# Principles of Polymer Synthesis

**Prof. Rajat K Das**
**Material Science Centre**
**Indian Institute of Technology, Kharagpur**

## Lecture - 33
## Synthesis of Industrial Polymers (Contd.)

Welcome back. In the last class, we have started talking about the synthesis of different industrial polymers. The first polymer that we are talking about is polyethylene terephthalate and we are still in the midst of discussing different synthetic routes. So, just for a quick recap, I actually have the script from the previous class.

So, basically, you have the polyethylene terephthalate, this is the structure of polyethylene terephthalate.

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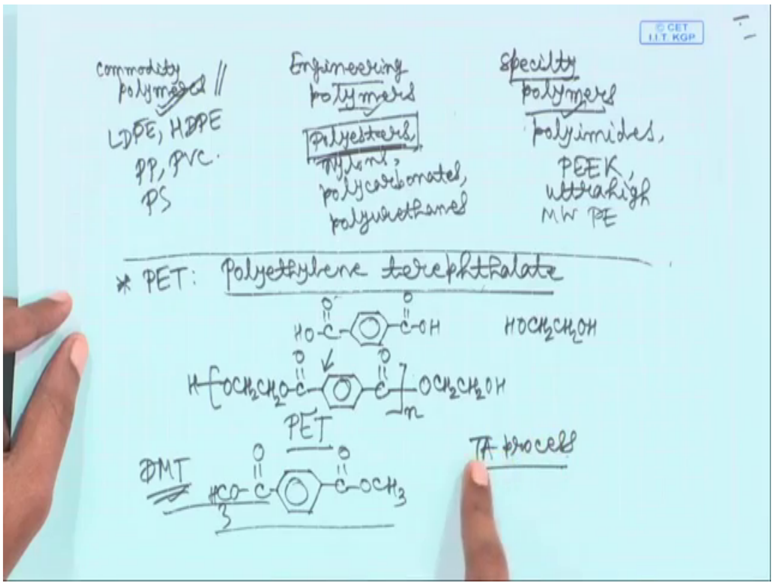

And there are two processes which you can use to synthesize this polyethylene terephthalate. One is DMT process that is dimethyl dimethyl terephthalate process. So, this is your dimethyl terephthalate. It is a starting material; another is TA process which is your terepthallic acid process.

So, we have discussed the dimethyl terephthalate route in the last class.

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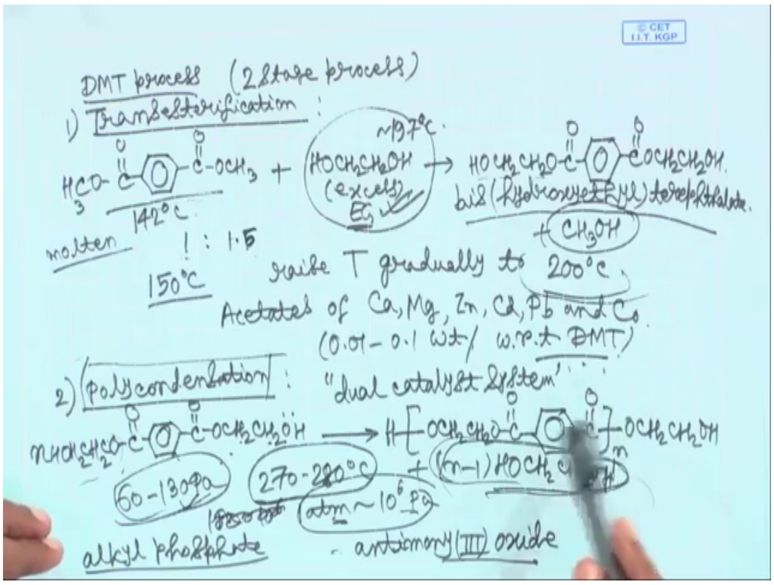

So, basically it is a two-stage process. The first stage is trans-esterification of dimethyl terephthalate with excess of ethylene glycol and typically what you get is BHET bis hydroxymethyl terephthalate. If you are using 1 is to 2 in this ratio, 1ne DMT and 2 EG ethylene glycol, then what you will get is exclusively this product and if you are using less amount of this; that means, less than 1 is to 2, maybe 1 is to 1.5.

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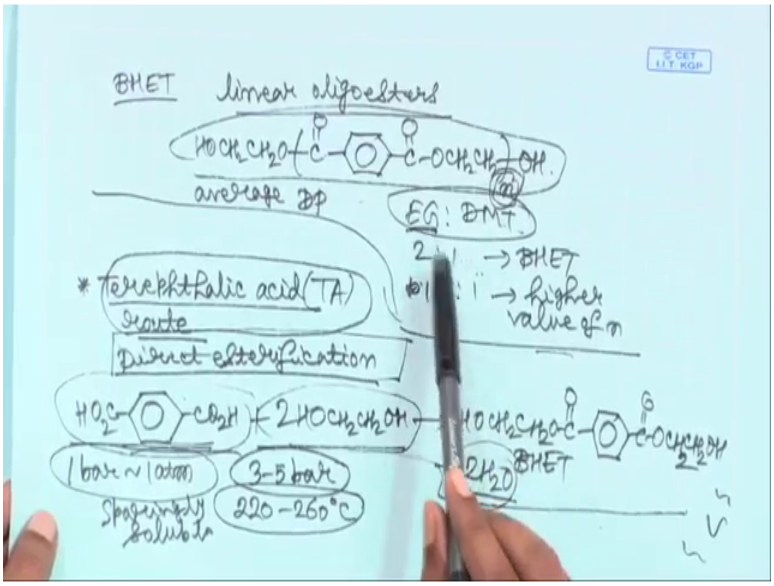

Or so, then you may get some oligomeric materials also or oligomers, like this oligomeric materials where n will have some value and depending on this ratio if the ratio is one is to two in that case you will get only BHET and if the ratio is less than that 1 is to 1.8; 1.5, the lesser it becomes, the higher the value of n becomes and then in a second step what you do is this BHET or the pre polymer the oligoester that I have shown.

So, it is a mixture of these two the reaction mixture. So, you do a poly condensation reaction by heating it up further and reducing the pressure; that means, applying some vacuum the catalysts used in the first step, they are not used for the second step you use alkyl phosphate to destroy that catalyst because the presence of that catalyst will reduce the thermal stability of your product PET and you add antimony oxide as a fresh catalytic system fresh catalyst for the poly condensation reaction.

That is why it is called dual catalyst system that you are employing. Now towards the end of the last class, what we started talking about is the other process of synthesis of teric PET polyethylene terephthalate. So, the other process is through terephthalic acid route.

So, this is your terephthalic acid and you do a direct esterification unlike your trans-esterification reaction that you did in DMT process, what you are doing here is a direct esterification of your terephthalic acid with ethylene glycol in glycol to increase its solubility the reaction at high pressure and high temperature up to this point we had discussed in the previous class.

So, now we will continue to have a more detailed understanding of this particular process.

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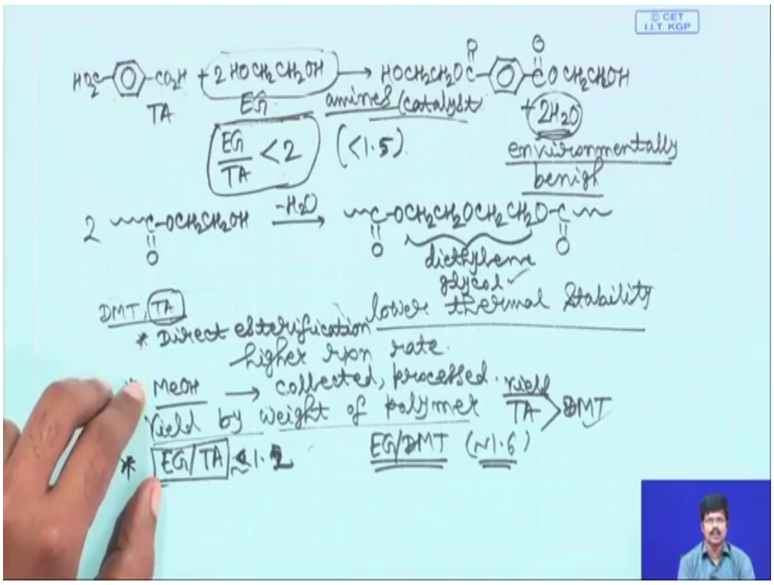

So, let me draw the scheme of the process once more. So, you have the terephthalic acid reaction with ethylene glycol. So, 2 molecules of that if it reacts, then you get your BHET, this is BHET and 2 molecules of water.

So, this water has to be continuously distilled off and the molar ratio. So, this is ethylene glycol and this is terephthalic acid. So, this molar ratio of ethylene glycol to terephthalic acid is basically less than 2, you are using it is the same thing that you are doing as you have done for the trans-esterification step in the DMT process and in most of the patents a ratio of less than 1.5 is specified.

Now, apart from the preparation of some of these oligoester species as you can see that if the ratio is less than 1 to 2, some of these oligoester species will be produced to the pre polymer, there are other reasons also, why you would like to have this ratio less than 2 and that is to suppress the following reaction I mean say you have an oligomer at the end of which you have this CH2; CH2OH, I mean the same reaction you can also envisage for two molecules of ethylene glycol.

So, I am just doing a general way here. So, two molecules of such entity they cannot react and one water molecule can be removed and the product that you will get is something like this OCH2 CH2 OCH2 CH2O because another molecule will have another OH CH2 CH2O unit on this side and that will have a condensation reaction with a water molecule being eliminated and then this is the product.

So, basically you will have a diethylene glycol unit dye ethylene glycol unit so. In fact, your two molecules of ethylene glycol can also react with themselves to produce a di ethylene glycol or some of these oligomers can have also this linkage diethylene glycol produced now this diethylene glycol that is produced this eventually leads to a lower thermal stability of the polymer finally, when you get the polymer this will be still present and this will lead to a lower thermal stability of the polymer.

So, in order to suppress the preparation of this kind of diethelene glycol units what you need to do is to have the ratio of ethylene glycol to terephthalic acid less than 2 because you do not have excess of ethylene glycol then ethylene glycol cannot react with itself to produce diethylene glycol.

So, as I told, I mean instead of this you can have just two molecules of ethylene glycol also and that will produce diethylene glycol. So, you want to suppress that reaction. Now the direct esterification, this reaction is possible without using catalysts, but if you use say some basic catalysts say some amines then this reaction can be accelerated.

So, this is a catalyst you can use or you could use some trans-esterification catalysts also, now what you do is that again once the esterification is done you have to distill off this ethylene glycol. So, and this reaction is done under high pressure of course, because this is not soluble very well in ethylene glycol.

So, what you do after the reaction, you reduce the pressure slowly I mean you release the pressure slowly; that means, it will come back to atmospheric pressure slowly and the temperature will be simultaneously increased and what will happen is that the excess ethylene glycol has to be distilled off and the second step is your poly condensation reaction of this molecule along with its oligoesters and that is exactly the same process as has been described for the dimethyl terephthalate route.

So, that process I am not going to discuss here just the first step is different when you are considering the dimethyl terephthalate process and the terephthalic acid process, the first step is different for DMT process the first step is a trans-esterification reaction using dimethyl terephthalate and for terephthalic acid process. The first step is a direct esterification reaction and of course, here for the first step you need high pressure and high temperature.

Now, if you want to compare between these two processes your DMT process and ta terephthalic acid process actually the terephthalic acid process has more advantages, but as I mentioned that previously since the economic process of synthesizing pure terephthalic acid was not developed, people used to do DMT process only because you have to see if it is economic also the process because you are synthesizing industrially. So, the starting material has to be available with a less cost as much less cost as possible.

Now, the advantages of terephthalic acid route or DMT route are multifold. So, one of the advantages is that the direct esterification route the direct esterification the first step direct esterification, this has higher reaction rate higher reaction rate than your trans-esterification that is done in the first step of DMT process.

Now, the second thing is that when you are doing a DMT process remember this is the DMT process trans-esterification reaction methanol is produced. Now, this methanol is poisonous and it has to be this methanol that is produced it is poisonous and it has to be collected and it has to be processed, I mean when you are doing an industrial synthesis, you want to look at the economy of the situation.

So, whatever byproducts are they are if possible you will collect them and you can process them and you can reuse them for other purposes so on and so forth. So, this methanol has to be anyway collected and it has to be processed and it is also poisonous, but if you compare these with a direct esterifications route, there water is produced this water is environmentally Benigh means; it is basically environment friendly.

So, this makes the DMT route more expensive than your terephthallic acid route because of because you have to process the byproduct methanol and here you do not need to do anything about this water. So, that makes the DMT route more expensive one more thing the yield by weight of polymer, if you just look at the yield by weight of polymers with respect to the monomer that yield is basically higher forty a route for the terephthalic acid route, the yield is higher than for the DMT route why because the terephthalic acid has a lower molecular weight compared to the dimethyle terephthalate.

So, when you are looking at the yield your yield value weight of the polymer is higher for terephthalic acid route, then for your dimethyl terephthalate route that is self explanatory because here the starting material had higher molecular weight. Here the starting material has lower molecular weight and you are actually aiming for the same molecular weight of polymer.

So, the yield is higher for the terephthalic acid route, next if you are looking at the ratio of ethylene glycol to terephthallic acid remember that the first step is ethalene glycol to terephthalic acid this ratio is less than 1.5, this this ratio is less than 1.5. In fact, it is close to 1.2, it is close to 1.2; around 1.2.

So, this is the terephthalic acid route because you are using terephthalic acid, if you compare that with your DMT process, in the DMT process your ethylene glycol to dimethyl terephthalate that ratio is around 1.6. So, that ratio is higher. So, this would mean that after the first step lower amount of ethylene glycol has to be removed before you go to the second step if you compare the terephthalic acid route with the dimethyle terephthalate route for the terephthalic acid route since this ratio is lower.

So, there is less amount of unreacted ethylene glycol present for the first step and of course, before you go for the second step poly condensation reaction, you have to remove whatever ethylene glycol did not react.

So, you have to move less amount of ethylene glycol in the case of terephthalic acid route, then in the case of dimethyl terephthalate route to achieve the same molecular rate of the polymer and also you do not need any trans-esterification catalyst to do this particular reaction, I mean of course, you can use some catalysts, but without catalyst also it will it will work because you have carboxylic acid present and the carboxylic acid can do a self catalysis, it can self catalyze the reaction.

So, you may not want to use catalyst also I mean if you want to reduce the expense. So, that. So, these are the advantages of the terephthalic acid route over the DMT process.

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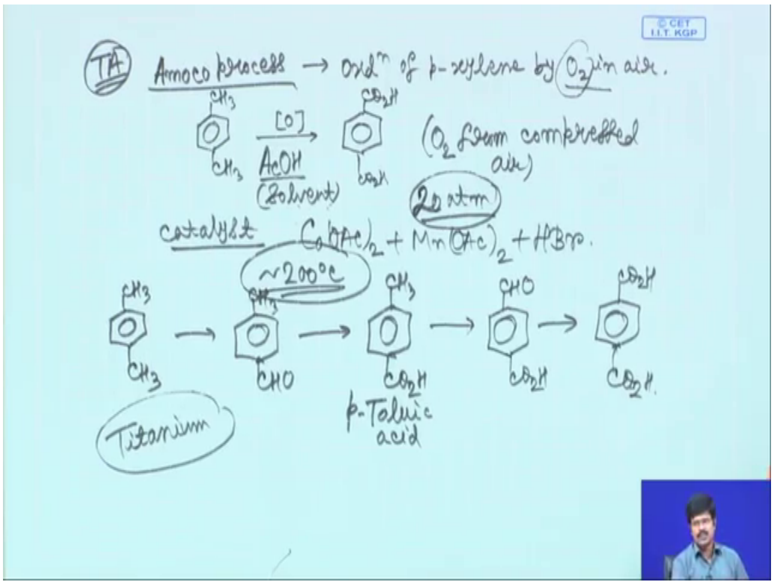

Now, what I thought will be also more useful is to tell you how the terephthalic acid, the starting material is prepared for this to affect this particular process of preparation of pet.

So, one of the main synthetic routes to terephthalic acid amoco process amoco process; so, this is basically oxidation of para xylene by oxygen in air. So, the main process is you start with para xylene and you do an oxidation and you will get your terephthalic acid your product. Now this particular reaction that I have shown here, this reaction is carried out in acetic acid in acetic acid acetic acid is a solvent here acetic acid is a solvent and of course, you are using oxygen for the oxidation.

Now, this oxygen from compressed air is used as oxidant; that means, the reaction is done under high pressure. So, the reaction is done actually at twenty atmosphere pressure. So, what you do for this reaction you use a catalyst system you use a catalyst system which is composed of the acetate of cobalt the acetate of manganese and hydrobromic acid.

So, what you do is you take your para xylene, you take your acetic acid para xylene acetic acid, you take the catalyst system and along with the compressed air you feed into the reactor, I mean along with the air you feed into the reactor and you apply 20 atmosphere pressure and the temperature is quite high, it is around 200 degree Celsius high temperature high pressure reaction and the reaction proceeds through an intermediate which is para taluic acid.

So, you start with your para xylene. So, the oxidation is basically sequential. So, in the first step you produce an aldehyde here and the CH3 is there. Now in the second step you have these molecules CH3, CO2H. So, this is the intermediate through which the reaction passes. So, para taluic acid and after this again sequentially the top methyl group will be oxidized.

So, CHO, CO2H and finally, it will be oxidized to terephthalic acid now and highly pure terephthalic acid can be obtained from crystallization and this reaction is done in a reactor which has a material, I mean which is made of titanium titanium reactors and these are very expensive reactors. The reason why you are using titanium is that you are doing the reaction at high temperature 2 degree Celsius and at this temperature, you have acetic acid as the solvent and this mixture as the catalyst the mixture of hydrochloric acid and acetic acid at this high temperature is highly corrosive.

So, that it can corrode your reactor wall also that is why you are using titanium to prevent that problem and that is why that process I mean the reactor is also the reactor is expensive ok. So, that completes our discussion of the preparation of polyethylene terephthalate. So, both the processes DMT process as well as the TA process terephthalic acid route both the processes we have discussed and we have also discussed the advantages of the terephthalic acid process and finally, we have talked about how the terephthalic acid itself is prepared from the raw material.

Now, we will still continue to talk about polyesters, but let us take a homolog of polyethylene terephthalate to understand the structure property relationship a little better let us talk about polybutylene terephthalate.

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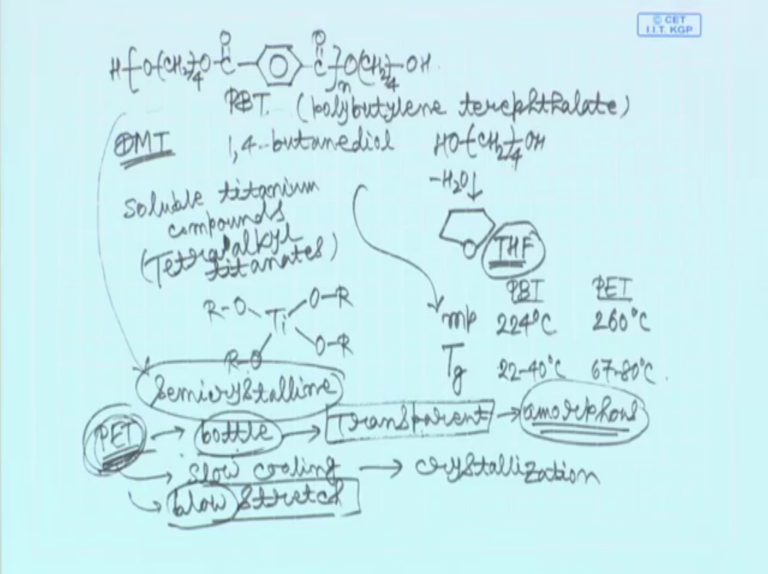

So, if you go to polybutylene terephthalate polybutylene terephthalate is this is your polybutylene terephthalate the preparation is. So, PBT poly butylene poly butylene terephthalate preparation is analogous to your PET and the currently preferred process for this is the DMT route dimethyl terephthalate route and basically instead of your ethylene glycol what you are using is 14 butanediol.

So, basically this is the alcohol that you are using you can understand from the structure. So, instead of CH2 whole two ethylene glycol you are using one for butanediol for the position of this compound and one of the main; the main byproduct of this particular reaction is tetrahydrofuran because this can actually cyclize by dehydration and it can produce tetra hydro furan and one more thing I need to mention that the second stage is poly condensation for the for the preparation of either PBT or PET.

So, the second stage basically you use catalysts they are typically soluble titanium compounds because if you remember for poly condensation we use catalysts we used antimony oxide for PET for PBT we use soluble titanium compounds I mean generally they are tetra tetra alkyl titanates.

So, they are of this kind of formula tetra alkyl titanates ok. Now, if you are looking at the structure of PBT viz a viz PET let us say, let us let us take a closer look. So, this is your PBT polybutylene terephthalate if you look at the PET polyethylene terephthalate instead of four CH2 units you have 2 CH2 units.

Now, the; so, if you look at PBT you have longer sequence of CH2 groups in the repeating unit you have two CH2 units more in the repeating unit. So, that gives a flexibility to this chain now remember this aromatic unit gives stiffness to the material because this aromatic unit is rigid it is on the plane of the paper let us say it is on the plane of the paper. So, more of the content of aromatic unit will indicate more stiffness.

Now, if you are looking at the PET versus PBT. So, PBT has more flexibility because of these extra CH2 units that are present and of course, PBT is also less polar because of this presence of extra CH2 units. Now all these things combined to make sure that the melting point and the glass transition temperature of PBT, they are basically lower than PET. So, PBT melting point is around 224 degree Celsius whereas, the melting point of PET is around 260 degree Celsius.

If you look at the glass transition temperature the temperature above which the chains become mobile the glass transition temperature is roundabout say 20, 22 to 40 degree Celsius. There is a range for PBT and for PET, it is around 67 to 80 degree Celsius and I mean this kind of thing happens because you know these chains are more flexible. So, if the chains are more flexible then you know they do not I mean and also they are less polar.

So, the interactions if you are looking at if they are less polar, then they will basically melt at a lower temperature, then a more polar component because they will have more interactions between the chains that way and also correspondingly your glass transition temperature will be lower because the interactions are less in a way that the polarity is less in the system and they are more flexible.

So, at a lower temperature I mean when you are heating the system up from below glass transition temperature at a lower temperature it will start to become mobile the chains will become mobile that is why the Tg is lower for PBT than PET.

Now, something more that I want to mention here is that lets say if you if you look at the crystallization capacity of PBT versus PET, what you will get. So, when you are processing the PBT almost always for polybutylene terephthalate you will get a semi crystalline material semi crystalline means this material is not perfectly crystalline some part is crystalline some part is amorphous, but some part the chains are quite nicely organized.

So, it is actually difficult under normal processing conditions to get polybutylene terephthalate which is completely amorphous they will always be semi crystalline and this is because of the fact that your chains are flexible here. So, they have a better chance to organize when you are cooling them from a higher temperature because when you are forming crystals basically from higher temperature you are cooling them down and then the crystalline zones will appear means the chains organized in certain zones that will appear. So, you will have a crystal unity in the system.

So, that kind of organization is possible in this system because of the flexibility of the chain now what happens because this is a perfect balance of the rigidity from the aromatic unit as well as the flexibility from this alkyl chain what happens with PET; PET also will crystallize, but the condition is that if you cool it down in a normal way or maybe if you cool it down faster then it will not crystallize it will form amorphous material.

In order to capture the crystallization of polyethylene terephthalate you have to cool it down slowly and also you have to maintain a high temperature in order for it to crystallize because of the reason that your chains are less flexible. So, they do not tend to organize that easily and form the zones of the crystal.

So, that is why you will almost always get PBT in a semi crystalline form actually the polybutylene terephthalate crystallizes faster than polyethylene terephthalate under normal processing condition and it is difficult to obtain amorphous form of PBT and PET depending on the processing condition you can obtain amorphous form or you can obtain semi crystalline form.

Now, keep in mind something that when you are looking for materials in which you will use say PET, you want to use PET in a crystalline form or you want to use PBT in a crystalline form the crystalline PET will always have a better property than crystalline PBT if you can crystallize the PET in the proper way it will have better property than the crystalline PBT that is because of the fact that the PET has more stiffness in the chain.

So, you will have higher stiffness and higher tensile strength of the crystalline material if you are comparing because you have to always compare apples with apples and oranges with oranges do not compare apples with oranges. So, when you are looking at the utility of your material you should compare them semi crystalline PBT with semi crystalline PET.

So, if you look at that if you have been able to make both semi crystalline of course, PBT is much easier to form semi crystalline we will talk about that little bit more after. So, both of them if you are looking at both are semi crystalline then PET will have better property in terms of say strength of the material in terms of stiffness of the material and in terms of thermal stability of the material of course, because the material properties are typically maintained right up to your Tg.

When you are heating the material up, once it is beyond Tg the material starts to become more malleable more processable. So, on and. So, forth the rigidity is lost. So, the mechanical properties also tend to get lost. So, if the Tg is higher that way, you can get a better a higher thermal range in which your properties are maintained. Once you have formed the crystals and also the crystallized material will have more stiffness and more tensile strength because of the reason that it has more stiffness due to the aromatic ring there is there is the distance between the subsequent aromatic rings is less is connected by 2 CH2 you have only two alkyl unit CH2 units rather than in PBT many of four CH2 units.

So, now this PET polyethylene terephthalate, this is very widely used in packaging industry as well as say in making bottles that contain water or soft drink. Now typically you will see that these bottles are quite transparent in this context, I should mention that transparency of the material is typically correlated with the amorphous nature of the material.

So, when you are preparing bottle from PET if you somehow get crystallization in PET then you will not get transparent material I mean depending on the applications you either want crystaline material or you want amorphous material when you are preparing bottles or that kind of stuff maybe. So, those materials you are not preparing to withstand say very high temperature; however, you want those materials to be tough and high input high impact resistance.

So, in that case, you would better look for an amorphous PET material because if PET starts to become crystallized then what will happen is that the material will gain strength, but it will have reduced toughness.

So, when you are plotting your stress versus strain curve suppose you are plotting on the y axis stress and the x axis strain and that graph that you are having if it is an elastic material then you have a linear graph now that if the slope is higher the higher the slope the higher is the stiffness you if you remember the slope is basically your Young's modulus.

So, higher the slope higher is the stiffness, but that does not mean that this curve will go on and on and on as you increase the strain it may just abruptly stop somewhere like this here because maybe the material is quite stiff, but the material is brittle. So, in that case the material will not go into higher strain regime it will somewhere break here.

So, the curve stress strain curve will stop abruptly here if the material is tougher then they basically can go further and further and further because it is the area under the stress strain curve that determines how tough the material is; that means, how much of energy it can absorb before it actually breaks or fails that is different from the stiffness because stiffness is about the initial slope of the stress strain curve that you have to keep in mind.

So, PET bottle. So, what happens is that if you do a slow cooling of PET slow cooling of PET then that will lead to crystallization if you do typically fast cooling you will have a more amorphous material. Now, what you normally do for the bottle preparation from PET is you blow and as well as stretch the material.

So, basically it is both blowing as well as stretching of the material. So, it is a blow molding blow and stretch molding. So, what you do here is the following you take your PET in the amorphous form and you heat it up beyond Tg. So, it will start to become malleable and when it starts to become malleable you take it in that range and then you start to blow into it and you start to stretch it. So, that so, basically there is something called a preform that you have prepared in the amorphous condition preform. So, you have a preform.

Now, when you are trying to prepare a bottle from this perform, the preform is a small thing when you are trying to prepare a bottle from this preform what you do is that you start to heat it up in you heat it up beyond your glass transition temperature and then at that temperature it can be molded now because it has now become more malleable it is not no longer rigid.

So, now what you do you start to stretch it as well as blow air into it. So, that it will start to become bigger inside as well as the length wise it will increase and when you are stretching it the walls will become thinner and the polymer chains will become more oriented which gives you the better material property and when you are doing all these things, you do not want crystallization to happen, but your question might be when I am heating why crystallization will happen I will come to that after.

You do not want crystallization to happen you want a material to remain amorphous because if crystallization happens your material will start to become cloudy because crystallization is associated with cloudiness and once the material starts to become cloudy under that blow and stretching condition the material becomes also brittle and it may actually shatter.

So, while making the bottle you do not want crystallization to set in you want perfectly completely amorphous material we will talk more about it in the next class we will continue to talk about it our time is up for the day. So, till then.

Thank you and see you in the next class.