Principles of Polymer Synthesis
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Lecture - 34
Synthesis of Industrial Polymers (Contd.)

Welcome back to the class again. We have been discussing the synthesis of industrial polymers since the last two classes and the topic remains the same for this class. So, where we left in the last class was the discussion on the process ability of polyethylene terephthalate and polybutylene terephthalate and we told that because of the structure, the I mean the structure that we have whether we have 2 CH2 units or 4 CH2 units that actually influences the ability of the material to crystallize from its melt and we told that the PBT is more prone to distillation than PET.

PBT is typically very difficult to obtain in amorphous form, but PET polyethylene terephthalate, if you cool it down in a normal way our fast way, it will form only amorphous material, you have to cool it down quite slowly, in order to get to the crystalline material; however, if you are comparing the semi crystalline form of PET with PBT and if you are planning to use one of them for an application.

Then the PET will have a better property in terms of its stiffness in terms of its tensile strength because the material is stiff by itself and lastly we were talking about this PET bottle preparation if the blow stretch molding process that we were talking about and we told that we typically choose a range, we choose a temperature which is higher than glass transition temperature and this is a temperature where you can actually blow the material, we can stretch the material we can change the shape of the material.

So, you basically have a preform. So, let us go back let us start right from there where we left in the in the in the previous class.

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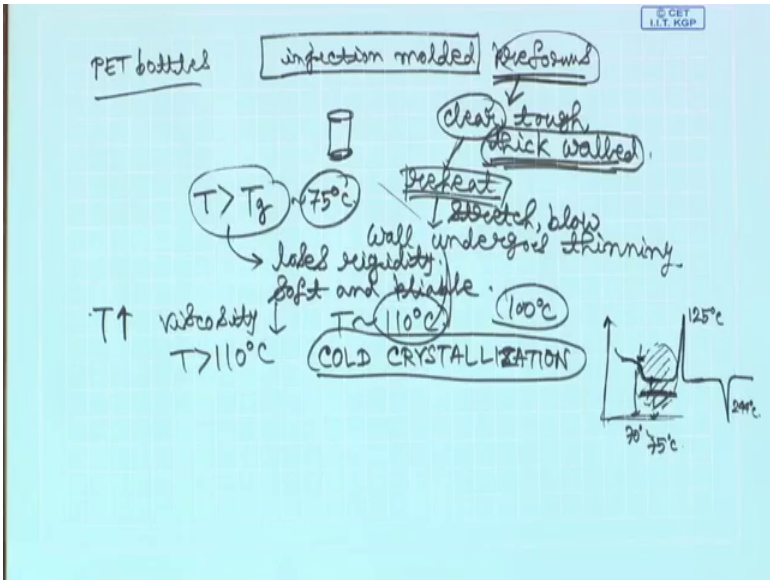

So, basically when you are creating the PET bottles how do you do that? So, first you start with what you call I will come to this process after injection molded preforms you start with. So, injection molding is a process through which you can prepare different kinds of shapes of the material. So, you start with what you call as a preform a small structure.

Now, this preform this preform is typically clear and it is tough and it is thick walled it could be something like this small preform and its thick walled because ultimately you are going to stretch it and the wall is going to become thin. So, in order to allow for that you start with thick walled reform and it is a clear material it does not have any crystalline in the crystalline zone in it.

So, what you do is that you reheat this material you reheat this material and then you stretch also along with that you stretch and blow air into the material. So, what happens is that the wall undergoes thinning and your temperature is basically higher than your Tg the temperature in which you are heating it.

So, Tg is approximately as I told it is a range approximately 75 degrees. So, what you do you go to T greater than Tg. So, at this temperature your material will lose loses the material who loses rigidity and it becomes soft and pliable now as T goes up, temperature goes up the viscosity of the material will go down until it reaches about 110 degree Celsius.

So, between 75 and 110, this is the range typically you will do the reheating step at around 100 degree Celsius, it do not want to go beyond 110, I will come to that. So, around this temperature you are going to have the opportunity to blow the bottle that that is made of PET and it will be amorphous it will be clear material and it will be tough material it will not have any crystallinity.

So, this material we cannot withstand very high temperature and it is not made to with stand high temperature, it is made to withstand impact resistance which is correlating with the toughness of a material how much energy, it can absorb before it breaks which is different from how much its thermal stability is that you have to keep in mind.

So, what happens if you go beyond 110 degrees, you will have crystallization occurring in the material surprise this is called cold crystallization. So, basically what is happening is that when you are heating beyond Tg your chains. Now, start to move around they now have so, if you keep heating beyond a certain temperature they become mobile enough. So, that they have a chance to organize together. So, that is why when you heat the material up it can also from crystals this kind of situation this kind of distillation phenomenon is called cold crystallization and this is something that you can observe for polyethylene terephthalate.

Now, you are doing the blow molding at 110 degrees say or hundred degree if you go higher than 110-115 what is the problem the problem is that at this higher temperature the chains will start to organize and crystallinity will start to appear. Once the crystalinity starts to appear the material will start to become opaque because as I told transparency relates to the amorphous nature of the material the more opaque it becomes it means actually the crystalinity has started to set in has started to get into the picture.

So, this is called cold crystalization because you are doing actually you are doing the process the opposite way typically, you get crystallization by cooling from the melt from a higher temperature, but here you are getting the crystallization by heating the material around 140 degree Celsius, you will have sufficient crystalinity and the problem is when you get beyond 110 or whatever you have this cloudiness developing and you are still stretching the material and still you are blowing air into it.

So, once the cloudiness develops once the material starts to gain crystallinity, it will start to also become brittle and so there is a chance that it may shatter and the bottle may break before, it has formed. So, it is very important to recognize that there is a region of operation beyond which you cannot operate. So, if you are looking at the differential scanning calorimetry curve, I mean I will just draw it is not according to scale you know on the y axis you have the heat change x axis temperature.

Now, you are heating it up so, around 70 degree. So, maybe this point is around 70 degree and this point is around 75 degree you have a trough like that. So, this change is basically because of the Tg and even though the average of these 2 temperatures maybe this is 70 degrees again approximately, I am saying just to tell you the concept the bottom of the trough is around 75 degrees and then it will go like this and it will show a peak like this an exothermic around 125 degree Celsius.

So, this is where the crystallization occurs and then if you heat it up further and further and further around 244 degree Celsius, it will melt it will melt. So, it is this range in which it is this range in which you can do the bottle preparation that is very important to keep in mind.

Now, what happens if you are so, now, I hope you understand this thing that when you are blowing the bottles from PET, why you have to work in this particular range and what is cold crystallization and as you have seen as I have told already that if you are looking at semi crystalline PET versus PBT, then basically you have a better property for PET polyethylene terephthalate.

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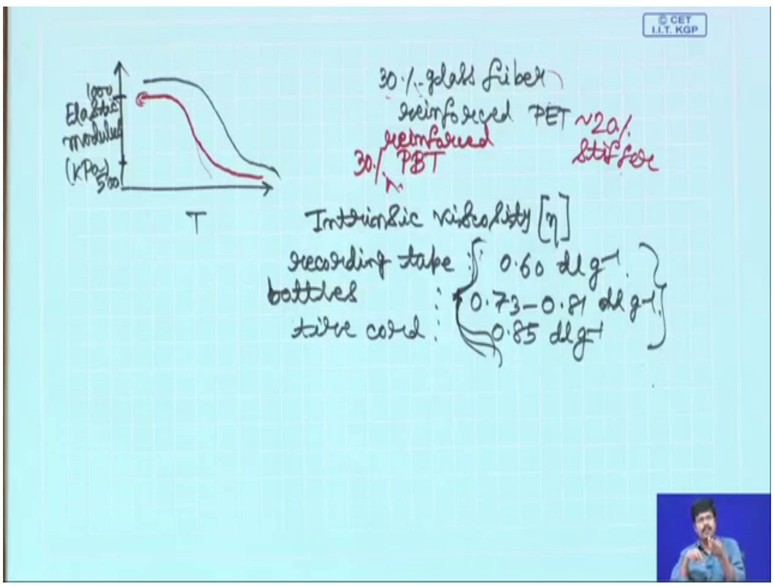

So, some experimental data are there say for example, if you are plotting say elastic modulus on the y axis I think it is in kilopascal that range and x axis is temperature and let us say we are working with thirty percent glass fiber reinforced PET which is in black and thirty percent glass fiber reinforced PBT which is in red you are reinforcing with glass fiber. So, you are increasing the material these are composite materials.

So, either you have thirty percent glass fiber reinforced PET or thirty percent reinforced PBT; that means, the 30 percent of the material is glass fiber rest is PET like that that now if you compare how the elastic modulus or the stiffness of these materials vary with temperature typically, what you will see is that it is something like this say, here you have 500 here you have again this is not exactly to scale here you have 1000. Now, this is for PE PET and of course, you see that right around Tg, this is somewhere around Tg, the property start to become poorer the material starts to become softer. So, your elastic modulus or the stiffness goes down.

Now, if you look at the thirty percent glass reinforced PBT it has lower stiffness. So, all through the temperature range, it has a it does not have as good material property as the as the PBT as the PET, you see the black is for PET and radius for the PBT 30 percent reinforced even the initial elastic modulus is lower and actually the polyethylene terephthalate 30 percent glass fiber reinforced polyethylene terephthalate is around 20 percent stiffer than 30 percent glass fiber reinforced PBT.

So, this material is around twenty percent stiffer than this material and it is all through this temperature range until they melt if that is the case and of course, the PBT starts to lose stiffness earlier at least 20-30 degree Celsius earlier because the Tg is lower for pbt. So, the temperature range over which the material property is maintained is also lower.

So, those things you need to keep in mind because the Tg of polyethylene terephthalate is around 30-40 degree Celsius higher. So, of course, the material property will be maintained up to that higher temperature ok, now and of course, if you have higher Tg, then you have improved mechanical performance over a over broad temperature range.

Now, something that you need to keep in mind is that if you indeed want to get crystallization in PET polyethylene terephthalate PBT it is not a problem you can get crystallization it is prone to crystalize, but polyethylene terephthalate, if you want to crystallize, what you have to do is that typically when you are making this crystallization you will add some nucleating agent in order to accelerate or facilitate the crystallization, it could be say magnesium oxide it could be clay from 0.00121 percent with respect to I mean the presence of PET that you have to add nucleating agent and more often than not you will also add some filler.

So, basically semi crystalline PET materials that you will have typically they are with filler, but PBT materials polybutylene terephthalate materials they are not there with fillers or without fillers, but for polyethylene terephthalate when you are trying to crystallize, you need this additional help you are using nucleating agent no doubt you can add also filler and when you are doing an injection molding, again I am going to come to injection molding right after this.

So, when you are doing the injection molding. So, there is a temperature of the mould at which you want your material to be there. Now, this temperature of the mold if you want a crystalline or semi crystalline part that is coming out of it a part a part a part of the machine, for example, that you want to fix that is made of PET maybe semi crystalline.

So, it has the shape of the mold now if you want to make a semi crystalline material typically the mold temperature at which the PET is coming that mold temperature has to be kept quite high around say 140 degree Celsius or so, because you want to have you want to cool down the polyethylene terephthalate from is from its melt state, you want to cool it down slowly, if you cool it down any faster, it will not crystallize, it will go to the amorphous state if you want to crystallize, it you better keep it at higher temperature and allow it to cool slowly.

That is why the mold in which you put it for the injection molding it has to be kept at higher temperature typically around 140-150 degree Celsius, you have to keep at higher temperature otherwise you cannot get the crystals, but PBT, you can keep at much lower temperature you can still get crystals.

So, these are some of the problems of course, for melt because if you are taking a mold which is say at room temperature and you have a molten PET coming and then going into the mold and cool down suddenly and takes the shape of the mold then you can take out the material which has the shape of the mold it cools down suddenly; that means, it does not have crystallinity you have to generate crystallinity because your objective is to get crystals say. So, then again you have to heat it up. So, system may not be homogeneous.

So, those kinds of problems will occur. So, you have to keep some of these things in mind. So, that is why many applications of polybutylene terephthalate, they are from processing by injection molding and extrusion say housings for heated domestic appliances. For example, coffee making machines, toasters, hairdryers, then plug boards, lamp sockets, those kind of things are made from polybutylene terephthalate bottles packaging these kind of things are made from polyethylene terephthalate ok.

So, that more or less completes our discussion on polyethylene terephthalate or polybutylene terephthalate, I hope you have got a flavor of the how the structural changes can affect the properties, if your thermal stabilities if your Tg is higher the glass transition temperature is higher one way it is good because you can maintain your mechanical property up to that temperature just like your PET polyethylene terephthalate it has a higher glass transitional temperature around 80 degrees.

So, up to 80 degrees; its stiffness can be maintained once you have got the crystalline material, but on the flip side if your Tg is higher typically you need to cool down material slowly in this case say for example, that you are looking at PET Tg is higher because of the material is stiff because the material is stiffer materials have higher Tg because they take more temperature in order to go to a more flexible regime.

So, the Tg the glass transition temperature is higher. So, for those kind of kinds of materials the crystallization also happens when you cool down slower and when you keep it at higher temperature. So, this is also a flip side; that means, your mold or the injection molding that mold temperature has to be kept at higher temperature.

So, that completes our discussion of PET and PBT for the study materials of course, I will add some notes and I will put some more applications along with that applications are just lists of applications that you can look at, but the principle ones you understand you will see and for example, depending on the viscosity different viscosities of PET might be used might be required for different kinds of applications and then you want to stop your reaction at that kind of particular melt viscosity.

So, those things are all I mean say for example, if you are looking for say for different applications of PET, let us say the intrinsic viscosity eta for different applications say for recording tape also they are used recording tape PET is used. So, the intrinsic viscosity that you want is 0.60 deciliter per gram for carbonated drink bottles, you want something like 0.73; 2.81; deciliter per gram for industrial tire cord you want higher around 0.85 deciliter per gram and of course, accordingly you will modify modulate your synthesis because the melt viscosity, you know is something that correlates with the power of the stirrer.

I mean the power that you are giving to the stirrer it correlates with that. So, accordingly you can stop your reaction and depending on what kind of usage you want you can modulate your process.

So, now what I will do since I have talked about injection molding I will give you a brief overview of injection molding this is little bit of deviation from what we are talking about synthetic processes, but this will always be the theme of these kind of courses, that that I am taking because it is like you know you have a holistic view before that we have to deviate a little bit. So, be it, but still it is part of synthesis is part of processing and all.

So, the topic and the theme they basically run along the same line ok, so, we will have a short and kind of dense discussion on injection molding process all right.

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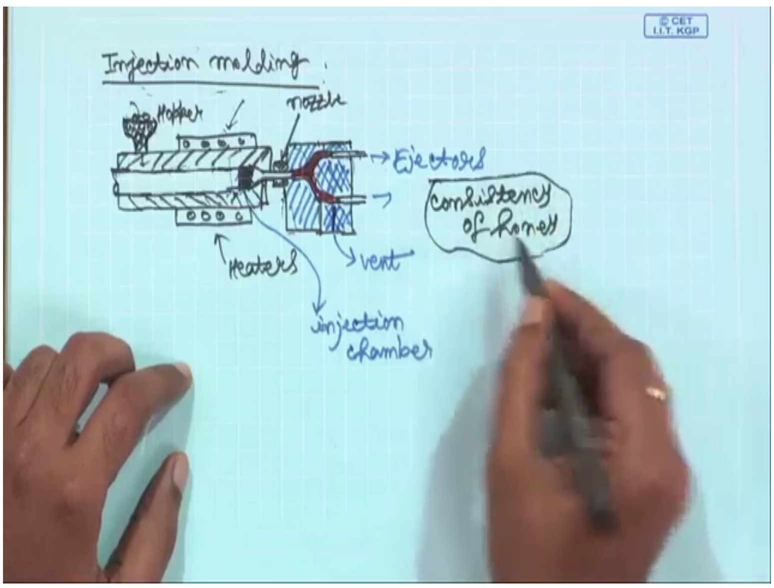

So, injection molding; so, basically what you do is that you inject your material you can say you inject your material into some kind of mold and then the material takes the shape of that mold. So, that is all this is over all your injection molding process.

So, I am going to draw a simple diagram for you. So, basically what you have is a chamber or a cylindrical or a barrel you have a barrel and into this barrel you put your pellets of polymer that has to be processed. So, you have these pellets of polymer are there and those pellets are put into what you call as a hopper. So, this is the hopper through this hopper these pellets pass into the barrel they will go into the barrel.

Now, in the barrel you have a piston all right you have a piston in the barrel that can push your pellets forward into what you call as an injection chamber. So, this is your injection chamber. So, this piston can actually move and it can push your material into this injection chamber and this injection chamber with the help of a what you call as a nozzle this is directly connected to your mold.

So, basically you have say something like this let me draw this full thing up and then I am going to explain to you in more detail. So, what you have here is a barrel a container into which through the use of a hopper. So, this is this shape is basically this is the hopper through the use of a hopper you put the polymer pellets inside this barrel and these polymer pellets are being pushed towards this side by this piston this piston is pushing the polymer pellets towards this side and here you have what you call as the this is your injection chamber. So, they are pushing these polymer pellets into the injection chamber and here you have heaters.

So, as the piston is pushing the pellets towards the; what you call as an injection chamber this black portion the injection chamber the pellets are also passing through this hot zone and they are being molten. So, it becomes molten and this molten material there is then pushed through a nozzle into your mold.

Now, this mold basically this mold has two parts you can see this part and this part and you see the liquid is coming like this and liquid is basically taking the shape of this particular space. So, the liquid is taking the shape of this particular space let us say and putting that space in red. So, the liquid is taking the shape of this particular space and you have two parts of your mold, you have two parts of your mold.

So, this is one part which does not move at all which is not movable this is another part let us say I am just crossing this part this part is movable this part is not movable now this mold basically and here you have some kind of vent you have some kind of vent here and these two are called here you can see these two lines here and these two are called ejector ejectors. So, these are called ejectors. So, what happens is that as you put the pellets inside this chamber or this barrel the pistons will push them towards the injection chamber.

So, this is your this black portion here is your injection chamber your injection chamber which is connected to this mold through the nozzle. So, then you have this liquid that is pushed through from the injection chamber through the nozzle by this piston and that fills up this area in the mold the mold has basically two parts one part is not movable this part is movable.

So, once this liquid fills up this melt fills up this particular place it takes the shape of this place and this particular this the mold is also cooled by passing some coolant fluid. So, this is at a low temperature. So, once this liquid goes into this mold it immediately cools down and becomes solidified. So, it takes the shape of the mold now what you do is that this part of the mold is basically movable. So, you pull this part out along with this part your solid material will also stick and come out along with this part then what you do is that you push the ejector pins if you push the ejector pins the solid material will just from this side of the mold that is the overall idea.

So, let us summarize the overall thing the plastic materials they are the pellets they are fed through the hopper into the barrel piston pushes the material towards the mold material is heated and melted in the injection chamber and this molten plastic is then injected into the mold through a nozzle. Now, what happens then when it is getting injected there might be some trapped air inside because it was there was nothing inside. So, there was air that air escapes through this vent and now it can go in.

Now, this vent basically they have tens of micrometers dimension. So, you might also ask when this melt has gone in this melt could also pass through the vent, but it cannot because the melt is quite viscous basically the melt has consistency of honey. So, it cannot pass through this vent the air can go out now once the melt has gotten in; what will happen is that it will start to cool down and once it starts to cool down in the mold it will start to contract and some more space will be generated so that some more of the liquid can come in.

So, the piston continues to push once the first installment of the liquid has gone in it, it cools down the plastic cools down becomes solidified and it contracts some more space is generated. So, some more liquid can go in and the cold water circulation through the mold will basically keep it cool and correspondingly it will also cool down this material after that you can take out this particular part and along with that the polymer shape will come out it will get stuck to this part it will come out and then you push this ejector pins which will allow this polymer shape or the mold polymer shape to come out.

So, it can detach the ejector pins can detach the plastic from the mold actually you can also see the you can also see how the mold structure varies I mean for example, if you if you look at the PowerPoint here. In fact, it is not PowerPoint, it is the PDF.

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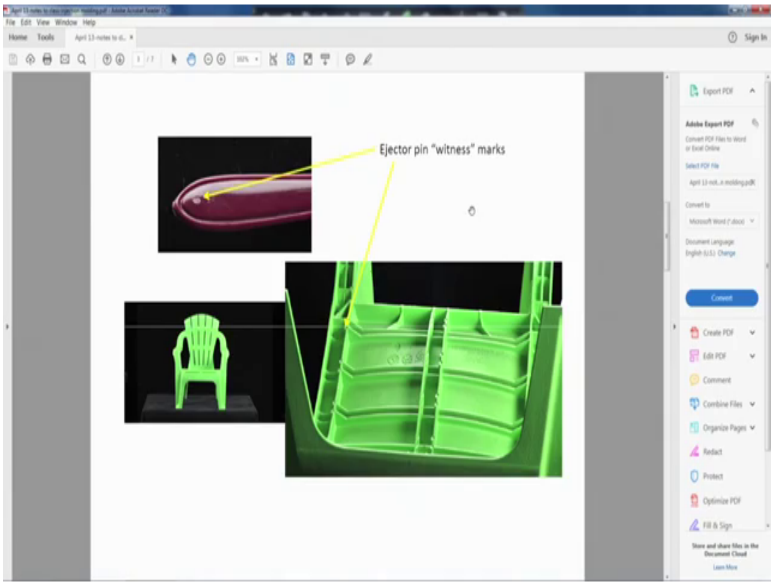

So, you will see that when you when you eject the molded parts from the mold by using the ejector pin you will have these kind of witness marks in the in the shape.

So, these kind of witness marks will be present that actually tells you the; you know the ejector pin has been used in these in those parts to detach these shapes ok. So, overall this is the process for the injection molding we will talk little bit more in detail about the

I mean some more intricate details about the advantages and disadvantages of such process in the in the next class. So, till then.

Thank you and good bye.