

Polymer Reaction Engineering
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Lecture - 01
Introduction to Polymerization Process-I

So welcome to the course of Polymer Reaction Engineering. And before we start this course, and we introduce our polymerization processes, let us have a brief look about the polymers. Now polymer occupies a very vital place in our day-to-day life. Now if you start your day right from tooth brushing to if you go to the bed, everywhere you will see there are variety of a spectrum of polymeric products.

Now if you are using day-to-day affair, you will see that they are having various kind of approaches in the polymeric application like flexible sheet to the bumpers of cars etc., they you require various kind of mechanical, chemical and thermal properties everywhere you go to the either PET bottle, whether you go for any kind of a packaging material, whether you go for any kind of a clothing etc., everywhere you will find there are a galaxy of a polymeric products.

Now when we talk about different kind of a polymeric products, then the things come into mind that what is the protocol for the development of such kind of a product. Second thing is that what is the science behind these kinds of a polymeric product.

Because if you see that, the flexibility in the polymeric sheet or if you go for the impact property of our car bumper or any kind of a thing which is required, any thermal, mechanical and chemical properties, you see that the protocol for the development of such kind of a variety of polymeric product is entirely different. Now as we go into the polymerization process, every process attribute to two type of a thing.

One is related to the process and second is related to the operation. Now remember operation always supported by the process. It is just like that if you are having two chemical products with two chemical reactants with you and if you wish to develop any kind of product through it, then you need to look into the various issues related to

this one. I am giving you a broad spectrum of ammonia synthesis example that like N_2 plus H_2 gives you NH_3 .

Now you see that if you are having any engineering background or a science background, this is an exothermic reaction. And it is not so easy to convert the nitrogen and hydrogen into ammonia because it is an exothermic reaction, it requires so many types of temperature and pressure control protocols etc. And sometimes if you got the product then you require some specific applications for of that particular product.

So, you require some specific characterization of that particular product. The same way it happens in the polymerization processes. Polymerization processes, because of the variety of a spectrum and variety of application, you require different type of polymerization steps. You require different type of things need to be carried out.

So, the basic theme because whenever we are having different kinds of reactants, when we are having different kind of a product demand in that case, it offers a wide spectrum and wide knowledge of reaction engineering concept. Sometimes reaction may be endothermic, sometimes reaction may be exothermic, sometimes you require certain higher molecular weight components.

Sometimes you may require any kind of a different product for this specific use. I am giving you a broad brief knowledge about polyethylene. Polyethylene sheets are always there. If you go for linear polymers, then you can develop the sheets. And if you go for some mechanical or stiff type of a polymer, then high density polyethylene etc., they offer wide spectrum.

Raw material is same, but the application point of view it is entirely different. So, based on various kind of application, based on various kind of specialty demands, there is a wide variety of polymerization product. So, based on this particular thing into our mind, first couple of lectures are attributed to the what is polymer and what is the history of polymerization.

Since it offers a wide variety, then every scientist across globe they try to develop their protocols, they try to develop various things like if you take the example of a toothbrush, there are two different type of polymers. One through which you use for the gripping, another one is for the brushing. So, the process for the development of these two things are entirely different.

And another thing offers that how you infuse them so that it may have a compatibility, it may have various application. Now if you go for further detail, then definitely you require certain specific things need to be carried out for those toothbrush applications like gripping you require certain light things and for brushing etc., you need to have some abrasion issues etc.


So based on this particular approach, you need to learn about that what kind of a protocol we need to adopt for different type of or development of a different type of polymeric products.

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Polymer Reaction Engineering

What we learn in this PPT?

- ❖ **Introduction to the polymerization process**
 - **Classification of Polymers**
 - **Based on Source of Polymer**
 - (1). Natural polymers (2). Synthetic polymers
 - **Based upon the behavior towards the heat**
 - (1). Thermoplastic polymers
 - (2). Thermosetting polymers
 - **Based on structure of polymers**
 - (1). Linear (2). Branched polymers (3). Cross-linked



So based on this particular thing, we are just going to have an outline that what we are going to learn in this particular lecture, that is introduction to the polymerization process. Then we will discuss about the various kind of a polymers or the classification of the polymer. Because when we try to develop a protocol for any kind of a polymerization process, then we need to know that how we can classify all those polymers.

And based on this particular information we can develop our protocol. Now see, one thing is that, if we talk about the classification issues, there are several methodologies given by various scientists like based on source of polymer, there are natural polymers. Nature gives me a number of polymers like if you take the example of a cotton etc., we will discuss this thing in due course of a time. These are the natural polymers.

Then we try to develop the synthetic polymers based on our own use. Then another classification can be given based on the behavior towards heat. This is a very common thing, thermoplastic polymers and thermosetting polymers. Now the more scientific way in which we can classify the polymer, polymers are linear, branched and cross-linked polymer. We will discuss this thing in due course of time.

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Introduction to the polymerization process

What are polymers?

- The term polymer can be defined as poly means 'many' and meres means 'part'.
- Polymers are large molecules having high molecular weight and complex in structure, formed by linking very large number of small molecules (monomers) together.
- Polymers have different chemical structures, physical properties, mechanical behavior and thermal stability than simple molecules such as common salt, sugar etc.



Now before we start, as I told you in a couple of minutes ago, that polymer occupies a vital spectrum in our day-to-day life. Then issue arises that what are those polymers. Now this term polymer this can be defined by as a poly means many and mers means apart. So, it is a building block of different type of monomeric substance.

Now these monomeric substances may be like a brick like structure and you need to join those monomers with the help of a suitable technique or suitable process to build the entire spectrum. Now usually, the polymers they are large molecules having higher molecular weight and then very complex in structure formed by linking a very large number of small molecules or monomer together.


They have a different chemical structure that is purely based on the requirement. Physical properties, I told you that you may have a plastic sheet or a polymeric sheet, they may offer a very good spectrum of flexibility to the car bumpers where you may have impact resistance etc.

Similarly, the physical properties, mechanical properties, thermal stabilities, you may have various kind of packaging material in which you see that there is a thermal stability so that there may be a minimum interaction between the inside the material and outside the atmosphere. So, these kinds of various applications can be attributed to the polymeric system.

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Introduction to the polymerization process

- Polymers exist in many forms and numbers due to large numbers and types of atoms present in their molecular structure.
- The smallest molecule which replicates itself many numbers of times to form a giant molecules i.e. polymer is termed as “monomer”. Such small molecules, which combine to form a big molecule, may be of one or more chemical compounds.
- Monomers are the raw material to form a polymer. The process of linking monomers via a covalent bond to form such a large molecule is called “polymerization”.



Now these polymers exist in many forms and number due to the large number of types of atoms or molecules present in their molecular structure. If you see that the automotive tires, they are a big molecule, but they are having the sulfur present in during the vulcanization process to offer many kinds of chemical, thermal, and mechanical properties.

Now the smallest molecule which replicates itself many numbers of times to form the giant molecule, this is termed as monomer. I in the previous slide, I refer that these are the building blocks of the polymeric substance. So, such small molecules, which combine to a big molecule may be one of the more chemical compounds.

Now trust me, this is the genesis of your polymer reaction engineering that how you can build up those empire of a polymer with the help of a small monomer units. What is the different kind of chemical process you need to adopt through which you can get your desired properties?

What kind of different things you need to or what kind of a different additives you need to add in those monomers, when they propagate itself to form a polymer, that is again a very good type of engineering, so that you can form a polymer which is which offers the desired properties which you are looking for. So, in nutshell we can say that monomers are the raw material to form a polymer.

And the process of linking of those monomers may be via covalent bond, maybe by the Van Der Waal bonds etc., to form such a large molecule, they are called the polymerization or the process of polymerization. Now when we talk about this process of polymerization, several things come into mind. That is it so easy to form this kind of a thing? Just if you go to the construction industry, there are small bricks.

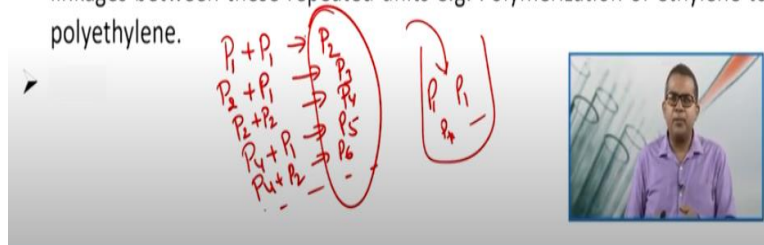
Now there is a set process that you require some cementing material through which you can join all those bricks to build either room or whatever house or whatever building you would like to have. And then you because the size of the brick, then the cementing material, one thing is essential, that always they offer the choice as that what kind of properties you are looking for that particular building.

So, in that case, similar things they are offering, because the polymers the monomers, they are just a building blocks or bricks, and the process through which you are joining all those things, they are called the process of polymerization.

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Introduction to the polymerization process

- The polymers are very high molecular weight compound their weight can range from hundreds to millions units.
- For polymerization to occur it is required that these small molecules (monomers) either have some reactive functional groups or unsaturated bonds (double or triple bonds) which can join to provide the necessary linkages between these repeated units e.g. Polymerization of ethylene to polyethylene.



So, when we talk about the high molecular weight compound, now their weight can be ranges from hundreds to the million units. That is purely based on the requirement. Now when we talk about the million units, then they offer a large molecular weight. It is just like that, if you compare one brick of your building unit, and if you try to imagine that if you are building a room, then you can calculate the cumulative weight of all those bricks.

Now when we talk about this polymerization process, it usually offers three different steps. One is the initiation; second one is the propagation and third one is termination. The reason for these three steps is that you must have any process through which you can trigger your poly process, because usually, these monomeric units are in situ they are having some inert properties.

So, whenever you talk about the initiation of the process, something you are require to trigger. And once they initiate the process that is called the propagation then they try to join different monomers all together. And they develop, then at that at you require one particular point where you need to truncate that particular reaction. Otherwise, they may combine together to form different type of blocks.

Now see, I am just giving you suppose I am talking about this P_1 . This P_1 is a monomer. Now if you are having a reaction mass, where all monomers P_1, P_1 and P_1 etc. Now if you start the things, then P_1 may combine with P_1 to give you P_2 . Now in

the next step, this P_2 may combine either with P_1 to give you P_3 . Or this P_2 may combine this P_2 to give you P_4 .

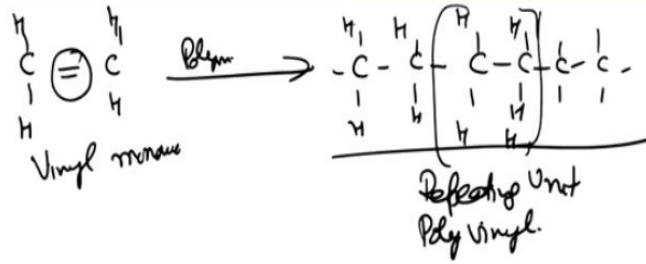
Now this is why I am emphasizing that we require the truncating step. We will discuss this thing in detail in subsequent lectures. Now this P_4 trust me, they may have a various variety of choices. It may combine with the P_1 to give P_5 . Similarly, this P_4 may combine with P_2 to give P_6 and like this.

So, if you see that this particular thing offers a wide spectrum and you would not be able to control the things unless otherwise all the things are being consumed. So that is why the truncation process or the termination process is required. Now the question arises that how we can see and how we can initiate the things because sometimes you may have a monomer which is having you can say the inert approach.

How you can trigger it to be to get initiated with the help? No doubt there are certain specific requirement of a temperature and a pressure and other catalyst. But for polymerization to occur, it is required that these small monomers or small molecules, they must have some reactive functional group or unsaturated bond, double bond or triple bond, which can join to provide the necessary linkage between these repeated units to form the polymerization process.

I will give you an example of polymerization of ethylene to polyethylene in due course of time. Now I am giving the example of polymerization of say vinyl monomer into forming the polyvinyl thing.

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Now here see this is the basic structure of vinyl monomer. Now if we perform the polymerization process, you will see that because it is having this double bond, it offers an opportunity to be get linked with other monomers of either same category or if you are having adopting any kind of special process, you can link or graft some other monomer to it. So, we go for the polymerization process.

Now here you see that this double bond is linked with other monomers to give you the this is the, now this is sometimes in literature, it is referred as repeating unit. So this vinyl monomer get polymerized to give you the polyvinyl. So based on this particular approach, up till now, we understand that what we require, first thing is that we require that what kind of a desired properties we are looking for.

We are having our monomer with us. Then to trigger the reaction, we require certain functional group to be added to this particular system.

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Classification of Polymers

1. Based on Source of Polymer

On the basis of depends on their origin, the polymers can be classified as synthetic and natural.

▪ Natural polymers

Polymers can be found naturally and can be extracted for commercial use. They are often water-based compounds.



Natural polymers



Now before we go into the details of these kind of a polymerization, process, initiation, propagation, termination, etc., let us have a look about the classification of polymer. As I told you that this classification of polymer offers a very good information through which you can assess the various properties attributed to your final product and what kind of process you require to have your polymerization process.

So, first thing as I discussed in the very first slide of this particular lecture is that based on the source of polymer, that is on the basis of their origin, these polymers can be classified as either synthetic or natural. Now natural why natural? Now see, if you see the photograph, nature offers various kind of polymeric product to our day-to-day affair or day-to-day life.

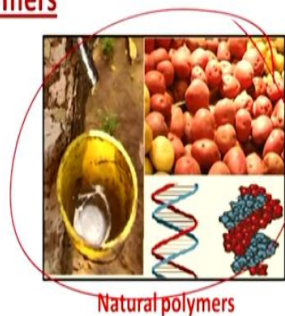
So natural polymers they can be found naturally and can be extracted for the commercial use. Usually, they are termed as water-based compounds.

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Classification of Polymers

▪ Natural polymers

Examples include; all kind of silks, wool, cotton, natural rubber, Living DNA, cellulose and proteins from plants and animals.



(The given picture showed natural rubber, starch and DNA)



And these examples, if you say that all kind of a silk, silk is a natural polymer. Wool, wool is a natural polymer. Cotton, natural rubber, living DNA, cellulose, proteins from plant, animal. Now these are, these things are you can say the natural polymers. And if you see that, like if you take the example of a natural rubber, it offers a very good spectrum of future kind of development like rubber tires etc.

So, you can see these types of things are available in your day-to-day affair, readily available. Now why we are talking about these natural polymers, because if you see that silk, at the start at the outset the silk was termed as a natural polymer, but it was giving I mean the people got an idea that because silk is a very useful product.

So, people thought that if we are having any kind of a product which is having the the properties like silk, can we develop in laboratory? Can we develop the things in the industrial scale? Similarly, wool. Similarly, if you see the cotton. Similarly, if you see the natural rubber. So, all kind of things or you can say the base material or thought process or school of thought process was the natural polymer.

And it gives an impetus to the scientists that we try to develop because they give you the usefulness to our day-to-day life. And that is why because to meet out the requirement of growing population and to offer more and more stability to the product, people thought to change the several polymerization process so that they can achieve the desired properties with respect to our day-to-day affair in different processes.


And that is the root cause of development of various polymerization process.

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Classification of Polymers

▪ **Synthetic polymers**

- The polymers synthesized from lower molecular weight compounds obtained from petroleum and natural feedstock are synthetic polymers.
- After World War II various advancements in science and technology happen. Synthetic polymers are also one great achievement attributed to 20th century.



Synthetic polymers

Now based on this particular thought process, people thought about the synthetic polymers. Now as the name implicates, that these the polymers synthesized from lower molecular weight compound obtained from either polymer products or a natural feedstock, they are termed as the synthetic polymer. And if you see that these are some of the products available as on date, which are attributed to the synthetic polymers, right.

So, see based on the requirement, based on the things available with you as a raw material, you can develop all those things. Now see World War II, they offer a very good, I mean the people like German, Americans, they just intended themselves towards the development of these product to carry out the requirement of those warriors, those army people etc.

So, after World War II, various advancement in the science and technology happened. Synthetic polymers, they may they got more and more impetus, more and more efficacy in our day-to-day affair. And that is why it is still this development process is going on. If you see, I mean if you are saying 15, 20-year-old or 25-year-old, you will see that there are various kind of development in the polymeric products are going on.


Like from bucket to the tubs, to the even if you see that nowadays we are talking about the personal protective equipments. So everywhere you will find. And now we are just one step ahead. i.e., we are talking about the degradable polymers or depolymerization or biodegradable polymers. So, this particular concept offers a very wide spectrum for the future entrepreneurs as well as the future researchers.

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Classification of Polymers

▪ **Synthetic polymers**

- Since that time, the production of polymers with different physical, chemical, morphological, and structural properties are advancing day by day.
- The reason being the fact that synthetic polymers can be modified according to the application.
- It can be formulated on dry basis, which opens a very broad domain to the application of such polymers.
- It can be formulated on dry basis, which opens a very broad domain to the application of polymers.



Now back to the synthetic polymer. Since that time, we were talking about the World War II, the production of polymers with different physical, chemical, morphological and structural properties are advancing day by day as I discussed, because for almost say 100 years, everyone those who are involved in the system of polymers, they are engaged themselves to develop a new and new protocol which are less energy consuming.

They are energy efficient, eco friendly, etc. So, because see, you cannot change the process of natural polymer, but you are having a various opportunity in the development of a synthetic polymer. So, the reason being for the fact that synthetic polymers can be modified based on the application, based on the requirement, it can be formulated on various dry basis, which opens a very broad domain to the application of various kinds of polymers.

It can be formulated either on a dry basis, it can be offered, it can be formulated on either on the wet basis, etc. So, you are having various routes, you are having a


various developed science and technology process available. So, you can develop a number of polymers with the synthetic polymer routes.

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Classification of Polymers

▪ **Synthetic polymers**

- This enormous growth in the production of synthetic polymers is due to several adherent factors like they are lightweight material, good flexibility, resistance to chemicals and can serve as electric and heat insulators and for fabrication into complex shapes in various colors.
- Polymers cover a wide range of applications ranging from soft packaging materials to fibres that are stronger than steel & allow simple processing.
- Synthetic polymers are basically derived from petroleum oil, which further synthesized to obtain desired products.



There are other factors, which are involved in the development of synthetic polymers that people are demanding the lightweight materials, they are demanding the good flexibility, they are demanding the resistance to chemical or to be more precise the resistance to environment so that they can be used in the packaging material, they can be used for storing the things.

By this way, they are not only supplement to the development of synthetic polymer, but also, they are serving to the other industries, like food industries, like other chemical industries through by providing the barrier to the atmosphere so that their shelf life or lifecycle assessment can be improvised. Even they can serve as electric or heat insulators.

If you see the wires over which there are PVC insulation or insulating materials or different kind of a color coding are there. So, what you require? You require that your product or your whatever things you are using will have more and more shelf life by this way by this approach because ultimately it will be the cost efficient. So, it offers various spectrum on the development protocol of the synthetic polymers.

Now these polymers cover wide range of applications like soft packaging I told you, to the fibrous material stronger than steel and allow the simple process. So basically,

as I told you, that the raw material for these synthetic polymers is petroleum oil, which can be synthesized to obtain in the various desired products.


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Classification of Polymers

▪ **Synthetic polymers**

Examples;

- ✓ Nylon 6, Nylon 6-6 (used in clothing, as conveyer and seat belts, parachutes, nets and ropes, etc.)
- ✓ HDPE and LDPE (used for making hard and soft containers, respectively and have several other uses)
- ✓ Polyesters (used in textile industries)
- ✓ Polyethylene (Master of packaging industries)
- ✓ Resins like Epoxy, Alkyd, Urea-formaldehyde, polyurethane, etc.



I am giving you a brief gist of these synthetic polymers although this list is not you can say the exhaustive. There are n number of product but just to synchronize the things into your mind that there are various examples like nylon 6, nylon 6-6, HDPE, LDPE, LLDPE, polyesters basically used for the textile industries and now we are always intended to have some blended fibers for our textile products like shirts, trousers etc.

Polyethylenes for the packaging industries, resin, epoxy, alkyd resins, urea-formaldehyde, polyurethane. Even you are using those water purifiers in your household applications they offer the various ion exchange resins. The base material for those ion exchange resins are polymeric products. So, you can see there is a wide spectrum of these synthetic polymers.

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Classification of Polymers

▪ Synthetic polymers

Examples;

- ✓ Polytetrafluoroethylene (remember non-sticky utensils in the kitchen, and tough seals used in industries)
- ✓ To understand the difference between natural and synthetic polymers, we can take the example of network polymers. Vulcanized rubber and pectin, both are network polymers.
- ✓ Pectin is a natural polymer which is water based and used as a settling agent in jams and jellies. While, vulcanized rubber is synthetically used to make durable tyres.



Other examples are PTFE. This is remembered as non-sticky utensils etc. You are having the coating to the utensil surfaces. They are usually PTFE coatings. Now to understand difference between the natural and the synthetic polymers, we can always take the example of network polymers, vulcanized rubber. Best example of vulcanized rubber is your automotive tires etc.

So, these are the things various kind of examples attributed to the synthetic polymers.

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Classification of Polymers

2. Based upon the behavior towards the heat

The oldest way to classify the polymers is based on the response towards heat. On this basis, polymers are two type- thermosetting and thermoplastic polymers.

▪ Thermoplastic polymers

Those who melt on heating and solidify on cooling, the heating and cooling cycle can be applied several times without affecting the properties of polymers.



Now sometimes people talk about that okay these are the things like natural polymer and synthetic polymers go away all those things. The oldest way is to classify those polymers was that purely based on their response towards heat. Now on the basis of

polymers, which are having the response towards heat, we can divide these polymers into either thermosetting and thermoplastic one.



Now thermoplastic polymers, those either melt on heating and solidify on cooling and heating and cooling cycle can be replicated to several times without affecting the properties of the polymer, they are clubbed under the head of thermoplastic polymers. Now again this particular approach offers a very good property that you can recycle the polymers.

Because nowadays, these plastic materials or a polymeric material, there are again people are talking about that they are danger to the human system or environmental system. So, if we utilize this particular property, then we can recycle those polymers to several times and if they are not affecting, this recycling approach is not affecting to the property of polymer, it offers a very good flexibility to the system.

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Classification of Polymers

- **Thermoplastic polymers**
 - Thermoplastics are used in the fabrication of many typical applications for plastics such as packaging and automotive parts, textile fibres and coatings.



Now as I told you that these thermoplastic polymers, they offer a wide spectrum towards the heat. Now this particular property can be utilized to develop different type of products, which are listed over here. So, we can fabricate the things many types of a typical applications like tubs, buckets, etc. Even the automotive parts. If you enter into your car and you will see that the dashboard other things, some of the things are manufactured with the help of a thermoplastic polymers.

So, they offer a very wide spectrum towards the product development. Now this particular thing is sometimes can say the disadvantageous because frequent heating and frequent melting sometimes may offer the breakage of the chain in that polymers and by the repeated recycling process, sometimes these polymers may not offer such properties which you are looking for.

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Classification of Polymers

- **Thermoplastic polymers**

Examples;
High-density polyethylene (HDPE), Low-density polyethylene (LDPE), Poly(vinyl chloride) (PVC), Polyethylene Terephthalate (PET), Polypropylene (PP), Polystyrene (PS), Polyamide (PA), Poly(methyl methacrylate) (PMMA) and Styrene copolymers (ABS) etc.

Applications of thermoplastic polymers

- ✓ The main thermoplastics include high-density polyethylene (HDPE) have applications in Industrial wrappings and films, pipes, Containers, toys and housewares.



So, by this way, we can have other examples of these thermoplastic polymers like HDPE, LDPE, polyvinyl chloride, polyethylene terephthalate, polypropylene, polystyrene etc. So, they offer a wide spectrum and we can have a different type of applications, which we will discuss in this particular lecture as well as in the subsequent lecture. Like these HDPE they are having the application in industrial wrapping, film, pipe, containers, toys, house wares etc.

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So, by this way, we will continue this particular classification in the subsequent lecture and we will discuss about the various application and nitty gritty of these thermoplastic polymers as well as the thermoset polymers and we will continue the classification scheme in the next lecture. Thank you very much.