Polymers: Concepts, Properties, Uses and Sustainability
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Lecture - 03
Process, Structure, Property

Hello and welcome to this course on Introduction to Polymers. We are looking at the concepts of polymers, their properties and usage and also sustainable aspects of polymers. In the week one, we are trying to answer question related to polymers and their unique features related to the structure of polymers.

And in this lecture, we will look at the essential relations, which are there in polymers which are called process-structure-property relations. So what do we mean by structure? What do we mean by process and what do we mean by properties and how they are all interrelated will be learning from this particular lecture. And the focus in this lecture will be on concepts.

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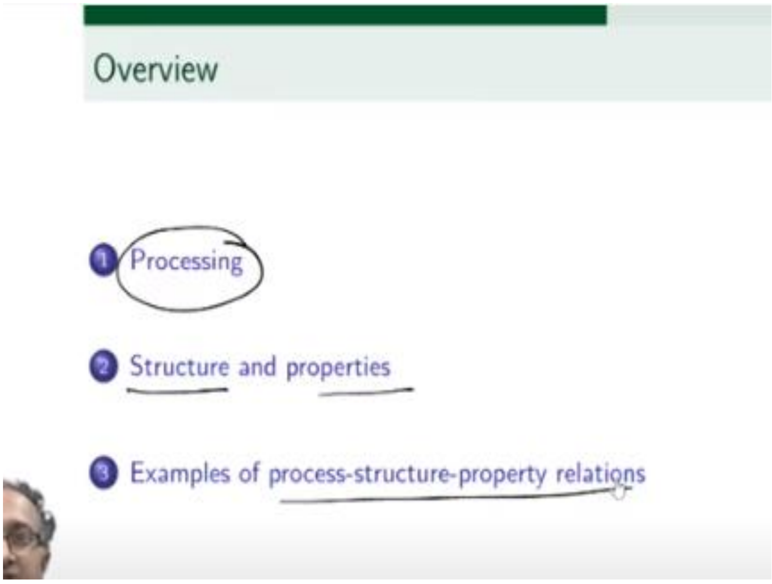

And how we are going to do this is by looking at what is processing in the context of polymers. What do we mean when we say we are processing the polymers? What do we mean by structure of these polymers and properties? And more importantly, how are they interrelated? So we will look at some few examples of process-structure-property relations in these polymers.

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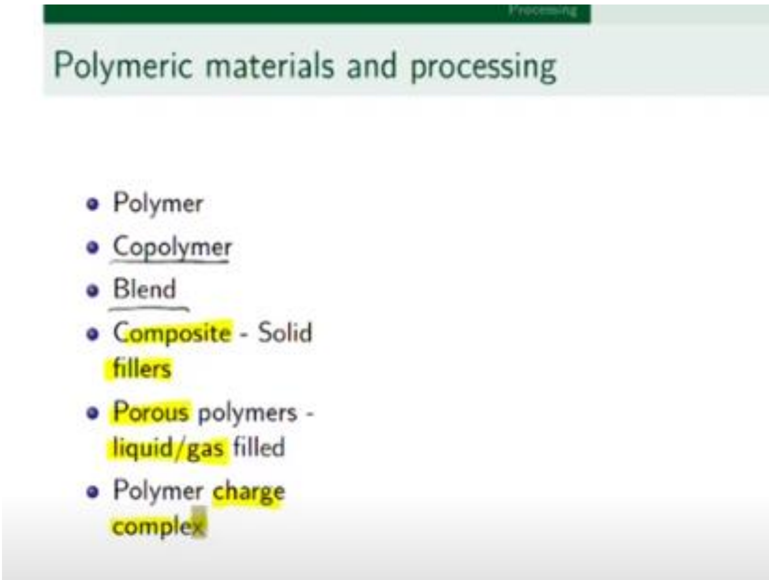

Let us first begin by trying to understand what do we mean by polymers. And what is the diversity of materials that are actually there when we talk in terms of polymeric materials. So we can process the polymer by itself. Or we can have the polymer made up of different monomers when it is called copolymer. We could mix polymers and make them into a blend.

We could also mix the polymer along with another filler, a fiber or a particle and in which case it is called a composite. We could also have a polymer membrane, for example for water purification. We know that many of the RO units which are there in our homes, or whenever we talk of purification of water, membranes are used and quite often, many of these membranes will be porous, in which case, they are either filled with liquid or gas.

Can you think of an example of a gas filled polymer? Styrofoam, of course, right? You can see that it is a very light form material where polymer and gas is together. And then we could also have a polymer along with some charges. So in which case, it is a complex of polymer and charge. So when we say polymeric materials, there is a variety of materials, diversity of materials that are out there, that have to be considered.

And sometimes polymer by itself is there but quite often it is mixed with other polymers or other sets of substances. So now what do we mean by processing of these polymers.

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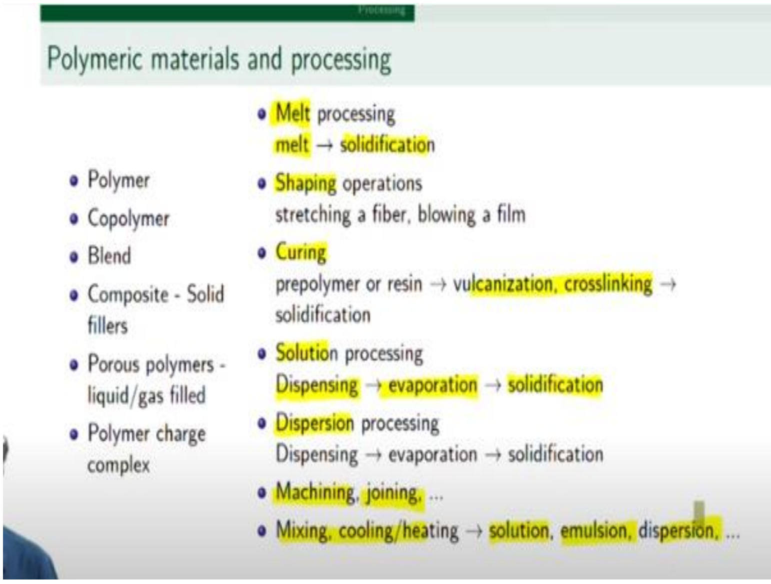

So we could have variety of ways in which polymers can be processed. For example, we can melt the polymers, which means we increase the temperature. So the one aspect we can look at is where we can melt the polymers, and by which we mean we increase the temperature, make them more fluid, so that they can flow and then mould them and so on. So what we have is melt of a polymer and then it will solidify.

So this is one aspect of processing. That is how a complex shape can be made. If we want to make a disc let us say, disc like object, so initially we start with granules. We melt it and then make it into disc shape by making it flow into a disc shaped mould. And of course, as I talked about different shapes, once we get a shape, we might have to manipulate the shape further.

So for example, we start with granules, we extrude a wire or a fiber and then we may want it to make it thinner. Or we extrude a sheet and we may want to make it very thin film. So in that case we have what are called shaping operations. An important class of polymers we start with what is called a prepolymer or a resin in which case the polymer is only an oligomer or small molecular weight, small molar mass molecules.

And then when we are actually processing and shaping it, curing happens or reactions happen. And so in this case, solidification happens because there is reactions happening in the material. There is alternate ways of processing polymers also. For example, if we are using in food applications and we want viscosity to be higher like a jelly in a jelly. In that case, we may be using what is called a solution processing.

So quite often, let us say in coating operation also, we want a polymer coating as a protective coating, then what we will do is we will form a solution, we will dispense it on the substrate where we are coating, then we will allow the solvent to evaporate and then the coating will, solid coating will form. So again this is an example of a processing operation. We need not have solution of polymer where there is an intramolecular mixing.

We could have just polymer particles like in case of paint, where we have particles of polymer, particles of pigment which is usually an inorganic oxide in a solvent. So this is called dispersion. And of course, when we are looking at engineering of these materials, we may have to cut, we may have to shape, give it a particular shape. We may have to join. Welding may have to be done or fastening may have to be done.

So many of these machining operations are also required as part of processing. And another aspect, we have to make solution, emulsion or dispersion, we will have to do mixing and cooling, heating and all of these operations. So when we say we are processing polymers, we are basically trying to fabricate objects out of these polymers.

And as part of the fabrication process, we have flow, we have heating, cooling, we have mixing and we have applications of stresses and application of several basically applied field so that we get a requisite shape that we want at the end. So this is called processing of polymers.

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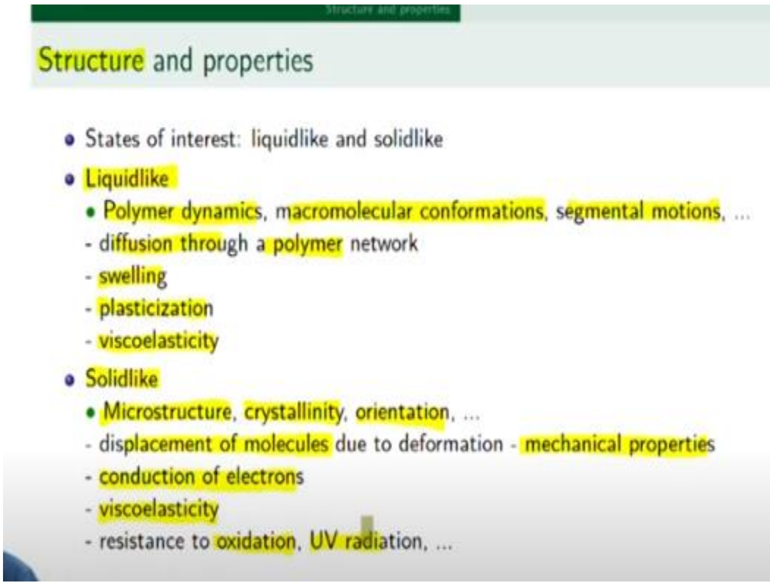

What about structure and properties? In case of polymers, basically there are two sets of states which are most important. And one important feature you can notice here is I am not calling them liquid and solid. I am calling them liquidlike and solidlike.

And this is something which we will have to continuously learn during the course that we will have solid polymers which will have some liquidlike features and we will have melt of a polymer or a solution of a polymer, which will have some solidlike features. So that is why rather than calling them solid and liquid, we will say they are more solidlike and more liquidlike.

So for example, a liquidlike state which could be a solution or a melt or even a rubber by the way has many features of liquidlike phenomena, because polymer molecules are dynamic objects in these situations, which means, polymer molecule can move around and if you think of a bowl of noodles basically the noodle are moving around and then you can think of a liquidlike state of polymer.

So therefore, the macromolecules or segments can move about. So there is a segmental motion possible or macromolecules can change conformations. And when are these important? For example, when I am looking at diffusion of a small molecule through a polymer, then how the small molecule diffuses, around these macromolecules, which are also moving about is an important consideration.

Or when, let us say in a diaper, where it is supposed to absorb, how much can it absorb? How much can it swell? And that is determined based on how much is the dynamics of the polymer. How flexible it is and so on. Similarly, when I make some object out of PVC, polyvinyl chloride as a polymer, I can make objects out of PVC only when I plasticize it. So I can add something to plasticize it.

I can heat something to plasticize it. Whenever I plasticize something I make segmental motion possible, macromolecular conformations possible. So these are liquidlike features, which make which we will have to understand. And of course, I have already highlighted the fact that when it is liquidlike it will certainly have some solidlike characteristics also. So viscoelasticity; viscous, elastic.

Viscous means liquidlike, elastic means solidlike. So viscoelasticity of polymers, the key feature associated will be polymer dynamics, which will give it the liquidlike characters. On the other hand, if we look at solidlike materials, then we need to know whether it is crystalline or amorphous material. What is the orientation of macromolecules? What are the ways in which molecules are arranged with respect to each other?

Or if we have a fiber and a polymer, how is fiber arranged within the polymer matrix, and so on. So it is called the microstructure of the material. So this is also aspect of structure of these materials. And the properties which are of interest due to the structures are, for example the deformation of polymer material.

So if it is more crystalline or less crystalline, it will be easy to displace molecules or more difficult to displace molecules. So therefore, mechanical properties will depend on the microstructure and how crystalline the material is. For example conductivity and in this course we learn about conducting polymers also. So whether crystallinity will enhance conductivity or whether amorphous material will enhance conductivity?

We will see, structure is again closely linked with property of these materials. And in the solid state though molecule seem to be frozen and therefore, we get a solidlike character, there is some liquidlike motion possible over long term or at high temperatures. Then therefore, solidlike materials will be viscoelastic. Which means they will be predominantly solidlike with lot of elasticity features, but with some viscous features also.

And of course, in solid state we also have to worry about for example, can oxygen come in? Is it resistant to UV radiation? Are chemical reactions happening in the solid state, because this will determine the overall performance of the polymer. So in a nutshell we have seen what is meant by processing of polymers, what are what is its structure and what are the properties.

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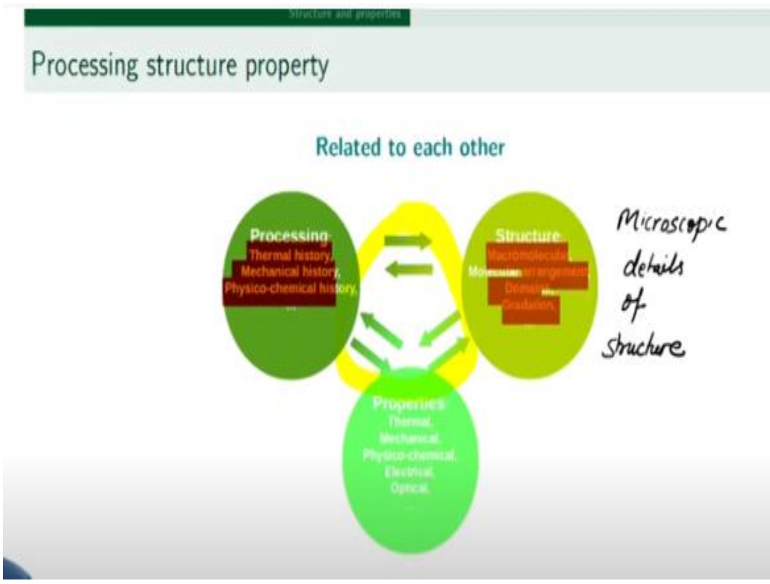

Now all of these are interrelated to each other. Generally this is called a process structure property triangle of the polymers. This is not unique to polymers by the way. Many material, most material scientists would talk of process-structure-property relations in the material. Because, the way you process them will determine their structure and properties.

Or depending on the structure of the material processing and properties will be determined. Or properties will determine what process and what structure do they have. So it is basically interrelations between all of these. When we say processing, we talk about what is the, what was it heated to, what was it cooled to, what was the thermal history of the material.

When we talk about processing, because we stretch the material we make it flow and of course, when we process it, it could be along with plasticizer, it could be along with a solvent. So there is always a physical, chemical, mechanical and thermal history associated with processing. And two different processing operations will therefore lead to a different two different sets of structures and therefore, different sets of properties.

When we say structure, we look at the molecular structure, in terms of arrangement of molecules, in terms of domains, whether it is crystalline domain or amorphous domain or maybe one particular polymer mixed in another polymer and also whether there is gradation in terms of there may be compositional difference. One part of the component may have lot more fiber compared to the other part.

So therefore, there is a gradation in terms of structure. One part of component may be more crystalline compared to the other part. So that is why it is called microstructure. We many times referred to not just structure, but microstructure because in this case, we are interested in microscopic details of the structure. And when we think of properties, of course, we think of all different properties.

Thermal conductivity, mechanical modulus of the material, conductivity, refractive index and so on. So now in the beginning, we looked at what is meant by process structure properties. Now we will close this lecture by looking at few examples of each of these as to how processing structure and property are related in case of polymeric materials.

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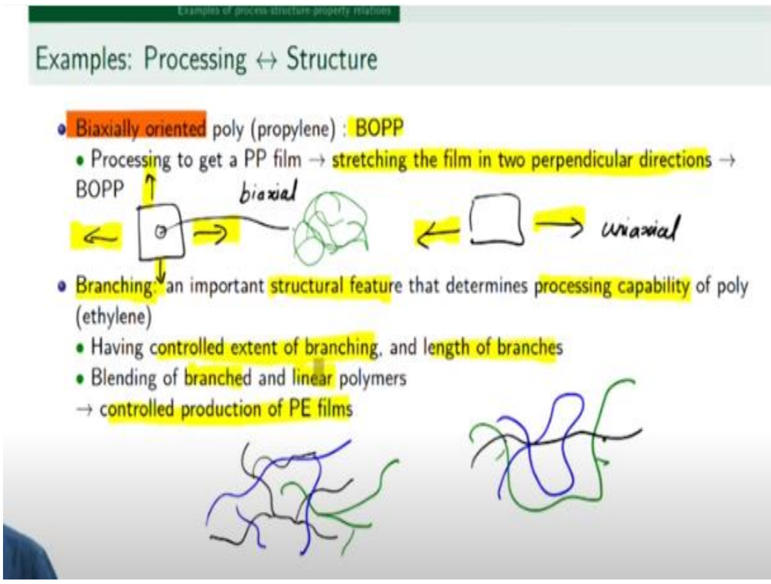

So let us start with processing and structure relationships. The first example that I am going to give is biaxially oriented polypropylene, BOPP. If you searched, you search this term, you will see that lots of suppliers are there in each and every country, which supply BOPP films, and it is different compared to polypropylene. And the reason is that this film is processed in a particular way.

What we mean by biaxial stretching is if I get a film, if I stretch it in two perpendicular directions. So what can happen during such a stretching operation? Remember that if I zoom in to this, what I might have is basically the macromolecules that I have talked about so far. Now what happens to these macromolecules when they are getting stretched into perpendicular directions?

How is this different compared to if I take a film of the same polypropylene but stretch it only in one direction? Clearly, you can see that these segments of these macromolecules will start aligning due to stretching. And alignment will be very different if it is this kind of stretching, which is called uniaxial stretching as opposed to this type of stretching, where we call it biaxial stretching.

So that is why what we have in this case is biaxially oriented polypropylene. And given that the molecules, macromolecules and segments have been oriented biaxially, the properties are far superior compared to just making a polypropylene film. And that is why this is such a important product. And you can see how in this case processing is influencing the structure, the orientation within the polymer.

Now let us look at an example where structure influences the processing. And branching is a very important indicator of how a material can be processed. So it is a structural feature that determines the processing capability of let us say polyethylene. So what is needed for a good processing of polyethylene is controlled extent of branching and also the length of branches.

So low density polyethylene is easier to process to make thin films compared to high density polyethylene. So branches in some ways help. Now the question that you could ask is why is this the case? So again, if we have a low density polyethylene, it is something like this, where there is very long branches on the backbone chain. And of course, we will never have one particular molecule in isolation.

We will always have multiple such molecules. And so what we have is basically another giant molecule with lots of branches also entangled with this molecule. And so with all these molecules entangled with each other, how the entangled mass of this polyethylene, branched polyethylene behaves, when we make it molten, and then making it flow for making a film.

And how is this different compared to let us say, an HDPE, where you have largely linear polymer with very small fragment at most, and this is entangled with other sets of macromolecules and you can clearly see that how a molecule can move about will be very different, because entanglement and these branch points will make very different motion in case of branched polymers as opposed to linear polymers.

And so therefore, for a controlled production of polyethylene films, many times blending of branched and linear polymer is done.

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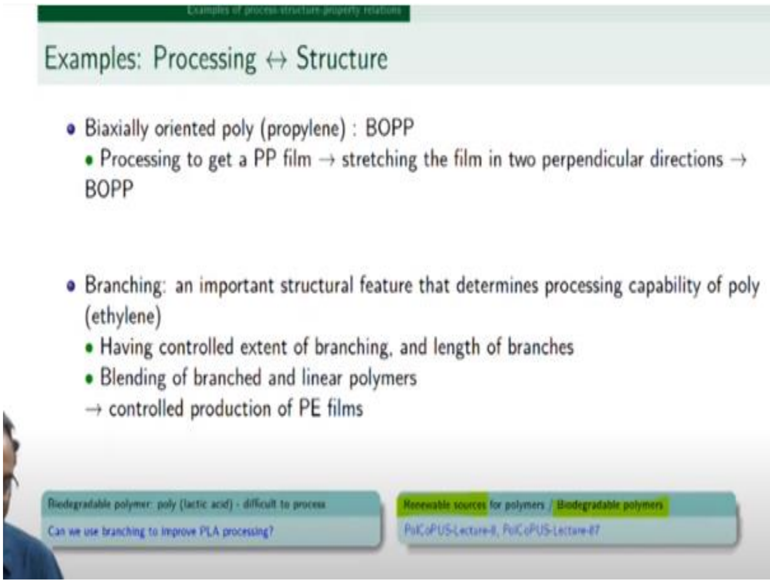

And this is such a popular case of improving processing of materials that polylactic acid which we will learn is a very promising biodegradable polymer for many of the packaging applications. But it is very difficult to process polylactic acid. So one of the key research question and practical question people are asking is, can we use branching to improve the polylactic acid processing?

Polylactic acid generally I get will be a linear molecule. So can I make it branched? Or can I mix some other branch molecule in it so that I can make film very easily like I can make films with polyethylene. And further on another aspect that we will continue to learn throughout this course, is related to when we are saying polylactic acid in which way is it biodegradable?

What makes polylactic acid biodegradable and polyethylene is not biodegradable? And also why is polylactic acid important because we are using renewable resource with it. So in next set of lectures during the course, we will also learn about these aspects.

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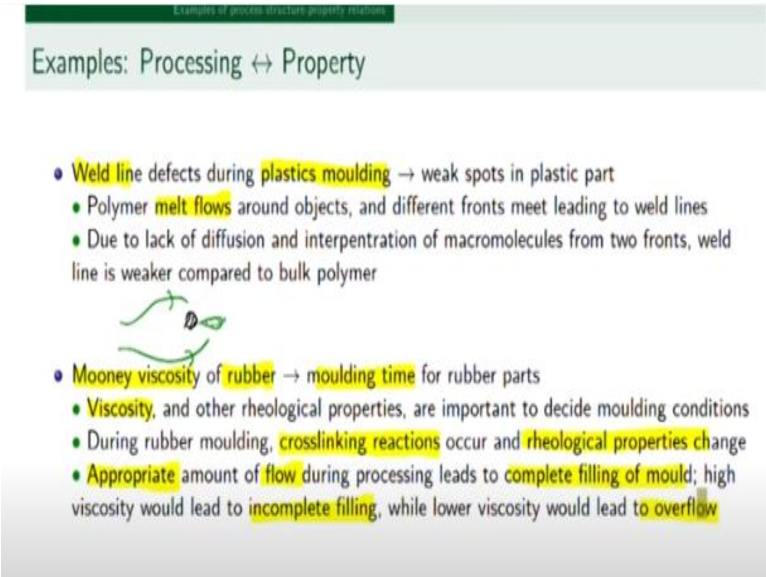

Now let us continue and look at the other examples of processing and property. For example, when we are doing moulding of plastic object, we will have flow. So when we do plastic moulding, there will be flow and melt flows, so for example, if we are making a cylinder with a hole in it. So basically an annular kind of object, then what will happen is we will have a solid block around which polymer will flow.

So polymer melt will flow like this, it will flow like this. And so the polymer in this region, polymer melt will come and flow and again join together. So that is called a weld line of a mould. So weld line is going to be the weak spot, because two polymer front melt fronts have to come and meet and then of course, macromolecules have to start entangling.

But depending on the diffusion rate, and depending on the temperature and pressure of our moulding operation, this interpenetration may not be sufficient. So in the end when we get a plastic object, everywhere else the properties will be very strong. But here since the polymers have not got enough chance to intermingle and interpenetrate there will be a weak spot.

So this is a case where processing is leading to a property issue in terms of weak spots. And that is where the part is likely to fail. So we need to know where the weld lines are and can we reduce the disadvantages of weld line. Can we improve properties around weld lines? So processing directly influencing the performance of a part.

You can also look at other example where Mooney viscosity of rubber is important in terms of finding out how will we process it. For example, how much time will the moulding operation take? Because, when starting viscosity will determine how the material is flowing and being shaped inside a mould. And more importantly in case of rubber, as the moulding is going on crosslinking happens and viscosity changes as a function of time.

So crosslinking reactions happens and rheological properties which are nothing but flow behavior properties of rubber keep on changing. And so we have to ensure appropriate amount of flow during processing, so that we have complete filling of the mould, which implies that we should not have incomplete filling or we should also not have too much overflow.

And this can be ensured if we make sure that we understand the viscosity of the material, the property of the material properly. So in this case the property of the material influences the processing conditions.

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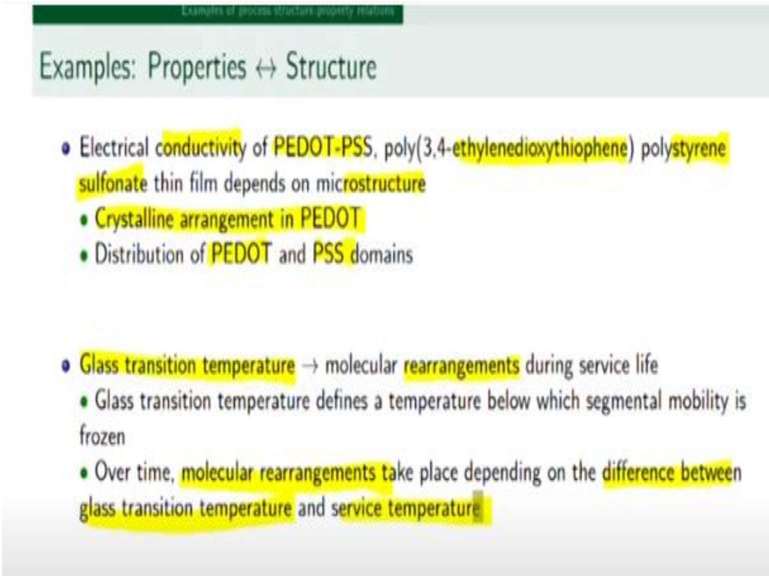

Let us complete the overall consideration by looking at the property structure. And as we will learn during this course, that it is possible to get a conducting polymer the example I have given here is called PEDOT:PSS. You can search for it and you can find lot of information related to PEDOT:PSS. In fact, it is available as ink. So I can use an inkjet printer to actually print electronic devices using PEDOT:PSS.

Very interesting, is it not? So the repeating unit in this case is ethylenedioxythiophene. And it is mixed with another polymer which is called polystyrene sulfonate. It is a very complex material and the conductivity in this depends very strongly on the structure of the material and in fact, the microscopic arrangement in the material.

So how is the crystalline arrangement of PEDOT, which is one polymer of this overall polymeric material and how are the domains of PEDOT and PSS distributed with respect to each other. So you can see that how structure of the material determines its property, in this case electrical conductivity.

And this gives a very rich possibility from an application, from a scientist and engineer point of view, can I manipulate my structure in a way to give me maximum property. So I need to understand the relation between what the microstructure is and what the property; in this case electrical conductivity. The last example we will look at is where a property in this case glass transition temperature, influencing the structure.

And in this case molecular rearrangements in the material. So a polymeric material let us say PET bottle, if we keep it at room temperature for 25 years. At room temperature means around 25, 30, 40, 30, 35 degrees Celsius, maybe 25 years it will be fine. But what if it is also subjected to 50 degrees Celsius? Will there be any molecular rearrangement? Will its structure change?

And that depends on its important property called glass transition temperature. And given that we will see that polyethylene terephthalate the PET bottle, the glass transition temperature is around 80, at around 60 degrees Celsius and around 55 degree Celsius structural changes are possible. If we take a polymer whose glass transition temperature is 150 degree Celsius, then at room temperature no structural changes may take place.

So clearly you can see a property will determine what its microstructure is going to be over time. So in case of many of the polymers rearrangements will take place depending on the difference between its glass transition temperature and whatever is the service temperature. So through this what we have seen is possibility of important correlations between processing structure and properties or in these polymeric materials.

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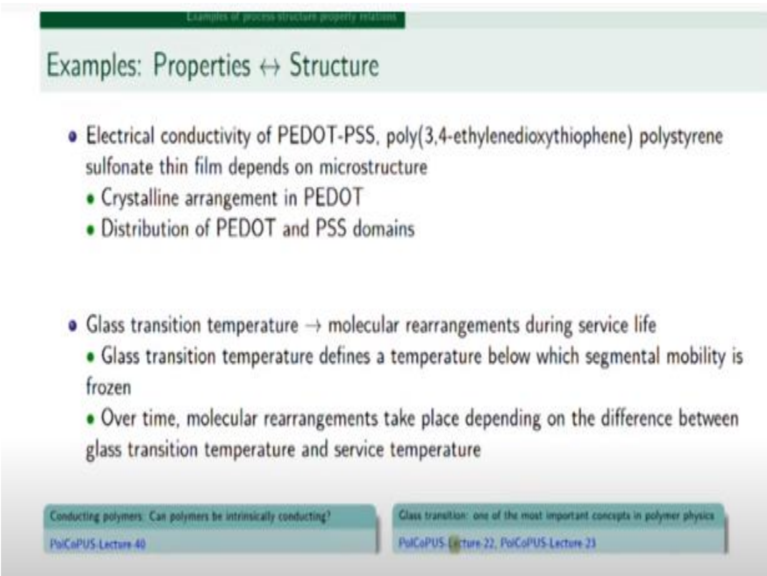

Just to remind you that conducting polymers we will look at in a separate lecture, where we will see can polymers are is it possible to get conductivity rather than adding a conducting material into it can I have polymer which are intrinsically conductive? And sure enough, we will see those later. And of course, glass transition is a very important property in polymers. And we will devote a couple of lectures discussing in this much more detail.

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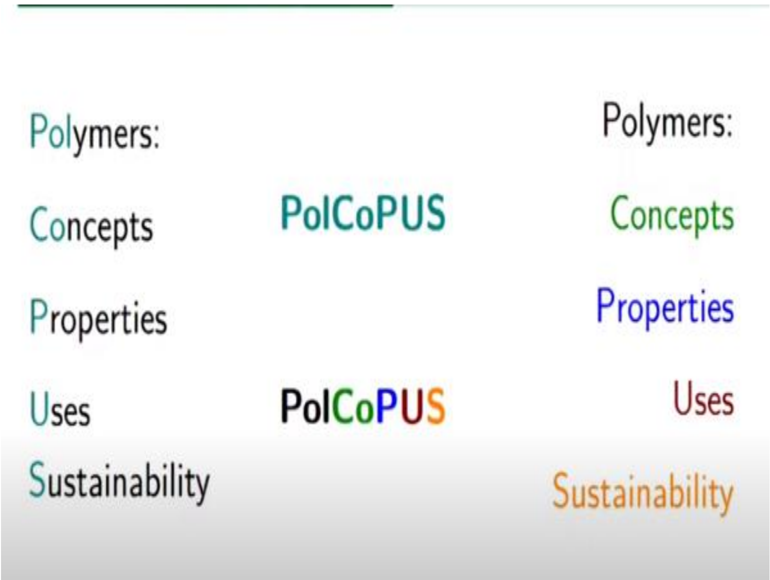

So with this we have come to the first three set of lectures in which case we tried to understand some basic nomenclature associated with polymeric materials. Thank you.