ethenic polymer processes we have polyethylene, polypropylene, polyvinyl chloride, polystyrene, acrylonitrile, butadiene, styrene polymers. Under the poly condensation processes phenyl formaldehyde resins, epoxy resins, etc. are there. So, let us start discussion on the manufacturing processes of these types of polymers. Polyurethanes are also there.

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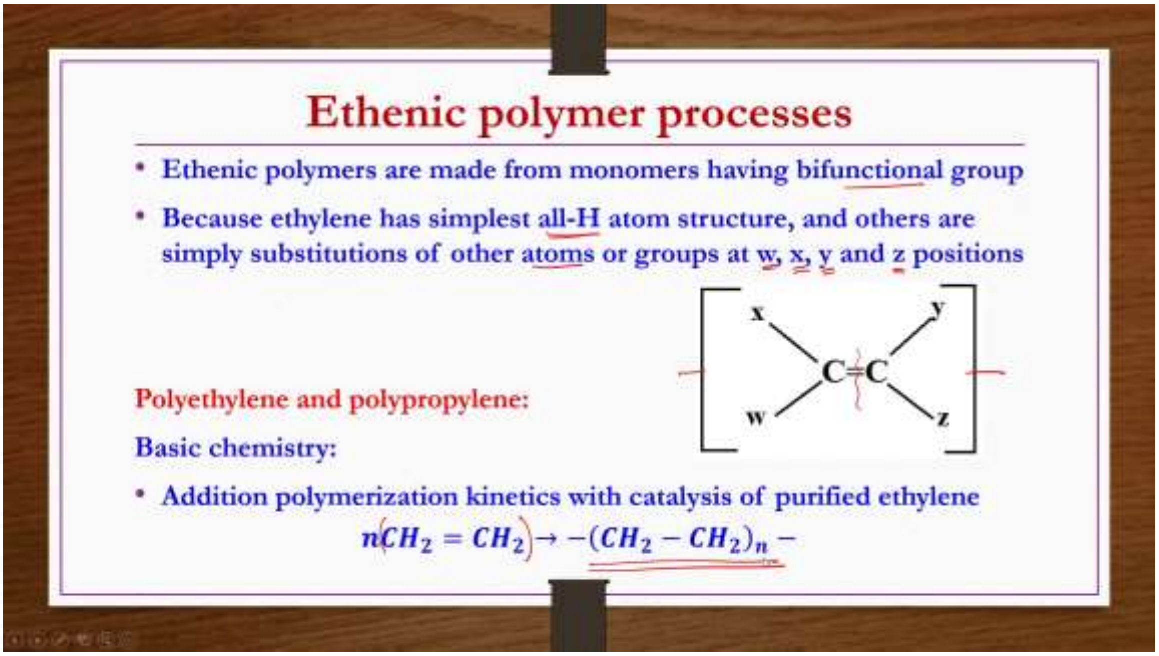

Ethenic polymer processes

- Ethenic polymers are made from monomers having bifunctional group
- Because ethylene has simplest all-H atom structure, and others are simply substitutions of other atoms or groups at w, x, y and z positions

Polyethylene and polypropylene:

Basic chemistry:

- Addition polymerization kinetics with catalysis of purified ethylene

$$nCH_2 = CH_2 \rightarrow -(CH_2 - CH_2)_n -$$

So, let us start discussion on ethenic polymer processes. Ethenic polymers are made from monomers having bi-functional group like ethylene because ethylene has simplest all H atom structure and others are simply substitutions of other atoms or groups at w, x, y and z positions as shown pictorially here. So, here this double bond would be breaking up and then you can have a monomer and then these w, x, y, z maybe you know substituted by other molecules or other atoms as well.

Polyethylene polypropylene manufacturing will be discussing first in this category of polymer processes. Basic chemistry addition polymerization kinetics with catalysis of purified ethylene is taking place. So, reaction is n moles of ethylene reacting together to form polyethylene as represented like this.

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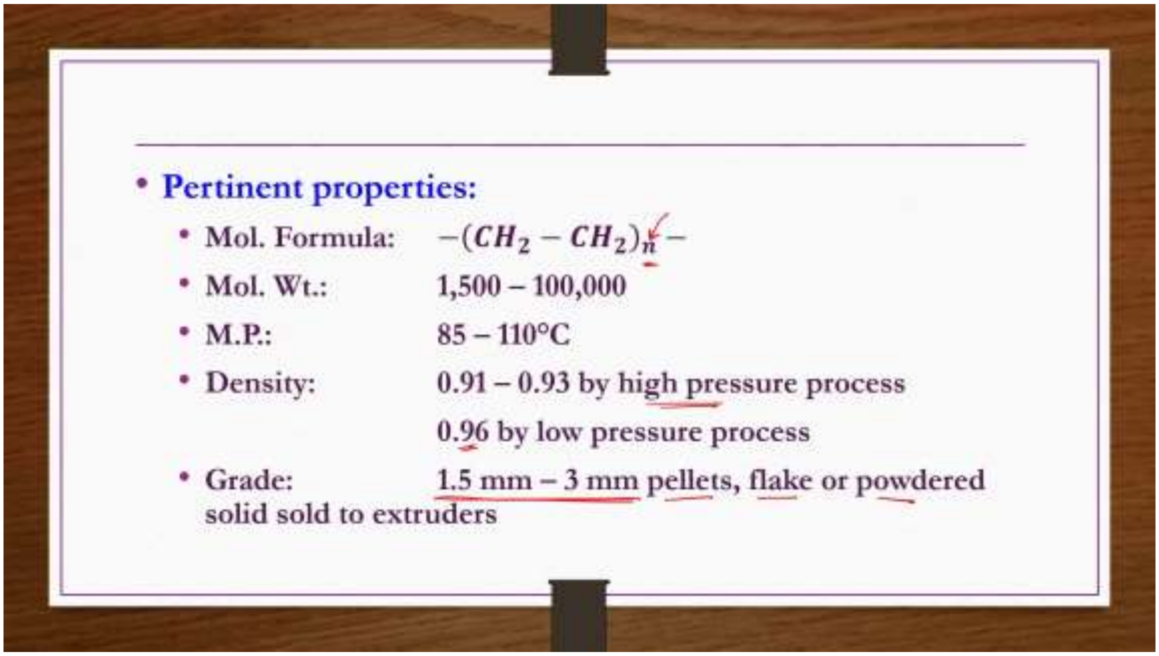

- **Pertinent properties:**
  - Mol. Formula: $-(CH_2-CH_2)_n-$
  - Mol. Wt.: 1,500 – 100,000
  - M.P.: 85 – 110°C
  - Density: 0.91 – 0.93 by high pressure process
    0.96 by low pressure process
  - Grade: 1.5 mm – 3 mm pellets, flake or powdered solid sold to extruders

Pertinent properties, molecular formula is -$(CH_2$-$CH_2)$- n times repeated. Molecular weight of the structure would depends on the number of repeating units n number that depends on that one molecular weight will depend.

So, molecular weight in general 1500 to 100,000 is possible. Melting point is 85 to 110 degrees centigrade. Density there are different processes high pressure, intermediate pressure and low-pressure processes to get the polyethylene and polypropylene. So, if you are doing high pressure process then density is 0.91 to 0.93. If you are doing low pressure process density is 0.96 gram per cc. Grates usually available in pellets, flake or powdered solid form. Size is in general 1.5 mm to 3 mm.

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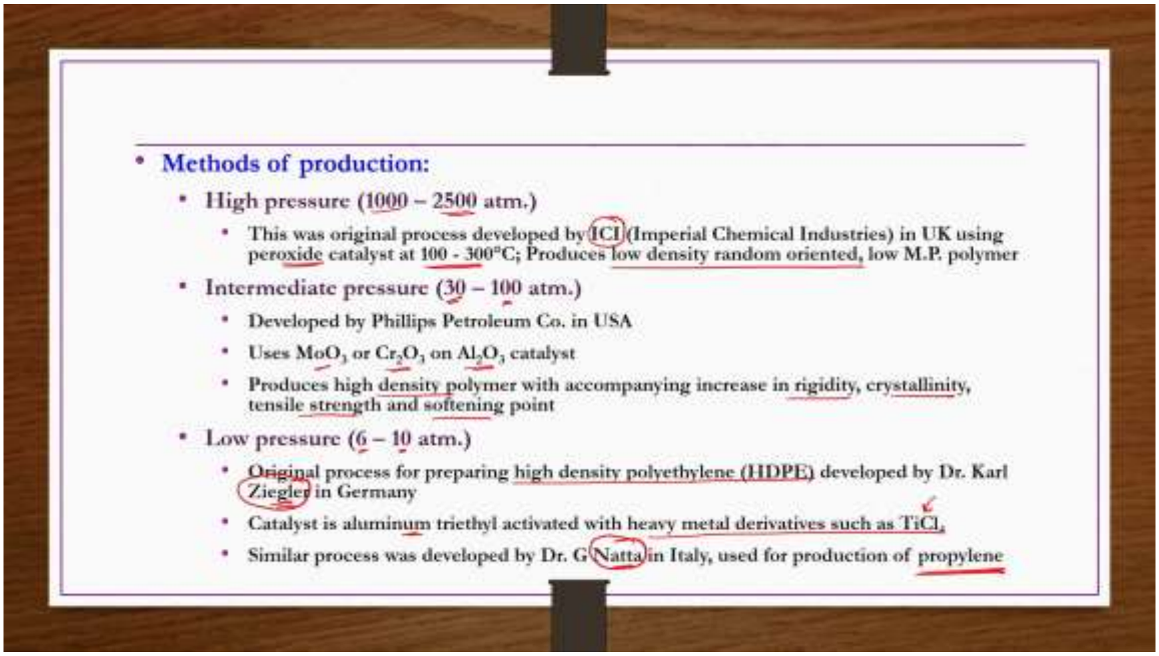

- **Methods of production:**
  - High pressure (1000 – 2500 atm.)
    - This was original process developed by ICI (Imperial Chemical Industries) in UK using peroxide catalyst at 100 - 300°C; Produces low density random oriented, low M.P. polymer
  - Intermediate pressure (30 – 100 atm.)
    - Developed by Phillips Petroleum Co. in USA
    - Uses MoO_3 or Cr_2O_3 on Al_2O_3 catalyst
    - Produces high density polymer with accompanying increase in rigidity, crystallinity, tensile strength and softening point
  - Low pressure (6 – 10 atm.)
    - Original process for preparing high density polyethylene (HDPE) developed by Dr. Karl Ziegler in Germany
    - Catalyst is aluminum triethyl activated with heavy metal derivatives such as $TiCl_4$
    - Similar process was developed by Dr. G Natta in Italy, used for production of propylene

Methods of production, three important types of methods of production are there.

High pressure methods where pressure is usually 1000 to 2500 atmospheres. Then intermediate pressure method where the pressure is 3200 atmospheres and then low-pressure method where the pressure is 6 to 10 atmospheres in general. High pressure method is the basic original process and then that was developed by Imperial Chemical Industries in UK. They have used peroxide catalyst; the temperature was around 100 to 300 degrees centigrade. The products were low density, random oriented, low molecular weight, polyethylene were produced.

Intermediate process developed by Phillips Petroleum Company in USA. It uses metal oxide catalyst like MoO_3, Cr_2O_3 supported on Al_2O_3 such kind of catalyst were used. Produces high density polymer with accompanying increase in rigidity, crystallinity, tensile strength and softening point. Then comes to the most important process, low pressure process which is original process for preparing high density polyethylene developed by Dr. Karl Ziegler in Germany. Catalyst is aluminum triethyl activated with heavy metal derivatives such as titanium tetrachloride, sometime titanium trichlorides are also used.

Similar process was also developed by Dr. G. Natta in Italy, but he used the method for the production of propylene. So Ziegler and Natta are two very famous personalities in polymer industry. So, there are a few topics based on their names or you know as a respect to their names, they are known as the Ziegler, Natta catalyst, etc. So now we see all these 3 processes by flowchart and then conclude the lecture.

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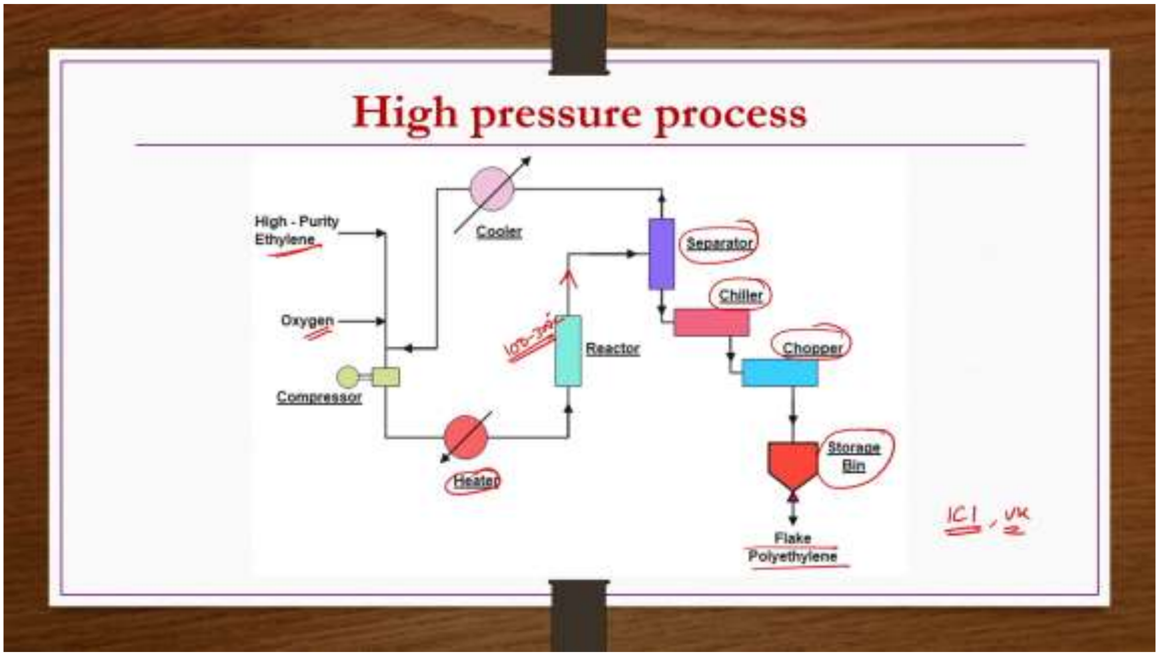

High pressure process

So first we see high pressure process which is the simplest one. What you have here high purity ethylene you take, mix with oxygen and then compress it to the required pressure of 1000 to 2500 atmosphere, preheat it because the reaction temperature is something 100 to 300 degrees centigrade.

So directly getting such temperature in the reactor may not be good enough from the yield point of view, that is the reason for most of the high temperature reactions preheating is used. The preheating enhances the yield in general. So, this preheated high-pressure ethylene oxygen mixture passes through the reactor which is at 100 to 300 degrees centigrade. Now the product mixture whatever is there that would be passed through a separator to separate out the unreacted oxygen and ethylene, etc. and then cool them and then feed them back to the compressor and then do the recycling. Whereas the polyethylene whatever form polymer that is formed that would be chilled, temperature reduced by the chilling then so that the solids would be formed then chopping, etc. would be done so that to get the required shape of the polymer then they would be taken to a storage bin. Flake polyethylene you can get like this. This is the high-pressure process developed by Imperial Chemical Industries UK.

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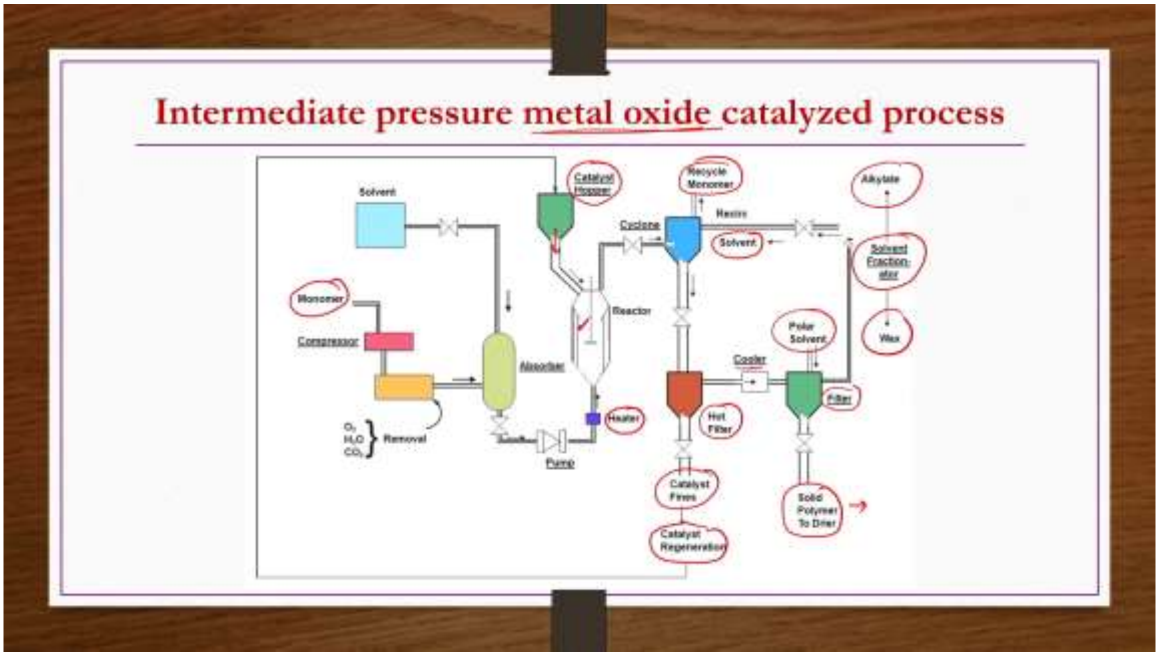

Intermediate pressure metal oxide catalyzed process

Now we talk about intermediate pressure metal oxide catalyzed process. This intermediate pressure process also known as the metal oxide catalyzed process because the metal oxide catalyst are used for this purpose. So here whatever the monomer that is there that you compress and then pass through some kind of separation, pretreating units to separate or remove sulphur, oxygen, water, carbon dioxide, etc. then send it to a reactor after passing through a absorber. So before sending to the reactor the mixture would be preheated as per the requirement of the temperature that is there in the reactor.

Then to this reactor from the top you are also supplying the catalyst. From the catalyst hopper continuously, you are supplying the catalyst. In this reactor continuously catalyst, solvent and then monomer are interacting and then required reaction takes place. Reaction mixture whatever is there that is taken to a cyclone separator where you separate the unreacted monomers whatever are there and then recycle back. Whereas the solvents, etc. along with the product mixture is there that you take to a hot filter where you try to separate out the solvents and then from the solvents you try to separate out the catalyst and then those catalyst you do the regeneration and then feed back to the catalyst hopper and then from there it goes to the reactor.

Whereas the product that is there after the hot filter they would be cooled in a cooler then pass it through a another filter where polar solvents are used to separate out the unreacted solvent, unreacted impurities or other kind of solvents that are present, etc. And then you get the solid polymer for the drying purpose from the bottom. Whereas whatever the solvents that you are separating out from the filtration unit they would be passed through a solvent extractor where the waxes and then alkylates are separated out and then solvent whatever is there that would be recycled back to the cyclone separator for the continuation of the process. So, this is the intermediate pressure metal oxide catalyzed process.

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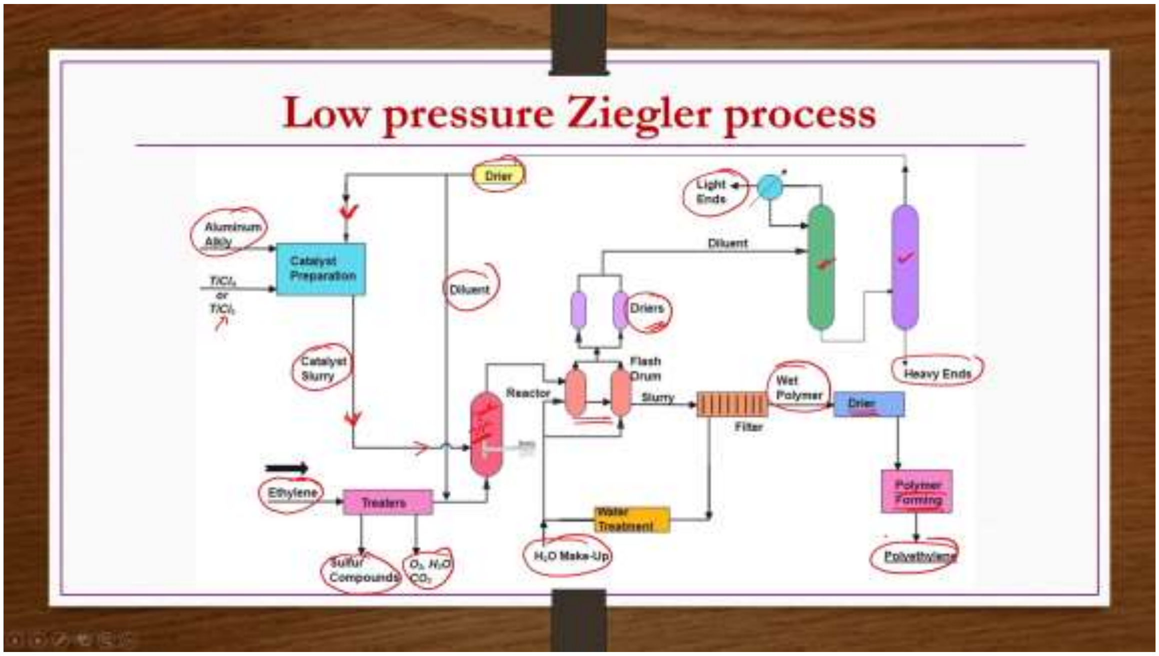

Low pressure Ziegler process

The final important process is the low pressure Ziegler process. Here what you have? You have the ethylene. This ethylene you may not be having the pure ethylene if you are taking from the hydrocarbon steam reforming processes, etc. So, then it may be having sulphurs, CO_2 and other kind of impurities may also be there. So, this ethylene would be pretreated to remove the sulphur, desulphurization takes place and then light ends are also being separated.

After this one the purified ethylene is sent to the reactor. To this reactor catalyst slurry is also supplied. What do you mean by catalyst slurry? Actually, $TiCl_4$ or $TiCl_3$ is only catalyst. But this catalyst is mixed with aluminum alkyl solvents so that a proper slurry can form and then if it is in a proper slurry form so then interaction with the gaseous ethylene would be better. So then here the interaction between the catalyst slurry and then ethylene takes place at 7 atmosphere, 7-8 atmosphere pressure and then 70 degrees centigrade roughly. So, then reaction takes place whatever the reaction product mixture is there that is passed through a series of flash drum to separate out the solvents and then to this reaction mixture where the flashing is done water is also added up. Why this water is being added up? Because the catalyst whatever are there under the dry condition they are very highly flammable that is the reason in order to control the flames.

So after the reaction or after the reactor whatever the product mixture is there that is mixed with water, a makeup water and then passed through series of flash drums where the solvents are recovered, dried and then passed through a fractionator to separate out the light ends and then heavy ends after separating the light ends and the heavy ends in series of fractionators whatever the solvents are there, they would be dried and then taken as a diluent and then sent back to the reactor along with the ethylene or they would be sent back to the catalyst preparation units so that to make the slurry of the catalyst. Whereas the slurry that is coming out from the flash drum that would be filtered to remove any water that is present that water would be pretreated or the water treatment would be done and then that water would be recycled back to the flash drums to control the reactivity or explosion of the catalyst. Whereas the wet polymer coming out after the filtration process whatever is there that would be dried and then sent to the polymer forming units if at all as per the requirement and then final polyethylene is being produced. This is the low pressure Ziegler process to produce polyethylene.

The same process may also be used to produce polypropylene but with a slightly modified conditions and then catalyst, etc.

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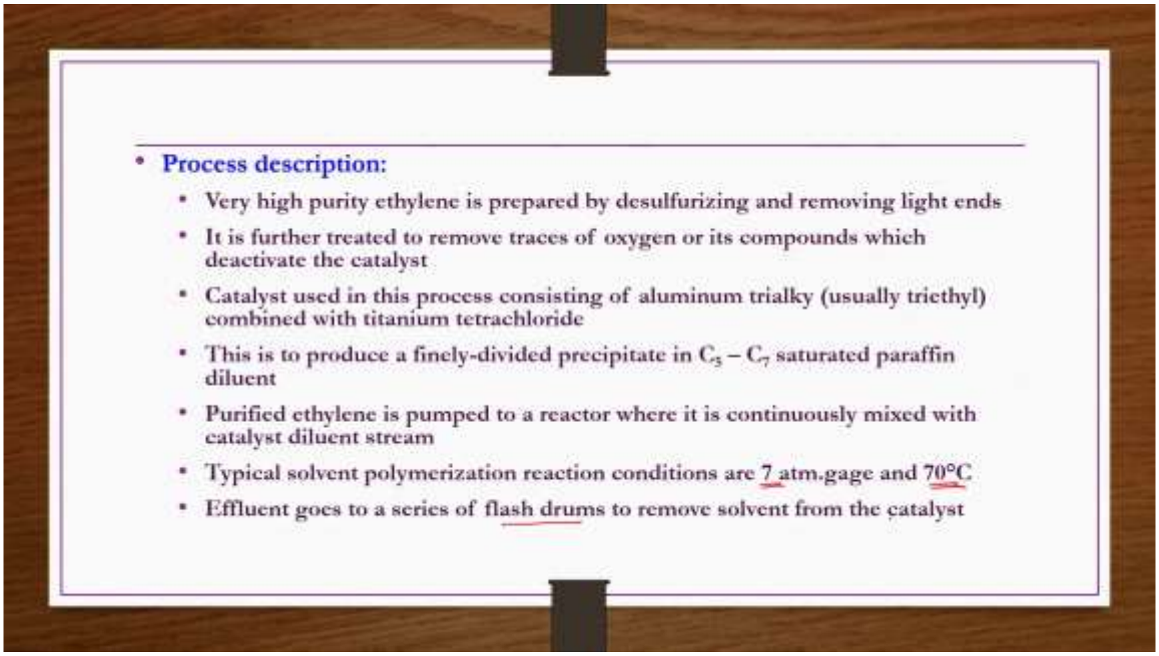

- **Process description:**
  - Very high purity ethylene is prepared by desulfurizing and removing light ends
  - It is further treated to remove traces of oxygen or its compounds which deactivate the catalyst
  - Catalyst used in this process consisting of aluminum trialky (usually triethyl) combined with titanium tetrachloride
  - This is to produce a finely-divided precipitate in $C_5 - C_7$ saturated paraffin diluent
  - Purified ethylene is pumped to a reactor where it is continuously mixed with catalyst diluent stream
  - Typical solvent polymerization reaction conditions are 7 atm.gage and 70°C
  - Effluent goes to a series of flash drums to remove solvent from the catalyst

Process description very high purity ethylene is prepared by desulfurizing and removing light ends. It is further treated to remove traces of oxygen or its compounds which deactivate the catalyst. Catalyst used in this process consisting of aluminum tri-alkyl usually aluminum triethyl solvents are used.

It is combined with a titanium tetrachloride catalyst. This is to produce a finely divided precipitate in C_5 to C_7 saturated paraffin diluent. Purified ethylene is pumped to a reactor where it is continuously mixed with catalyst diluent stream. Typical solvent polymerization reaction conditions are 7 atmosphere gauge pressure and then 70 degrees centigrade. Effluent goes to a series of flash drums to remove solvent from the catalyst.

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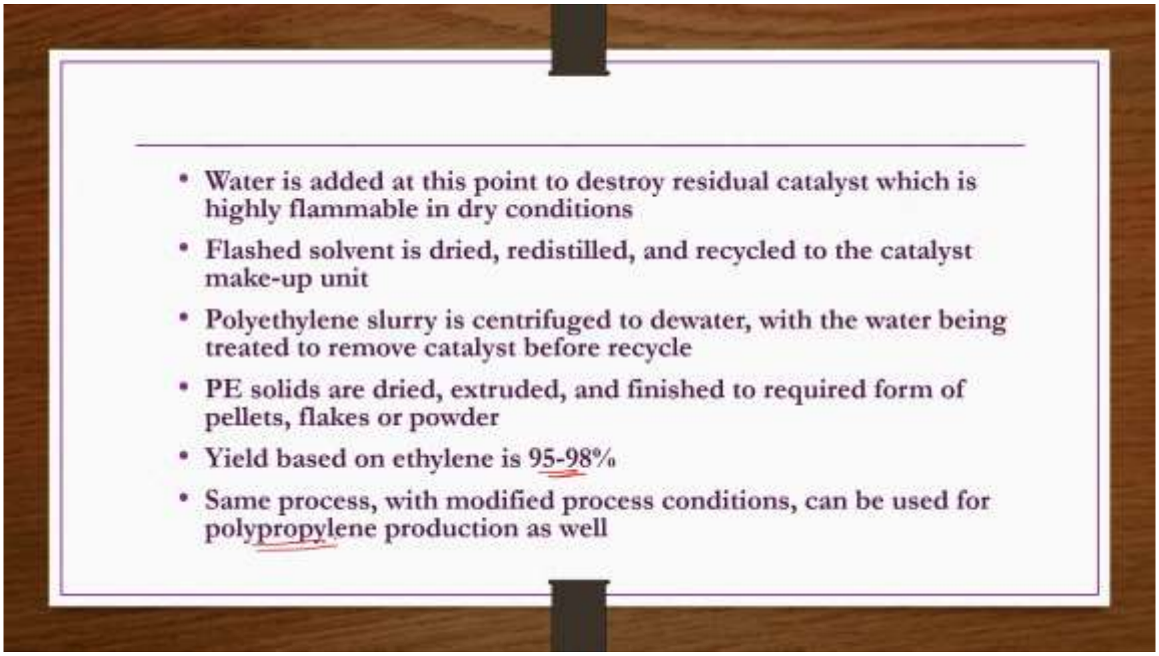

- Water is added at this point to destroy residual catalyst which is highly flammable in dry conditions
- Flashed solvent is dried, redistilled, and recycled to the catalyst make-up unit
- Polyethylene slurry is centrifuged to dewater, with the water being treated to remove catalyst before recycle
- PE solids are dried, extruded, and finished to required form of pellets, flakes or powder
- Yield based on ethylene is 95-98%
- Same process, with modified process conditions, can be used for polypropylene production as well

Water is added at this point to destroy residual catalyst which is highly flammable in dry conditions.

Flashed solvent is dried, re-distilled and recycled to the catalyst makeup unit. Polyethylene slurry is centrifuged to dewater with the water being treated to remove catalyst before recycle. Polyethylene solids are dried, extruded and finished to required form of the pellets, flakes or powder. Yield based on ethylene is approximately 95 to 98%. Finally, same process with modified process conditions can also be used for the production of polypropylene as well.

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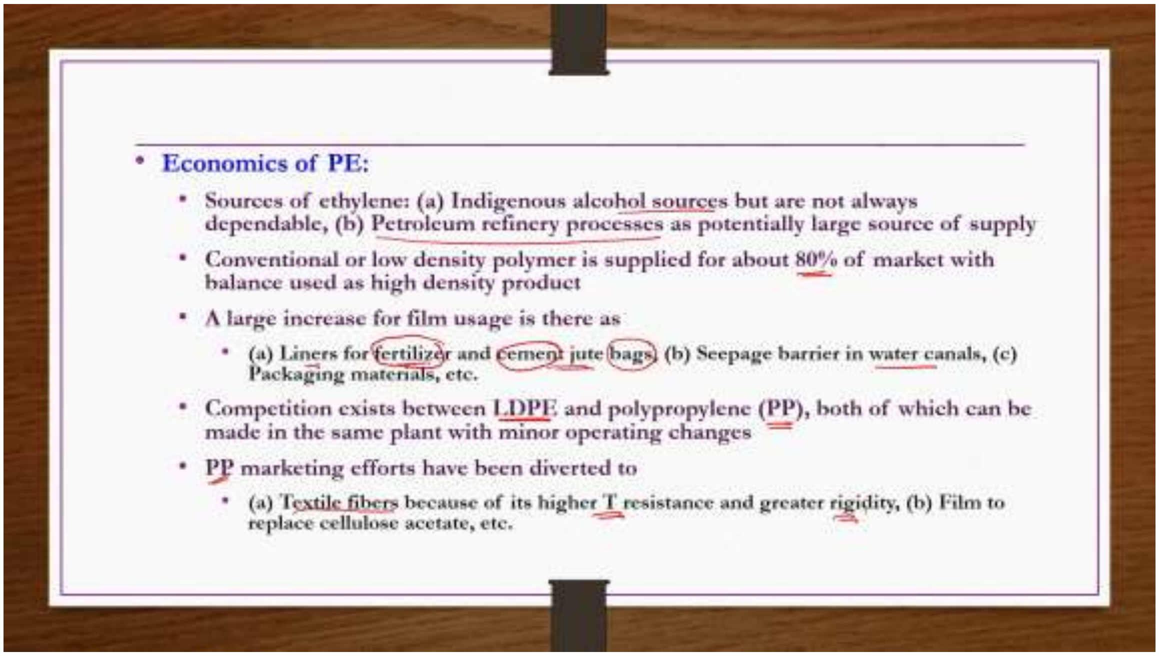

- **Economics of PE:**
  - Sources of ethylene: (a) Indigenous alcohol sources but are not always dependable, (b) Petroleum refinery processes as potentially large source of supply
  - Conventional or low density polymer is supplied for about 80% of market with balance used as high density product
  - A large increase for film usage is there as
    - (a) Liners for fertilizer and cement jute bags, (b) Seepage barrier in water canals, (c) Packaging materials, etc.
  - Competition exists between LDPE and polypropylene (PP), both of which can be made in the same plant with minor operating changes
  - PP marketing efforts have been diverted to
    - (a) Textile fibers because of its higher T resistance and greater rigidity, (b) Film to replace cellulose acetate, etc.

Finally, we conclude the lecture with economics of polyethylene. Sources of ethylene are indigenous alcohol sources for India but are not always dependable in general. Other important source or the largest source of supply of ethylene is the petroleum refinery processes. Conventional or low-density polymer is supplied for about 80% of the market with balance used as high-density product. A large increase for film usage is there as liners for fertilizers and cement jute bags.

Bags actually, in general bags are used for the packing of fertilizers and then cement. So, for those bags these polyethylenes are used as liners. Then seepage barriers in water canals and then packaging materials purpose also it is used. Competition exists between low density polyethylene and then polypropylene both of which can be made in the same plant with minor operating changes. However, PP or polypropylene marketing efforts have been diverted to mostly towards the textile fibers because of its higher temperature resistance and greater rigidity and then film to replace cellulose acetate, etc. So that is all about the production of polyethylene and polypropylene.

In the next lecture we will be discussing production of different types of other types of polymers.

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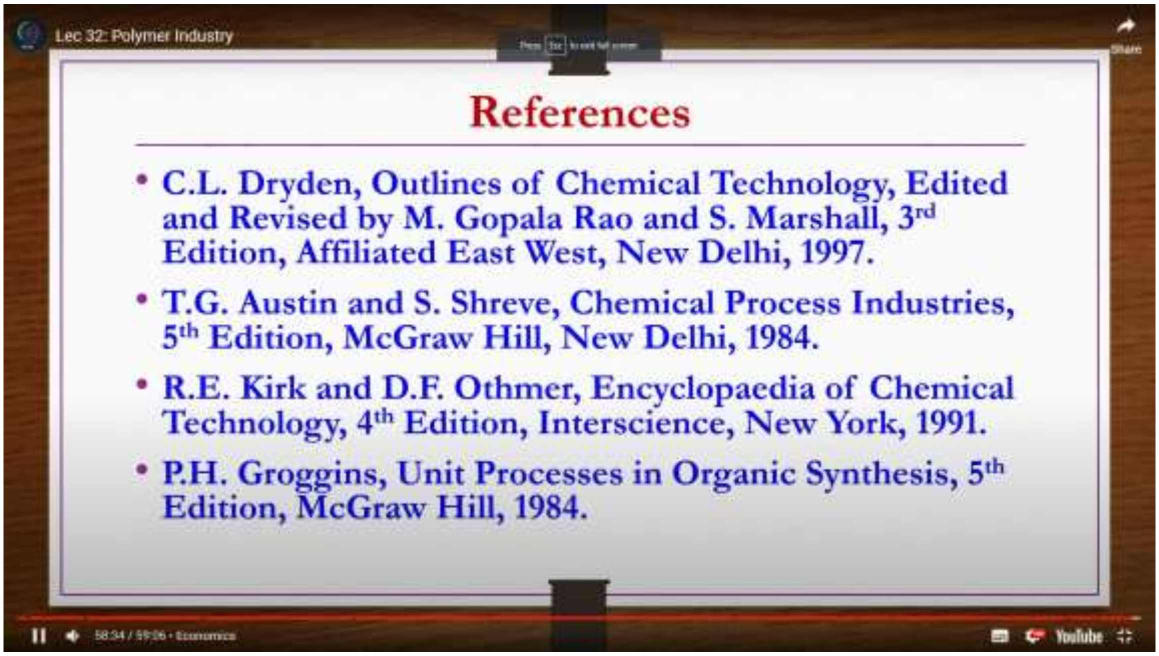

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References for today's lecture are provided here. Thank you.