Polymeric Materials of Different Kind
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Lecture - 25
Liquid Crystalline Polymers

Hello, welcome to the lecture on polymers in this lecture, we will look at liquid crystalline polymers. And this is an interesting state, which we have not discussed so far, where there are liquid like characteristics, but there is crystalline order in the liquid like system. And of course, we are familiar with the liquid crystal displays. So, in small molecules and in inorganic systems, liquid crystals are well known, but we also see that along the macromolecules there can be small moieties or small segments which can have liquid crystalline order.

So, therefore, in polymers also we can have liquid crystal empty just to remind you that this week we are discussing polymer materials of different kind, we will look at co-polymers and blends and composites as we look at the use of polymeric material in all different applications. And in so, this lecture also we will focus on some of the key uses of liquid crystalline polymers. These are materials which are used in small quantities compared to the overall polymers usage, but, given the advantages they give provide, it is used in niche applications.

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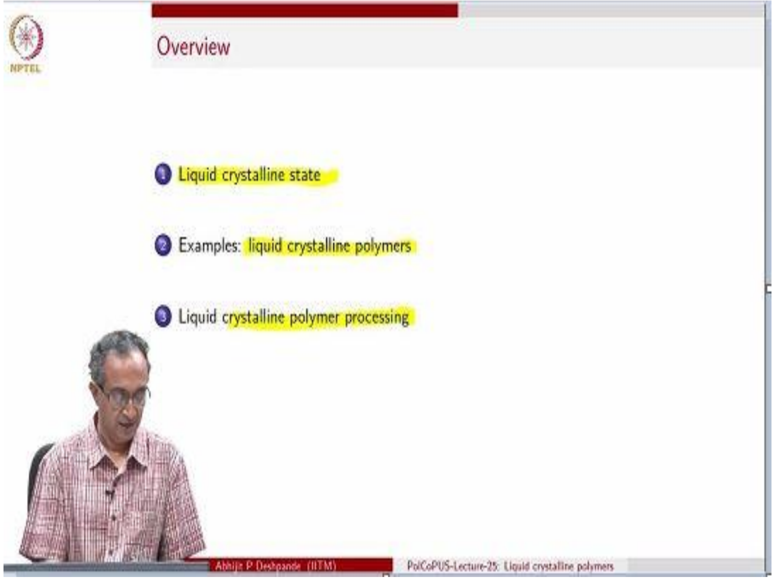

Overview

1. Liquid crystalline state
2. Examples: liquid crystalline polymers
3. Liquid crystalline polymer processing

So, we will look at these liquid crystalline polymers, but by first looking at what is meant by the liquid crystalline state, and then look at few examples of some commercial materials and what gives them liquid crystalinity and in the end, we will also see given that, we have rodlike segments in liquid crystalline polymers, how can that be exploited in polymer processing to orient the rodlike segments.

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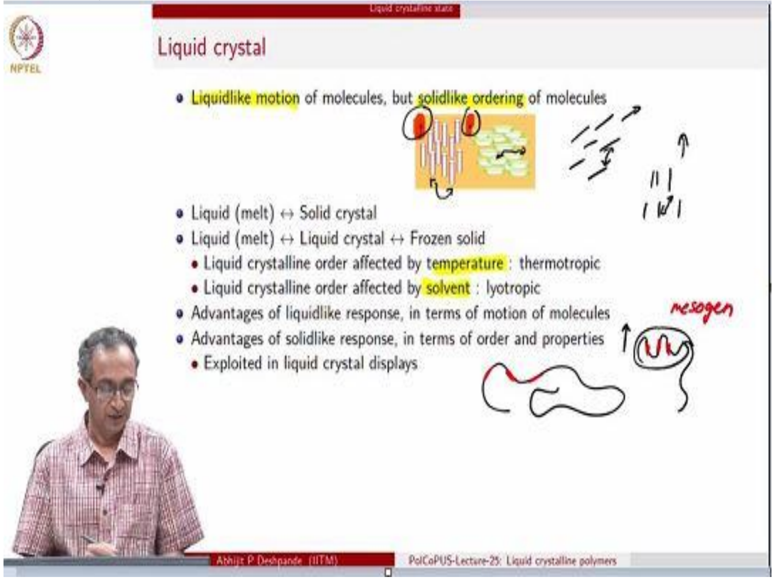

Liquid crystal

- Liquidlike motion of molecules, but solidlike ordering of molecules
- Liquid (melt) ↔ Solid crystal
- Liquid (melt) ↔ Liquid crystal ↔ Frozen solid
  - Liquid crystalline order affected by temperature : thermotropic
  - Liquid crystalline order affected by solvent : lyotropic
- Advantages of liquidlike response, in terms of motion of molecules
- Advantages of solidlike response, in terms of order and properties
  - Exploited in liquid crystal displays

And so, liquid crystal are materials where there is a liquid like motion of molecules, but at the same time there is solid like ordering. So, here for rods or discs, the ordering is clear. For example, with the arrow which is shown here, you can clearly see that there is an orientation which we can assign for the disc or for the cylinder. But what is crucial about this state is the fact that there can be exchanged between these rods or between 2 discs.

So, therefore, what is translation and the motion of these entities is possible, however, orientationaly they remain more or less fixed. So, in this case, the director vector as it is called is pointing to the to one particular direction, of course, we could have a liquid crystalline order in which the direction could be different in one place, and it could be different in another place. And within these domains, there is exchange of molecules which are possible.

So, you can read the bit more about these liquid crystalline material, and how there are different types of liquid crystalline material depending on whether it is a solvent, which leads to the formation of liquid crystalline order or disruption of it, or whether it is related to temperature. So, these are textbook related information on liquid crystals of small molecules. Now, given that we are looking at a macro molecule in this course, what we are looking at those set of macro molecules where in parts there is rigid rod like moieties.

So, now, what can happen once you have this kind of a system is the fact that some amount of ordering can take place between these rigid entities and so, just the way we drew a director vector for a small molecule liquid crystal, now, these segments of polymer chain can align themselves and therefore, we can again look at a director vector. So, these small groups which are present which prevent bond rotation or which are leading to chain being rigid locally, are called mesogens.

So, depending on what kind of macromolecule we have, we could have mesogen along the backbone, the way it is drawn here or it could be as a branching point or it could be as a side chain and so on.

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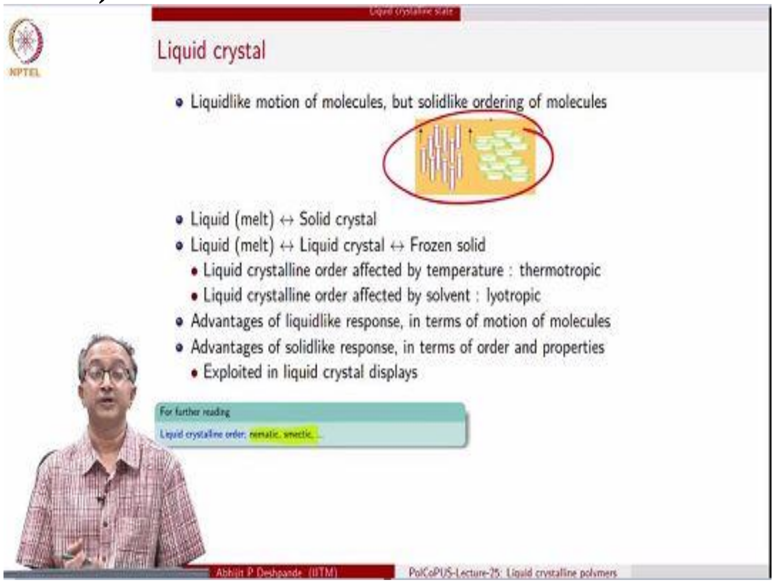

Liquid crystalline state

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For further reading

Liquid crystalline order: nematic, smectic, ...

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So, there are various possibilities of liquid crystalline polymers. Also, the ordering is of different type. And again you can go through and familiarize yourself with nematic and smectic. And in fact, if you do just an image search, you will see beautiful pictures of how some of these materials can organize themselves in variety of different ways. Of course, liquid crystal given these kinds of arrangements have very interesting optical properties.

And that is why liquid crystal displays and there are so many products, which are related to optical properties of these materials. In case of polymers, so, we will see, mechanical performance is what is the biggest advantage.

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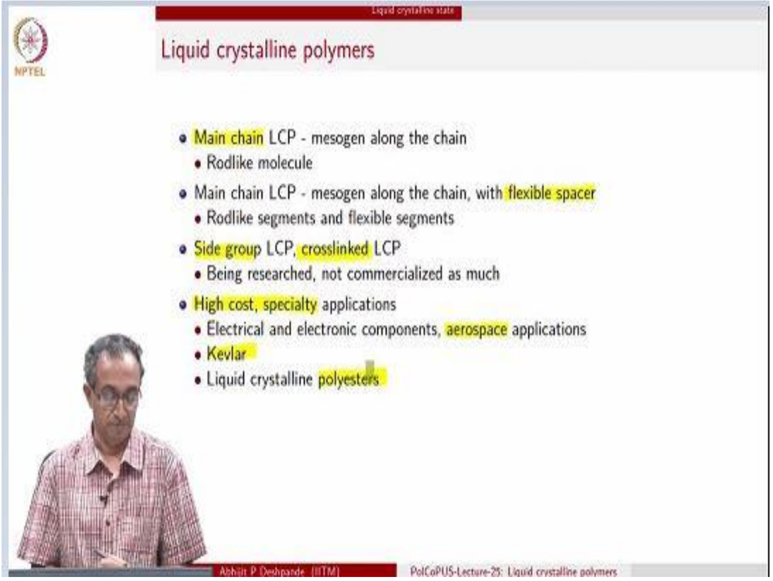

Liquid crystalline polymers

- Main chain LCP - mesogen along the chain
  - Rodlike molecule
- Main chain LCP - mesogen along the chain, with flexible spacer
  - Rodlike segments and flexible segments
- Side group LCP, crosslinked LCP
  - Being researched, not commercialized as much
- High cost, specialty applications
  - Electrical and electronic components, aerospace applications
  - Kevlar
  - Liquid crystalline polyesters

So, the liquid crystalline polymers can have the mesogen along the main chain or they can also have in between a spacer. So, we can have mesogen which is rigid rod like entity and then in between there can be spacers. So, for example, if there is a copolymer of ethylene and other components, then the ethylene component will be flexible and the other components will be rigid given our discussion so, far, can you try to guess what would these other components be? What kind of bonds along backbone might make the chain more rigid or less flexible?

And if you think and recall some of our earlier discussion, if you do not have single carbon carbon bond along the chain, that will immediately start leading to some amount of rigidity in macromolecular chain. So, couple of slides down you should not be surprised looking at the groups that we will see which are part of the mesogens. So, therefore, mesogens can be on the side group, they can be a crosslinked polymer can also have a the liquid crystalline mesogens on them. And generally these are fairly high cost speciality applications kind of material.

But given the requirements, let us say in electronic industry or aerospace applications, we use some of these materials. Of course, Kevlar is the most prominent example of these kinds of liquid crystalline material. And we also polyesters, of course, are very common material used in variety of applications. We also have liquid crystalline polyesters, which are quite common.

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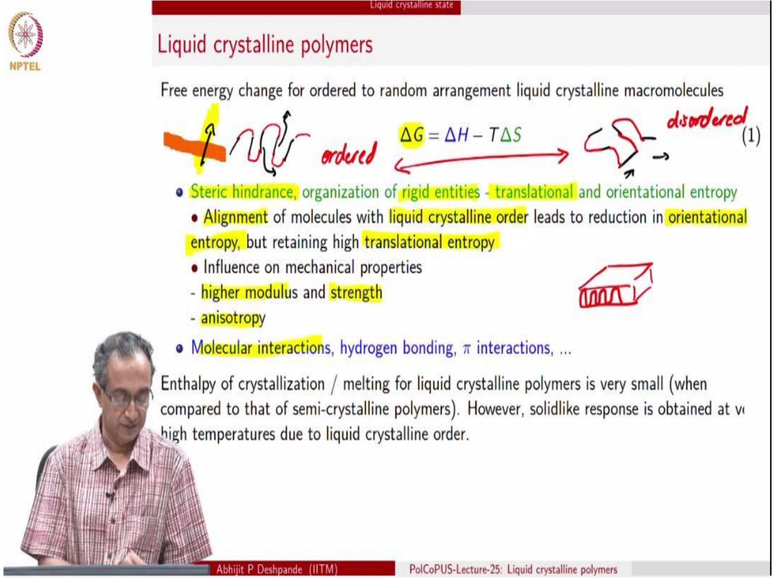

Liquid crystalline state

Liquid crystalline polymers

Free energy change for ordered to random arrangement liquid crystalline macromolecules

$$\Delta G = \Delta H - T\Delta S \quad (1)$$

- Steric hindrance, organization of rigid entities - translational and orientational entropy
  - Alignment of molecules with liquid crystalline order leads to reduction in orientational entropy, but retaining high translational entropy
  - Influence on mechanical properties
  - higher modulus and strength
  - anisotropy
- Molecular interactions, hydrogen bonding, π interactions, ...

Enthalpy of crystallization / melting for liquid crystalline polymers is very small (when compared to that of semi-crystalline polymers). However, solidlike response is obtained at v high temperatures due to liquid crystalline order.

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So, we look at them. Before we go on there, let us just look at thermodynamically what it means to have this liquid crystalline order, if you look at the free energy change for this transition between disordered mesogens of a macromolecular chain, so, I am not drawing the overall macro molecular chain, but you can understand that you know, this is part of let us say a macro molecule, and then we are the looking at the rod like segments ordering themselves.

So, you could have an ordered state or you may have disordered state and so, in both of these cases, so, this is a disordered state. So, we had when we look at these transition we are looking at from disordered state to an ordered state. And so, the Gibbs free energy change for this as we know can be thought of as 2 different components one is related to enthalpic component, which is based on interaction between macromolecules.

And the other one is related to the entropic component, which talks about the ordering as well as the number of different ways in which these macromolecular segments can be positioned with respect to each other. So, therefore, depending on the macromolecule that we have, and depending on the kind of steric hindrance that is present or in these organization of rigid entities, we will have differences in terms of the entropy, what we have as I mentioned is there is exchange possible between so, between different segments.

So, this can diffuse this can diffuse and so, therefore, they can change place, but the overall orientational order remains fixed. So, macromolecular change and especially the red part here can move around and because of that the rigid mesogens can also move about while still maintaining their orientation. And of course, in this case, they are all randomly oriented in any case, and they will continue to be randomly oriented even if the red segments move.

So, therefore, the alignment when happens of these mesogens, that leads to a decrease in orientational entropy, because instead of these being oriented randomly they are all oriented and in one direction, but at the same time translational entropy is still possible. So, therefore, high degree of translation entropy is retained and this is the liquid like character. So, we have a solid like character which is orientational entropy being lost. And we have translational entropy still being high, which is a liquid like character.

So, molecules and mesogens in this case can exchange places and they can diffuse around. And so, the influence of this orientational order is on very high modulus and strength. So, therefore, very good mechanical properties, the other feature that ends up being attributed to these polymers is because of this orientation anisotropy comes in, so, the properties in one direction, so, in this direction are going to be very different compared to properties in this direction.

Of course, in a bulk sample, we may have many such domains and they are all randomly oriented. So, in that case the overall bulk samples still may be isotropic, but, we will see at the end of this class that how we can try to purposely orient most of the liquid crystalline order especially, let us say in a fiber, when you have a fiber and if you want all the orientational order in the fiber direction, we can get a very strong fiber if we do that.

So, therefore, this orientational order is exploited for achieving very good mechanical properties. Now, over and above this entropic considerations of organization and assembly of these mesogens we also have molecular interactions. And of course, these molecular interactions could be in the form of hydrogen bonding or in the form of pi interactions, we will see that variety of these mesogens and rigid rod like entity will have benzyl groups.

And so, therefore, there is pi pi interactions or stacking possible, so benzyl group can be part of as a disk and therefore, this can stack as we just saw. So, therefore, these interactions are important also. So, the overall Gibbs free energy for whether liquid crystalline order will occur or not will depend on both of these factors. However, one thing we need to keep in mind is the enthalpy of crystallization for disorder to order liquid crystalline system is much less compared to a crystalline melt to crystalline order that we already discussed in 17th and 18th lecture earlier and that is because the orientational order is only present translational entropy is still present and therefore, there is flexibility of molecular motion. While in case of a crystal, what we saw is there will be a folded chain crystal and of course, this will be only vibrations around mean positions is permitted. So, therefore, this is a perfectly solid like material while what we have in liquid crystalline cases is still liquid crystalline order present.

And so, the overall energy change when we go from random to liquid crystalline order is much less compared to a melt to crystal transition.

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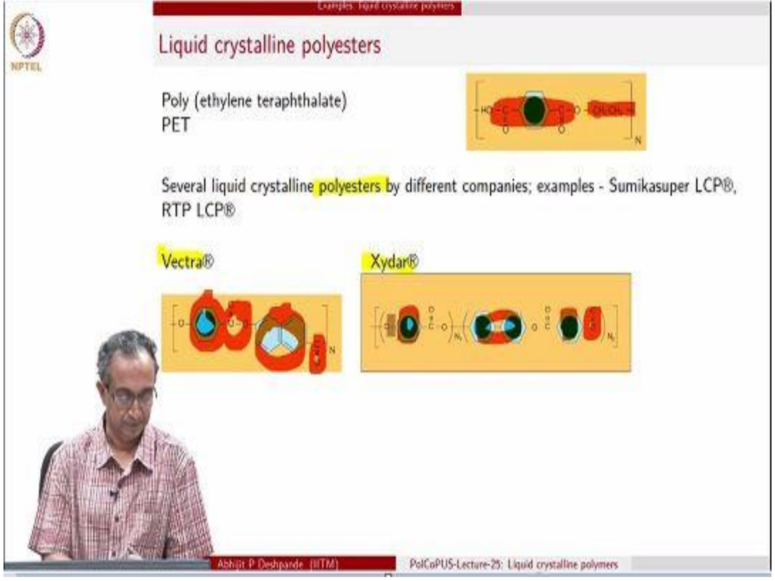

Examples: liquid crystalline polymers

Liquid crystalline polyesters

Poly (ethylene teraphthalate)
PET

Several liquid crystalline polyesters by different companies; examples - Sumikasuper LCP®, RTP LCP®

Vectra®

Xydar®

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So, now, let us look at some of the commercially available examples of these. And just to compare, let us look at polyethylene terephthalate. So, the ethylene group of course, gives it the flexibility but we also have the terephthalic acid associated group and so, polyethylene terephthalate of course, has a glass transition temperature of 75 to 80 degrees Celsius as opposed to polyethylene which is in - 60 to - 80 degrees Celsius.

So, therefore, PET already has molecular rigidity much higher than polyethylene. However, still because of the polyethylene groups, cc bond being present bond rotation around that is possible. Now, instead of these if we look at other polyesters, which are commercially available, and here, there are 2 examples of it, you can see that now, we have the same way, bulkier groups along the backbone. And also we have ketone linkages, which actually will prevent any rotation.

So, that is the key to get liquid crystalline order. So, this molecule has lot more rigidity compared to the ethylene segments that are there in PET. So, therefore, we have polyesters which is PET and polyester which is let us say Sumikasuper LCP or RTP LCP or these Vectra and Xydar and the cleverness here is in terms of introducing mesogens or rigid entities along the macromolecules chain, using similar chemistry of forming basically acid and alcohol reaction to get polyesters.

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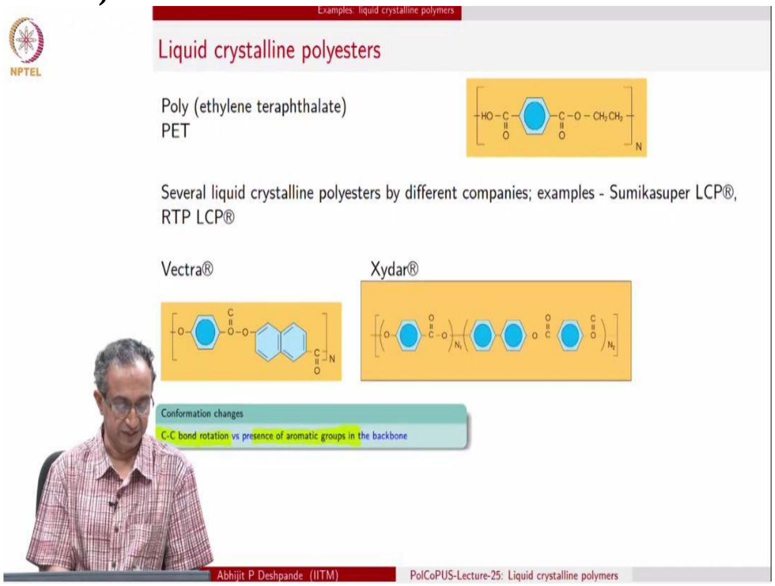

Examples: liquid crystalline polymers

Liquid crystalline polyesters

Poly (ethylene teraphthalate)
PET

Several liquid crystalline polyesters by different companies; examples - Sumikasuper LCP®, RTP LCP®

Vectra®

Xydar®

Conformation changes

C-C bond rotation vs presence of aromatic groups in the backbone

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So, one of the key feature in summary is to say to basically avoid the carbon-carbon bond rotation and then presence of bulkier groups along the backbone to improve the chain rigidity.

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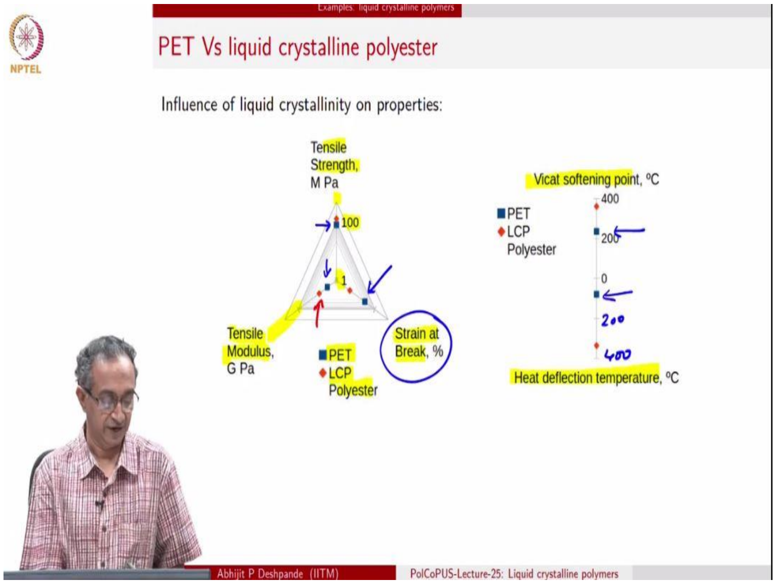

Examples: liquid crystalline polymers

PET Vs liquid crystalline polyester

Influence of liquid crystallinity on properties:

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So now, just to give you how much difference does this make by just me introducing these mesogens, and in this slide, I have taken commercially available data based on PET and liquid crystalline polymer, just to give you an idea of how much difference does it make, and this is a slightly complex diagram. So, just spend some time looking at what is being tried to say. So, we are looking at 3 different properties, tensile strength, tensile modulus and strain at break.

So, we are looking for 2 different materials, PET, PET bottle, PET, and then liquid crystalline polyester. And let us look at tensile modulus first you can see that the scale goes from 1 to 100. And then of course, this is 200 also. So, you can clearly see that the LCP polyester has higher modulus compared to PET. Similarly, you can also see tensile strength of PET is less compared to the LCP polyester. And this is a logarithmic scale, by the way, so, the difference between the 2 is quite huge. It is more than 3, 4 times some of these property changes.

But on the other hand, if you focus on strain at break, you can see that strain at break for PET is much higher. So, clearly, therefore, the PET is less stiff, it is less strong, but it is more flexible compared to the LCP polyester. You can also look at the thermal response of it. And we have already seen that, instead of looking at glass transition temperature as a transition, many engineering applications, people look at the vicat softening point or the heat deflection temperature.

And in both cases, you can see that the PET is much less compared to the transition points. You can see here the difference if so, this is 200, and this is 400. So, you can see what the deflection temperature increases by 200 300 degrees Celsius. So, that is the advantage that you can get by introducing liquid crystalline order in a material. And while processing you introduce this order, and then bring it below glass transition temperature, and now, because of that order, which is present in the sample, the mechanical properties get a tremendous boost.

The thermal stability of the sample also increases very significantly. So, that is why you can see the other claim that I made that even though these materials are expensive, due to the chemistry and processing of them, they are still used in a fair number of niche applications.

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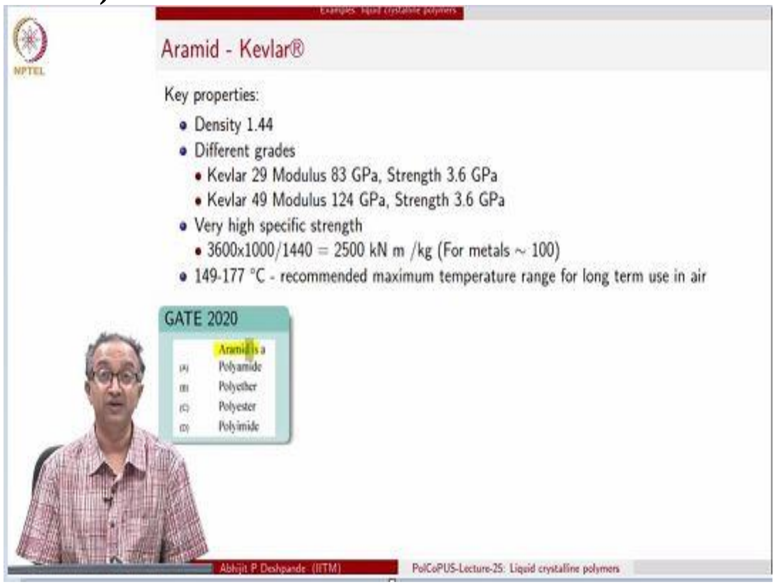

Examples: liquid crystalline polymers

Aramid - Kevlar®

Key properties:

- Density 1.44
- Different grades
  - Kevlar 29 Modulus 83 GPa, Strength 3.6 GPa
  - Kevlar 49 Modulus 124 GPa, Strength 3.6 GPa
- Very high specific strength
  - 3600x1000/1440 = 2500 kN m /kg (For metals ~ 100)
- 149-177 °C - recommended maximum temperature range for long term use in air

GATE 2020

Aramid is a
(A) Polyamide
(B) Polyether
(C) Polyester
(D) Polyimide

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And Kevlar which is the most commonly known and popular example, because of its spectacular properties is useful, because of this liquid crystalline order. And basically its properties are extremely high. So there are different grades of Kevlar which are present and property can be as high as 130 Giga Pascal's and, more importantly, its specific strength. And by specific strength, we mean the strength or any mechanical property, per unit mass per unit weight of the polymer.

And you can see that in aerospace applications, this will be such a premium, quality to have that if your specific property is very high, which means you need to use less of your material in terms of mass, and which is the key characteristic for a material being very light and useful. So, for metals, for example, this is around 100, but for Kevlar, it is 2500. So, there you can see 25 times specific mechanical properties.

And the temperature range for long term use in here is also very significant. So, you can use, for example, in a variety of applications, where temperature can be as high as 150 degrees Celsius. So, just to let you know that, you know, since, as polymer scientists and engineers, this is one of the successful examples of manipulating molecular level details to achieve spectacular performance. And so, Aramid you can look up and try to see which family of polymer does it belong to? Is it a polyether? Is it a polyamide? Or is it a polyimide.

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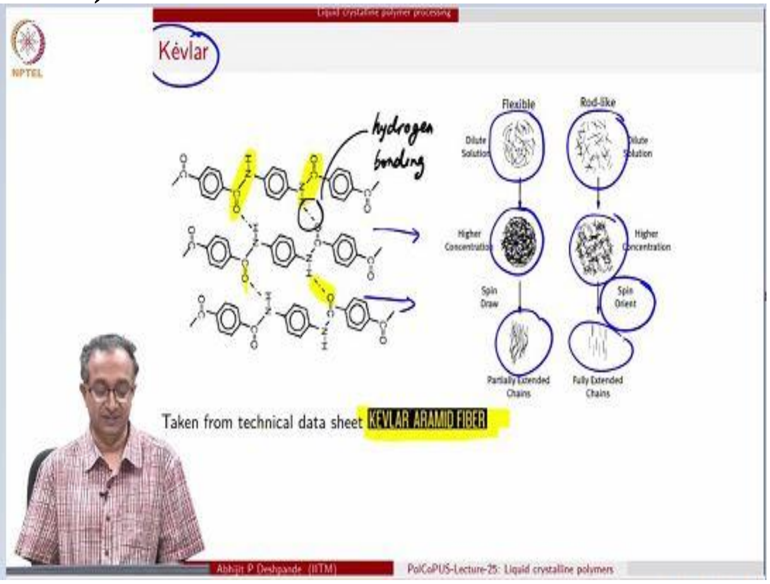

Liquid crystalline polymer processing

Kevlar

Taken from technical data sheet KEVLAR ARAMID FIBER

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And the other thing about Kevlar, and this is taken from the commercially available datasheet as to how you can exploit this liquid crystalline order during processing to organize the order. And then once we bring it below glass transition temperature, the order gets frozen. And we have excellent mechanical properties. So, in case of Kevlar, if you notice these groups, you can answer the question which is there on the previous slide.

And the key feature here is these hydrogen bonding between these moieties I am not going to take the name of these moieties because I want you to think about the answer on the previous slide. But you can see that basically there is a stacking of these chains because of these strong interactions between different chains of polymer, and so, you can see that there is therefore an orientational order which is present.

So now if you look at any macro molecular system and if let us say it is a flexible macro molecular system in dilute systems basically there will be macromolecule orientation in all random direction, even if you increase the concentration, the randomness will remain. And if we now extrude this polymer out of a narrow opening, and then if we stretch it to make a fiber, let us say then what we will end up getting is of course, partially extended chains.

And this we have seen orientation of macromolecular systems, we looked at in a quite a bit detail in lecture 20. And now, instead of this flexible segments, if we have rod like segments, so, in case of dilute solution also these will be present but randomly organized, even when we increase the concentration, there will be some tendency now, because of the concentration is too high, instead of them being criss crossing each other, there will be some tendency for them to start ordering themselves.

And if you now do processing, where you try to extrude them spin them through a very narrow opening, and also then stretch them. So then what happens is you will get a perfect, fully extended orientational order. And so this is what is the key to the performance of Kevlar and variety of other liquid crystalline systems.

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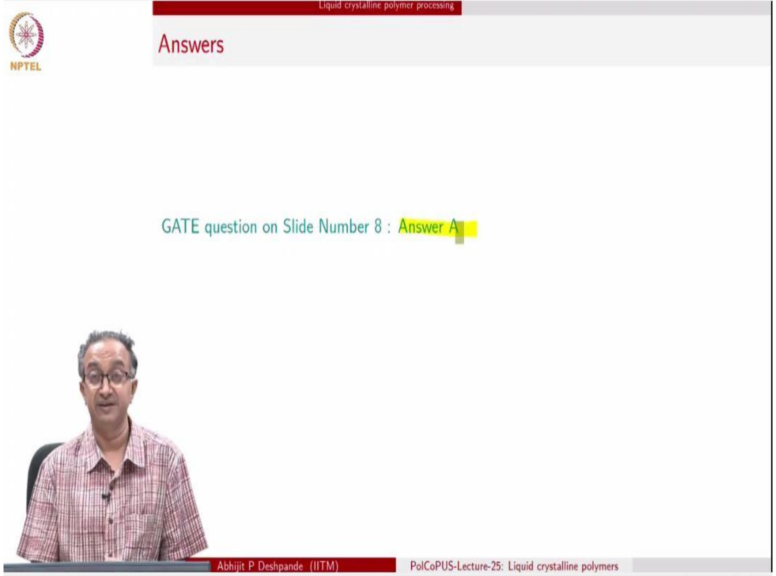

Liquid crystalline polymer processing

Answers

GATE question on Slide Number 8 : Answer A

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And so with this, we will close this lecture, and I am sure all of you have already narrowed down what family of Kevlar does belong to thank you.