Molecular Arrangement and States of Polymers
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Lecture - 19
Orientation

Hello, welcome to the 3rd week of this course on polymers. We are looking at molecular arrangements and the states of polymers. And one of the important aspects of the solid state of polymers is related to the state of orientation. And in this lecture we will look at the presence of orientation in polymeric materials from the point of view of applications.

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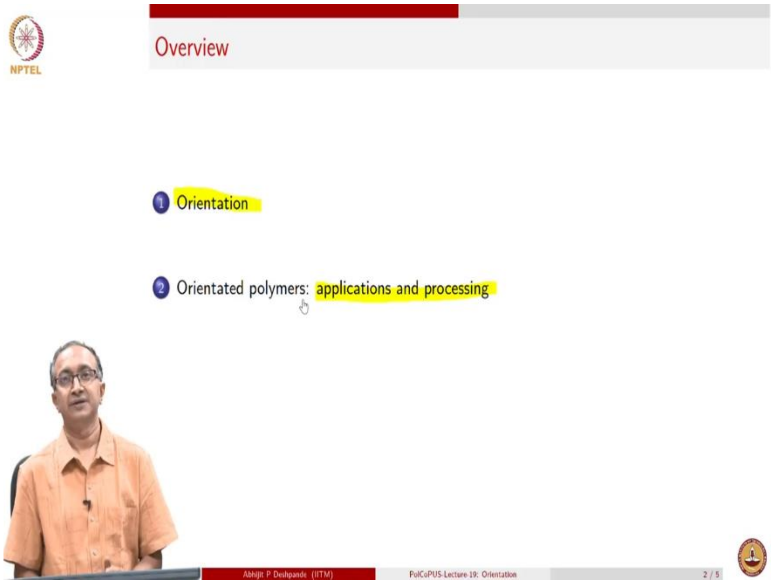

Overview

1. Orientation
2. Orientated polymers: applications and processing

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And we will do this by first quickly reviewing what is meant by orientation and what can orient. and then we will look at few examples of where such oriented systems are used and also where we can process them.

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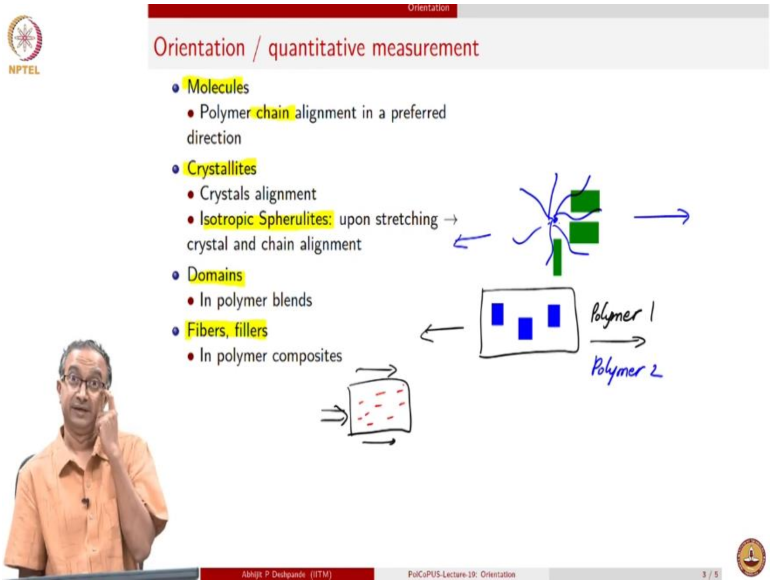

Orientation

Orientation / quantitative measurement

- Molecules
  - Polymer chain alignment in a preferred direction
- Crystallites
  - Crystals alignment
  - Isotropic Spherulites: upon stretching → crystal and chain alignment
- Domains
  - In polymer blends
- Fibers, fillers
  - In polymer composites

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So orientation is basically can be of molecules, macromolecules in our case, it can be the orientation of crystalline segments, crystalline domains of the macromolecules. If we have mixture of two polymers then one polymer will be distributed in another polymer, there will be domains of one polymer and another polymer, so these can also be oriented. And in composites when we add short fibers or when we add whiskers so then these can also be oriented.

So therefore when we speak of orientation in polymeric materials, it can be of all these different things. In case of macromolecule it is the chain itself which is aligning in a preferred direction. And why would this happen? Why would chains align in a particular direction? So can you think of if you have actually experienced the alignment of chains during your day to day use of polymers?

If you think about it when you take a grocery bag or any of the plastic films and if you start stretching, initially it will stretch easily and then as you stretch more and more it becomes more difficult and then it will also not spring back. So in such cases what is happening is polymer molecular chains are getting aligned. Similarly if you have a semi crystalline sample and we have seen the structure of spherulitic arrangement in case of polymers, what we have is the crystalline lamella which are growing in all three dimensions. And so if we try to stretch this sample then what will happen is the crystallites will also get oriented and the amorphous region where there is between two lamella there is of course amorphous region, so, that also will start getting oriented.

And if we have a polymer blend then what we have is let's say a polymer 1 and then we have polymer 2 and this polymer 2 is distributed in with the domains in polymer 1.

So if we stretch this sample then again these blue domains will start orienting, so therefore different orientation is possible. For example in case of composite sample what we have is if I have a geometry in which a polymer melt is made to flow like this and this polymer melt has also short fibers and we will denote those short fibers and since the flow is in this direction the short fibers will also predominantly start getting oriented in the flow direction. So therefore orientation of short fibers is also possible. So, all of these are different examples of orientation.

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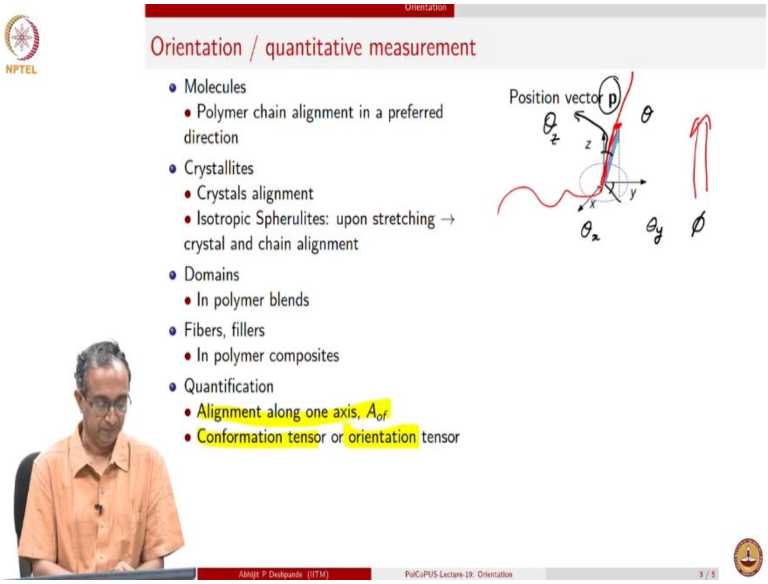

Orientation

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- Domains
  - In polymer blends
- Fibers, fillers
  - In polymer composites
- Quantification
  - Alignment along one axis, A_{of}
  - Conformation tensor or orientation tensor

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And we can quantify this orientation by trying to ask two different questions. So basically what we are looking at is let's say if there is a chain and then there is an orientation of the chain, so we can take a point on the chain and then we can have the position vector of that point. And then we are asking the question as to what is the orientation of this chain with respect to some coordinate system that is of our interest.

So let's say if this is one axis and let's say flow is happening in this direction z direction and so we are interested in knowing with respect to that flow direction the z direction what is the orientation. So in that case this angle between this and so this angle θ will be of interest, but generally this orientation can be quantified if we know the angle that this position vector makes the projection that is made on x axis, y axis and z axis.

So if I denote this as θz then there will be projections on θx, x axis and θy which is on y axis. So this is one way of quantifying. The other way of quantifying this orientation is also by our usual spherical coordinate system kind of description where we say that the with the z axis the θ is the angle and then we do the projection onto the x, y plane and then the angle which is related to the projection on x and y and which we usually do not by phi.

So these two different ways in which we can look at what is the orientation and therefore quantify what is this position vector. Now the complication is that when we have a bulk macromolecular, sample a sheet or a molded part what we have is lots and lots of macromolecules. So when we say orientation we are interested in average orientation. So therefore the quantification factors which are there, one is called the orientation factor or the confirmation or orientation tensor these are necessarily average quantities which can quantify and tell us on average what is the orientation in the sample.

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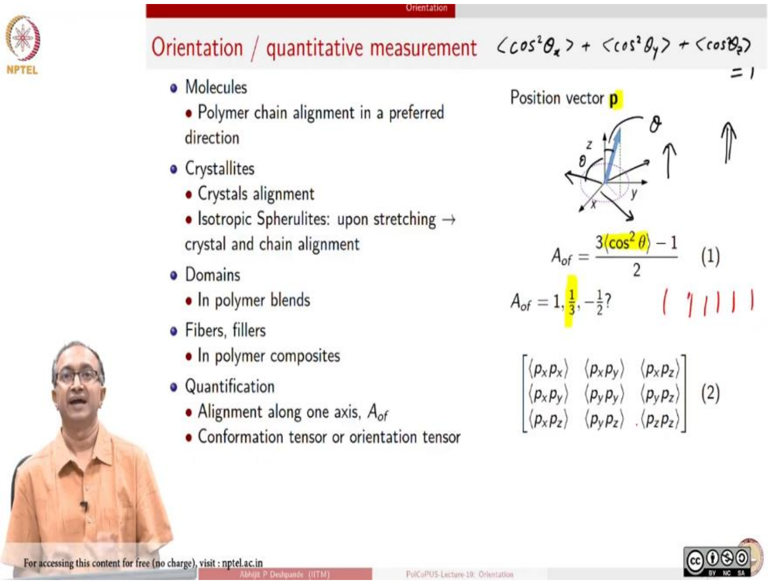

Orientation

Orientation / quantitative measurement $\langle \cos^2\theta_x \rangle + \langle \cos^2\theta_y \rangle + \langle \cos^2\theta_z \rangle = 1$

- Molecules
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Position vector **p**

$$A_{of} = \frac{3\langle \cos^2\theta \rangle - 1}{2} \quad (1)$$

$A_{of} = 1, \frac{1}{3}, -\frac{1}{2}$?

$$\begin{bmatrix} \langle p_x p_x \rangle & \langle p_x p_y \rangle & \langle p_x p_z \rangle \\ \langle p_x p_y \rangle & \langle p_y p_y \rangle & \langle p_y p_z \rangle \\ \langle p_x p_z \rangle & \langle p_y p_z \rangle & \langle p_z p_z \rangle \end{bmatrix} \quad (2)$$

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So for example this orientation factor has average of what is the cosθ for all different macromolecules. So here we already talked about that θ is the angle which is made by the projection of the orientation vector onto the z axis. So what we need to do is take all such macromolecular segments which are oriented in lot of different random directions, we need to take all such θ, evaluate $\cos\theta$ for all of them, because that will tell us how much is the projection along that direction.

For example if the fiber is in x, y plane then its projection on z will be because θ is pi/2, 90 the projection will be 0, of course when the fiber is an x, y plane it is not going to project anything onto the z axis. So similarly if the fiber is aligned already in z direction then its whole length will be projected. And so therefore this curly brackets which in indicates ensemble average as we have discussed earlier, this tells us what is the projection of each and every macromolecular segment along the direction of interest, in this case which is the z direction.

And as I said this is because of the flow may be happening in z direction and we want to find out how many macromolecules or how many fibers are getting aligned in the flow direction. And if you look at the definition of this what happens when $\cos^2\theta$ is 1/3, the average $\cos^2\theta$ if it is 1/3 then the orientation factor is 0. So this is in fact the sample where there is random orientation.

Can you think why? Why is $\cos^2\theta$ equal to 1/3 implies random orientation? So in this we are also looking at x and y being identical. And because there is flow direction in z, z is different compared to x and y. So if you have a random orientation then we discussed that there will be θx on to x axis θy into y axis and θz into z axis. And given that all the macromolecules are randomly oriented each of them will contribute equally. And what we will have is in that case we will see that, this average and this average this of course always has to be 1 irrespective of any situation but when they are randomly arranged all 3 will be equal and each of them will be 1 third. So therefore in that case A o f is 0. So you can think about how justification of A of being 1 or – 1/2 implies. The other way to completely keep track of this is to just take this orientation vector and its different components p x, p y and form this orientation tensor. So if let's say all of them are organized only along z direction, so let's say if we have all the segments and they are all like this all the segments are like this. So in that case we will only have p z. p x, p y are zero. So therefore you can arrive at this orientation tensor and then that will tell us what is the state of orientation.

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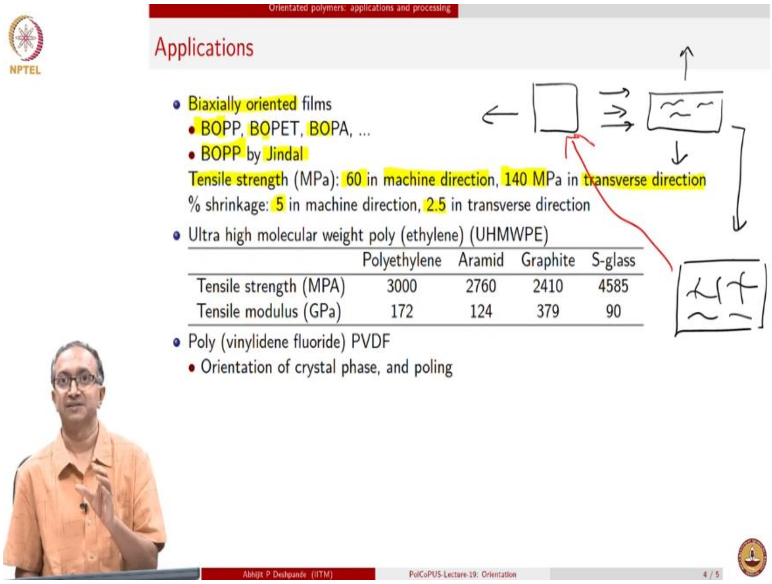

Applications

- Biaxially oriented films
  - BOPP, BOPET, BOPA, ...
  - BOPP by Jindal

  Tensile strength (MPa): 60 in machine direction, 140 MPa in transverse direction

  % shrinkage: 5 in machine direction, 2.5 in transverse direction
- Ultra high molecular weight poly (ethylene) (UHMWPE)

	Polyethylene	Aramid	Graphite	S-glass
Tensile strength (MPA)	3000	2760	2410	4585
Tensile modulus (GPa)	172	124	379	90

- Poly (vinylidene fluoride) PVDF
  - Orientation of crystal phase, and poling

Now from the practical point of view this is used in a lot of different ways. One of the most important set of products which are there where orientation is mentioned in commercial names itself are biaxially oriented films. So BOPP, polypropylene or polyamides or polyethylene terephthalate and here is an example from Jindal group the polypropylene that they make, in fact they give their tensile strengths in two different values and they are also saying different directions. So what this implies is this film which is made from polypropylene it is actually being stretched but it is stretched in two different directions. So initially the film is stretched in this direction and once the stretching happens then transverse direction stretching is also involved so that the sample becomes stretched in both direction. And so this kind of a direction stretching make sure that macromolecules get aligned in the direction of stretching.

And in this case by doing biaxial stretching orientation is being done in both the directions. So you can think of if we do just one single uniaxial orientation then macromolecules more will be aligned in this direction, but if you do biaxial orientation then we have orientation in both the directions and therefore the film will be stronger in both components. However you can see that there is a difference in the two directions.

And in fact percentage shrinkage is also a different. Percentage shrinkage here implies that if I heat the polymer film, it shrinks. Now, can you think why would that be? Why is this film which is oriented where we have forced the macromolecules to orient themselves from their random configuration, as soon as we heat them there is a shrinkage. And so effectively what you have to think of, is why does this oriented sample want to go back to shrinkage. And if you can think in terms of molecular flexibility whenever thermal energy is available you have got the answer. So we will discuss this more later on in the course.

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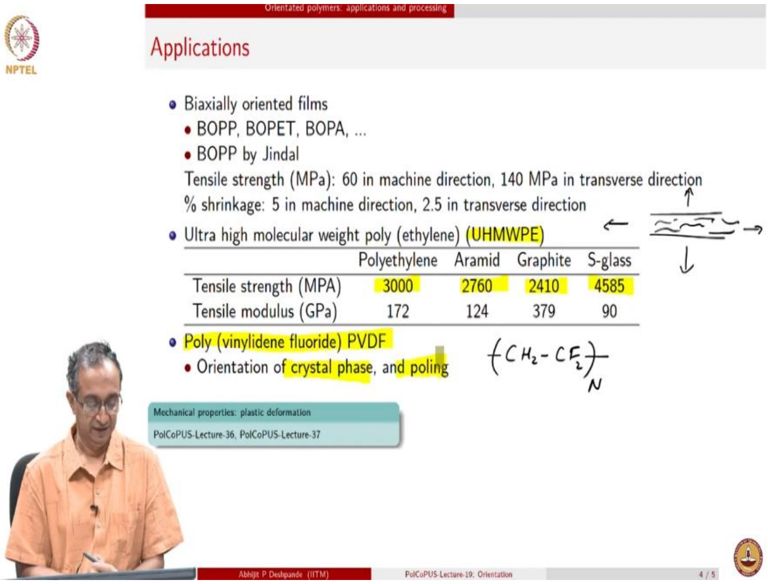

Orientated polymers: applications and processing

Applications

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$-\!\left(CH_2-CF_2\right)\!-_N$

Mechanical properties: plastic deformation

PolCoPUS-Lecture-36, PolCoPUS-Lecture-37

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So this orientation is very crucial in terms of mechanical properties, for example in case of polyethylene and we have a commercial grade of polyethylene called Ultra-High Molecular Weight Polyethylene (UHMWPE). And these are used in fiber form where stretching is done so that all the macromolecules of polyethylene get align in the fiber direction, the stretch direction and look at the strength that polyethylene can get.

Generally we think of polyethylene as a material for grocery bags and where the mechanical properties are not that significant but look at one of the most strong fiber known graphite or glass fiber and aramid which are strongest fibers known, in fact polyethylene can reach similar strength. This is because along the fiber all the molecules are organized. So if this is the fiber the macromolecules are all organized.

And you can see why there will be anisotropy of mechanical properties in such cases because if you were to pull the polymer along this way then the covalent bonds have to be broken if the sample has to be broken. But if I try to break the sample in this direction then secondary bonds between macromolecules only need to be broken. So orientation therefore will necessarily always bring in anisotropy and this is the anisotropy which can be also exploited in case of shrinkage or many other mechanical properties.

And other example of orientation is in case of an electro active polymer poly vinylidene fluoride and this is a CH2-CF2. And because of the strong polar group of CF when crystals are formed and one type of morphology or one type of unit cell when it is formed, then we have all the possibility of the poles the dipoles being arranged and oriented along one particular direction. And because of that orientation of dipoles then when current is applied to this sample it deforms or when you deform it current forms.

So therefore orientation of crystal phase is very important in this case and the phenomena of orienting the dipoles is called polling. So we have in this case orientation of not only chains but also dipoles themselves which is important.

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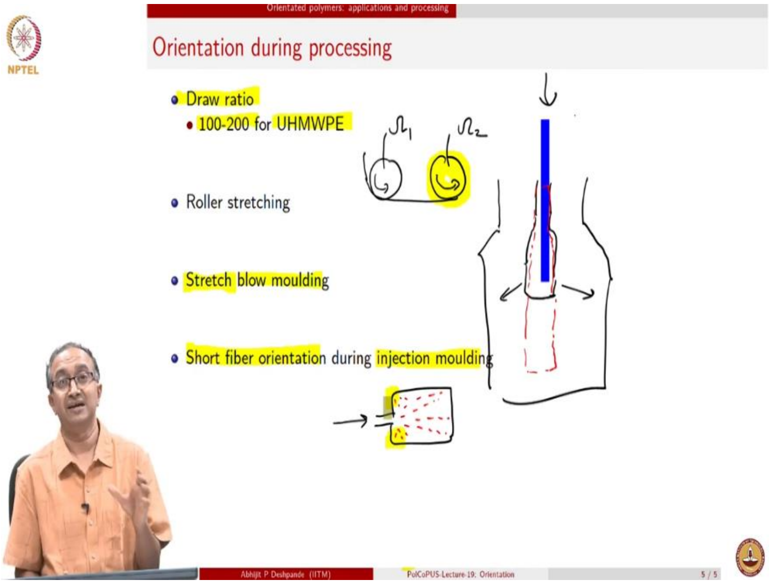

Orientated polymers: applications and processing

Orientation during processing

- Draw ratio
  - 100-200 for UHMWPE
- Roller stretching
- Stretch blow moulding
- Short fiber orientation during injection moulding

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So in terms of how this is achieved for practical applications, there are several ways and one of the most important factors which processors talk about is the draw ratio.This is the change in dimension when we are stretching. So if I take a fiber and stretch it 100 times then its draw ratio is 100. I have basically drawn it 100 times. So you can see that for ultra high molecular weight polyethylene, draw ratios can be 100 to 200. So that’s the amount of orientation and stretching that is being done to a sample to get the maximum mechanical properties.

We can do the stretching for sheets also based on roller. So if I have let’s say rollers and they are this one is rotating and then supplying a polymer film to this and this one is rotating but if the rotation rate of this is much more higher so that this film is this roller is rotating lot faster then what happens is this film will start getting stretched.

And so therefore roller stretching is one of the common examples of introducing orientation in polymers. Even in case of making bottles, so blow molding is a process in which case bottles are made and if you look at a typical bottle shape initially what happens is parison is made and then we blow air or other gas into it so that this stretches and then there is a mold and this mold is actually the eventual bottle shape.

So then this polymer flows and then it will come into contact with the mold surface. And that’s how blow molding is done. Now in addition to doing this blow molding, I can do stretch. What is implied by that? I can stretch the macromolecules in a particular direction first before doing the blowing. So what is done at times is we take a plunger or a rod kind of a thing and we push that so that this parison will get stretched and I will just indicate that using the red. So there will be a stretched parison and then blowing can happen. So in all of these cases it’s the orientation which is being manipulated and it’s a very practically sound way of making sure that certain parts of the bottle becomes stronger and which is what is desirable from an application point of view.

Similarly if we have a mold in which injection molding is being done and there are short fibers then short fibers orientation during injection molding is also equally important. So for example if I have let’s say a mold opening and then the mold is there and then polymer melt is coming in with all the fibers then what you might end up seeing is some of the fibers being oriented this way while here fibers will be randomly oriented. So if you look within the part itself the way the flow happened of the polymer melt the fiber orientation will be similar way.

Now the challenge in injection molding and orientation here is, let’s say if I want this particular corners to be stronger but they are the fiber orientation is random. So clearly then this kind of mold flow is not appropriate so I will have to change my injection points or I will have to change the way the mold shape is, so that I can achieve preferential orientation of fibers so that maximum mechanical reinforcement can be obtained. So therefore what we have seen is orientation is practically very important in case of polymeric materials and from polymeric chain onwards to fillers and reinforcement orientation is important.

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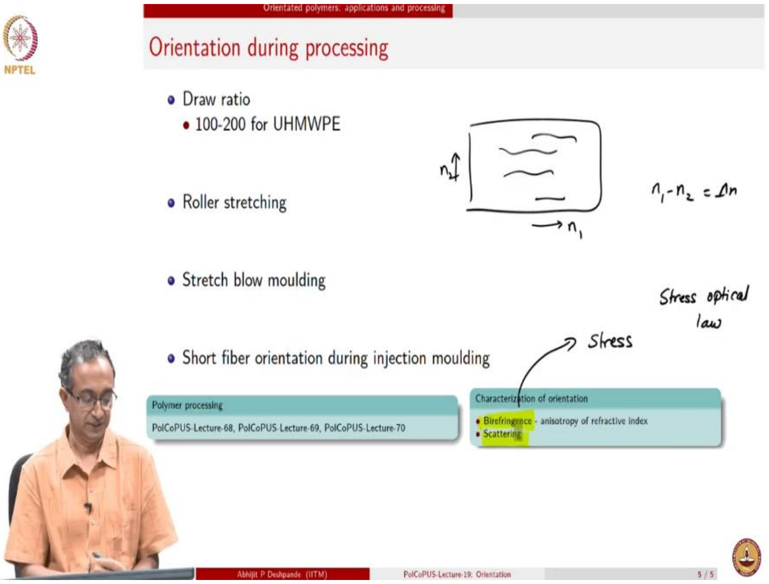

Orientated polymers: applications and processing

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n_2

n_1

$n_1 - n_2 = \Delta n$

Stress optical law

Stress

Polymer processing

PolCoPUS-Lecture-68, PolCoPUS-Lecture-69, PolCoPUS-Lecture-70

Characterization of orientation

- Birefringence - anisotropy of refractive index
- Scattering

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And with this we will close the lecture with a reminder that some of these processing aspects that we mentioned, we will be looking at much later in course where we look at many of these polymeric processing techniques and how we manipulate the status of macromolecular chains to obtain the best possible properties that we want. Also the characterization of this orientation experimentally can be done by measuring refractive index for example.

So since the polymer chains are all oriented in one direction, if I look at refractive index and if I say refractive index in one direction as opposed to another direction in fact there is an anisotropy, so this refractive index difference which is called birefringence is one common way to measure orientation in polymers. So much important this birefringence is that actually it is an indication of the state of stress in the polymer.

Can you think of why? Why do I say that if I measured the birefringence, I can get to know what is the state of the stress during let’s say flow of a polymer melt? And the key connecting point here is again the flexibility and rigidity of macromolecule. So the more the stretching is, it implies that more the stress was applied in the flow direction so that macromolecule can stretch. More the stretch is more will be the birefringence.

So therefore stress gives you more orientation, more orientation gives you birefringence and therefore birefringence can be connected back to stress. So therefore this is something very important to note that connection between stress and birefringence and in fact it is also referred to as stress optical law. So you can read more about it to know this interesting aspect of how orientation can be directly used to get some information about state of stress in the material.

And of course given that chain orientation and crystal orientation involves ordering we can use scattering techniques also to do the measurement of orientation. So with this we will stop here and continue our discussion of the structures of macromolecular system systems in the solid state.