Polymers: Concepts, Properties, Uses and Sustainability

Prof. Abhijit P Deshpande
Department of Chemical Engineering
Indian Institute of Technology – Madras

Lecture - 52

Impact and Energy Absorption

So let us continue our deep dive into viscoelasticity of polymers and while we are discussing properties of viscoelasticity at different times temperatures frequencies, in this particular lecture we will focus on high strain rates and high strain rates is when impact and the energy absorption capability of polymeric materials is very important and application wherever you want to prevent the energy transferred due to impacts, so where the material should absorb the energy. So in some sense, these are sacrificial materials, so they absorb the energy; they might start fracturing; they might get damaged, but this is classically what is expected of a helmet also, so which is an energy absorbing material on impact. So polymers are used very strong, very commonly in these applications because of their strength in terms of high impact properties. So we will discuss these properties by keeping their applications in mind.

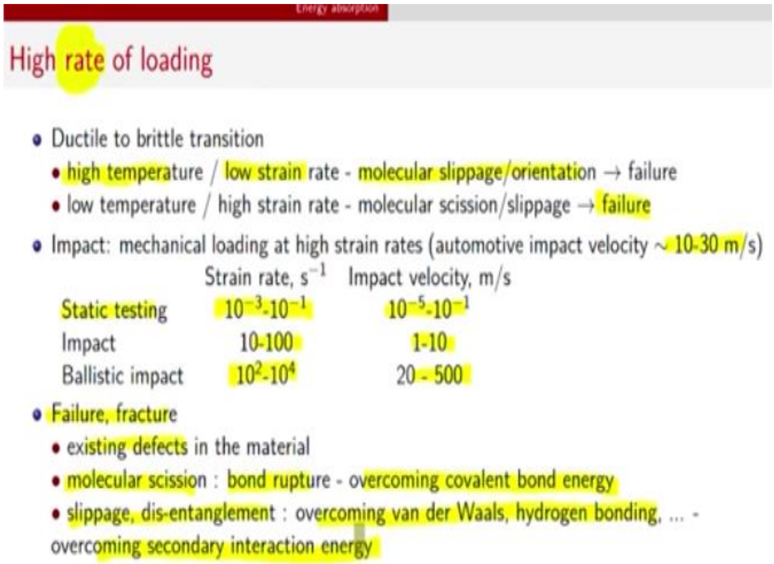
(Refer Slide Time: 01:19)

Overview

1. Energy absorption
2. Impact testing

By first examining the phenomena of energy absorption and then specific testing which is done to assess the capability of energy absorption in polymeric materials by doing what is called impact testing,

(Refer Slide Time: 01:30)



Energy absorption

High rate of loading

- Ductile to brittle transition
  - high temperature / low strain rate - molecular slippage/orientation → failure
  - low temperature / high strain rate - molecular scission/slippage → failure
- Impact: mechanical loading at high strain rates (automotive impact velocity ~ 10-30 m/s)

	Strain rate, s^{-1}	Impact velocity, m/s
Static testing	10^{-3}-10^{-1}	10^{-5}-10^{-1}
Impact	10-100	1-10
Ballistic impact	10^{2}-10^{4}	20 - 500

- Failure, fracture
  - existing defects in the material
  - molecular scission : bond rupture - overcoming covalent bond energy
  - slippage, dis-entanglement : overcoming van der Waals, hydrogen bonding, ... - overcoming secondary interaction energy

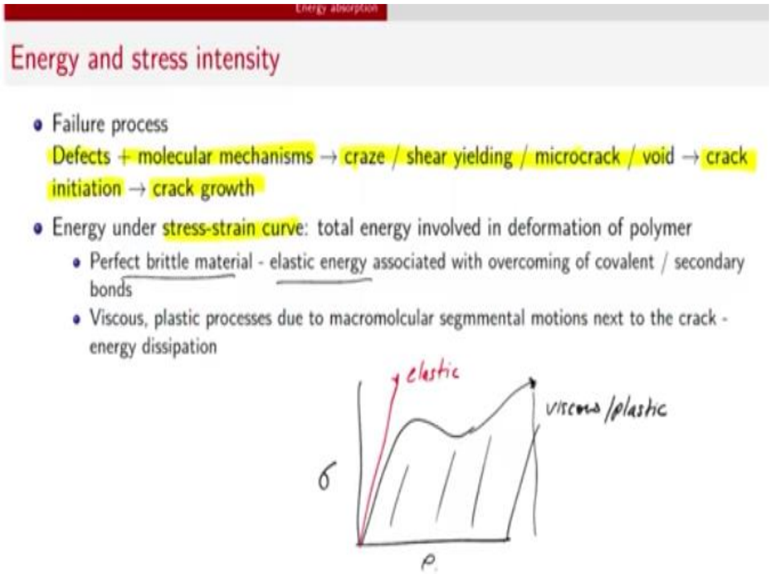
And so generally, the rate of loading is an important factor. How high is the rate of stress or strain application and in fact, this can lead to the behavior changing and we have already discussed this that at low temperature you might see a very brittle material, but at high temperature you might see a flexible and soft material and so if you go to high temperature or you go to low strain rates, basically these mechanisms of molecular slippage and orientation start happening and eventually failure happens.

But at low temperature or very high strain rates, the slippage and orientation all of these processes cannot take place because the rate of fluid loading is very high. So consequently what happens is the molecular breakage or some of the phenomenon which has to happen for failure to happen and just to give you an idea of how different rates are; you know the bus or truck or car or two wheeler velocities are 10 to 30 m/s. When we do static testing, we are doing it at fairly low velocities or the strain rates are 10^{-1} and lower. Impact testing on the other hand is at much higher loads and of course, this is where, let us say, accidents or something which falls. This is where impact may be of relevance, but we also have ballistic impact in case of a bomb explosion, in case of a bullet. So there the rates are even more higher and so the velocities are higher and the strain rates are higher.

So generally when we think of impact, its high strain rate but not extremely high, which is called ballistic. So when we discuss impact we are going to confine our attention to non-ballistics or high strain rates, but more from the point of view of impact to some collision or impact due to impact that can material withstand when it falls and so on. So there the velocities of 1 to 10 m/s are typical. And so we just should remember that failure in the material is because of the existing defects that are already there in the material. There will be voids. There may be some micro cracks during processing. Because of aging effects in the material certain amount of defects may have accumulated. So all of this is always there in the material and when processes of failure and fracture starts happening in case of macromolecules, macromolecules have to start breaking. So bond rupture or overcoming the covalent bond energy between different monomers is a key phenomenon, which has to happen for fracture to take place and of course by overcoming the secondary interactions we can also have other processes which again are precursors to eventual failure. So overcoming secondary and interaction energy is also important. So failure involves all of these and this probably can then give you an idea as to why rates matter.

Because depending on the rate which is there, some of these will take place and some of this may not. So depending on the kinds of defects which are there in the material, depending on what are the segmental flexibilities and whether slippage and disentanglement is possible or not, the overcoming of secondary interaction may be possible in a given rate of loading or it may not be possible. So therefore, different rates of loading lead to different kind of mechanical response from the material.

(Refer Slide Time: 05:14)



Energy absorption

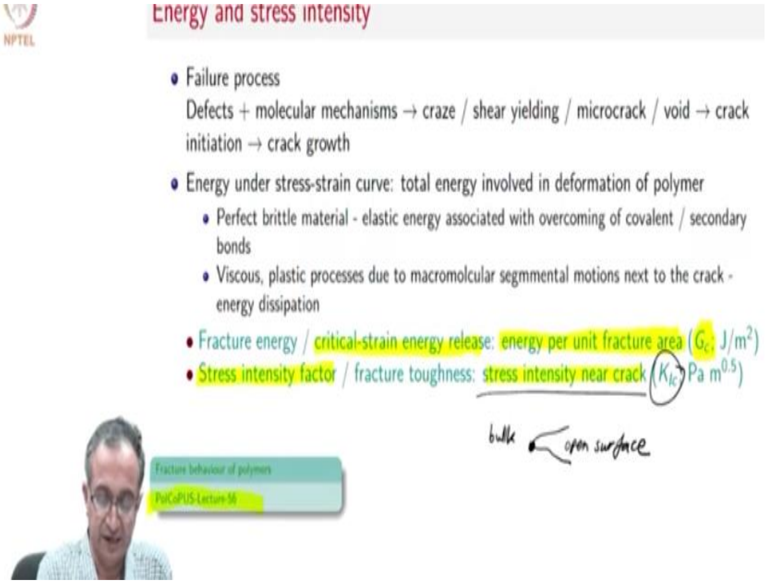
Energy and stress intensity

- Failure process
  Defects + molecular mechanisms → craze / shear yielding / microcrack / void → crack initiation → crack growth
- Energy under stress-strain curve: total energy involved in deformation of polymer
  - Perfect brittle material - elastic energy associated with overcoming of covalent / secondary bonds
  - Viscous, plastic processes due to macromolcular segmmental motions next to the crack - energy dissipation

So generally therefore, a failure process the defects and molecular mechanisms together and leads to certain microstructural features, which could be a micro crack, which could be avoid, which could be a shear inlet zone or crazing in the materials and eventually when accumulation of these happens, a crack starts and generally we try to distinguish as a micro crack and a macro crack. So macro crack is when the failure is eminent and then this crack can grow leading to failure. So this phenomenon can be analyzed using the stress strain curve also that we have discussed earlier, because if you remember we had discussed stress as a function of strain and depending on the kind of materials you have stress strain may vary and we had also talked about the overall energy, which is involved in the stress strain curve is basically some amount of a measure of how much energy can the material absorb before it eventually fails.

So a perfect brittle material will have only elastic energy associated. So if at all let us say we have a material, which is a perfectly brittle material, basically till failure there is only elasticity involved; but on the other hand many of the polymeric materials will have other processes which are viscous and plastic and so crack propagation and how the crack grows is very different in these two materials; but generally lot of fracture mechanics initial concepts are developed based on elasticity or elastic materials. But many of these have been now extended to viscous and plastic materials, because near the crack what happens is very different in case of an elastic material, which has only energy storing capacity while for a viscous plastic material there is energy dissipation and structural rearrangement of macromolecules is possible.

(Refer Slide Time: 07:22)



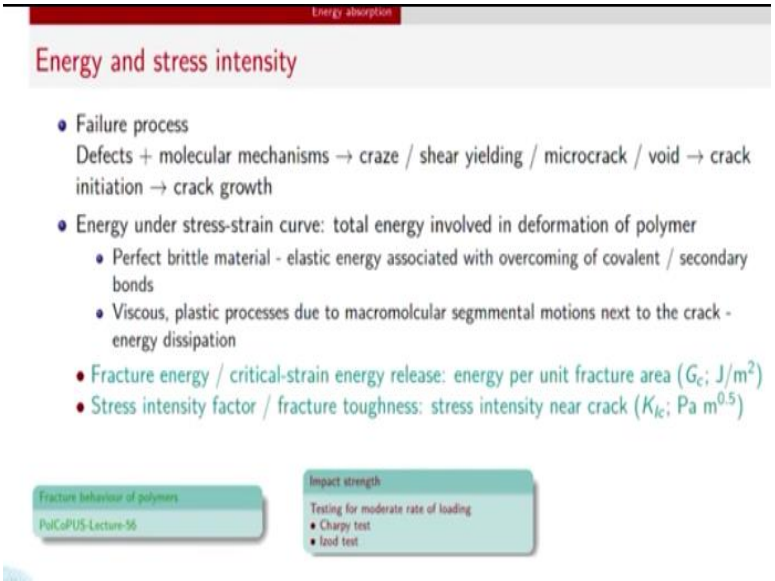
Energy and stress intensity

- Failure process
  Defects + molecular mechanisms → craze / shear yielding / microcrack / void → crack initiation → crack growth
- Energy under stress-strain curve: total energy involved in deformation of polymer
  - Perfect brittle material - elastic energy associated with overcoming of covalent / secondary bonds
  - Viscous, plastic processes due to macromolcular segmmental motions next to the crack - energy dissipation
- Fracture energy / critical-strain energy release: energy per unit fracture area (G_c; J/m^2)
- Stress intensity factor / fracture toughness: stress intensity near crack (K_{Ic}; Pa $m^{0.5}$)

So given that there are several ways in which we can analyze this fracture phenomena; one is by looking at what is called a critical strain energy release rate and this is factor G. It is basically energy per unit fracture area. So one measure we saw earlier which was based on stress strain curve and the overall integral of that, but that is completely talking about elastic, plastic all of the deformations in overall energy involved. But more importantly we would like to know that given there is a crack growing in the material and crack implies that some area of the material is getting exposed, because crack is nothing but generating new surface in the material. So what is the energy absorbed per unit area of this crack surface, which is opening up? So that is why energy per unit fracture area is quantified using this variable called critical strain energy release. The other way we analyze this problem is by looking at what is called stress intensity factor, which is basically the stress intensity near a crack; because near a crack there are there is a singularity. There is a point at which there is one phase and then there is another. So crack is basically nothing but here, so this is open surfaces of the material and here is the bulk material. So at the crack tip basically stresses get intensified and that is what is quantified using stress intensity and it is a factor called K_{ic}.

So using both of these approaches, we can look at the fracture phenomena, what happens when a crack is there in the material, how does the crack grow, what is the energy required for stress crack growth in the material and so on. So these concepts of fracture energy and stress intensity factor, we will discuss in a subsequent lecture related to the fracture behavior of polymers.

(Refer Slide Time: 09:27)



Energy absorption

Energy and stress intensity

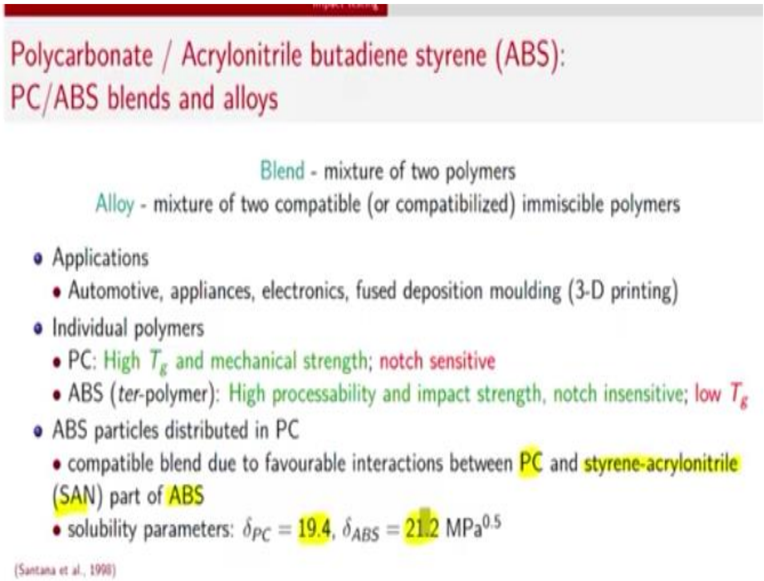
- Failure process
  Defects + molecular mechanisms → craze / shear yielding / microcrack / void → crack initiation → crack growth
- Energy under stress-strain curve: total energy involved in deformation of polymer
  - Perfect brittle material - elastic energy associated with overcoming of covalent / secondary bonds
  - Viscous, plastic processes due to macromolcular segmmental motions next to the crack - energy dissipation
- Fracture energy / critical-strain energy release: energy per unit fracture area (G_c; J/m^2)
- Stress intensity factor / fracture toughness: stress intensity near crack (K_{Ic}; Pa m$^{0.5}$)

Fracture behaviour of polymers
PolCoPUS-Lecture-56

Impact strength
Testing for moderate rate of loading
- Charpy test
- Izod test

In this particular lecture, we will focus more on the impact properties, which are loading at a range which is not very high so that it is ballistic or it is not low, so that we get the overall stress strain curves in the material and generally the impact stress strength is measured using trade tests. So these are tests where Charpy and Izod where you take a specimen of a given dimension and subject it to a particular test and get the numbers in terms of impact strength.

(Refer Slide Time: 09:58)



Polycarbonate / Acrylonitrile butadiene styrene (ABS):
PC/ABS blends and alloys

Blend - mixture of two polymers
Alloy - mixture of two compatible (or compatibilized) immiscible polymers

- Applications
  - Automotive, appliances, electronics, fused deposition moulding (3-D printing)
- Individual polymers
  - PC: High T_g and mechanical strength; notch sensitive
  - ABS (*ter*-polymer): High processability and impact strength, notch insensitive; low T_g
- ABS particles distributed in PC
  - compatible blend due to favourable interactions between PC and styrene-acrylonitrile (SAN) part of ABS
  - solubility parameters: $\delta_{PC} = 19.4$, $\delta_{ABS} = 21.2$ MPa$^{0.5}$

(Santana et al., 1998)

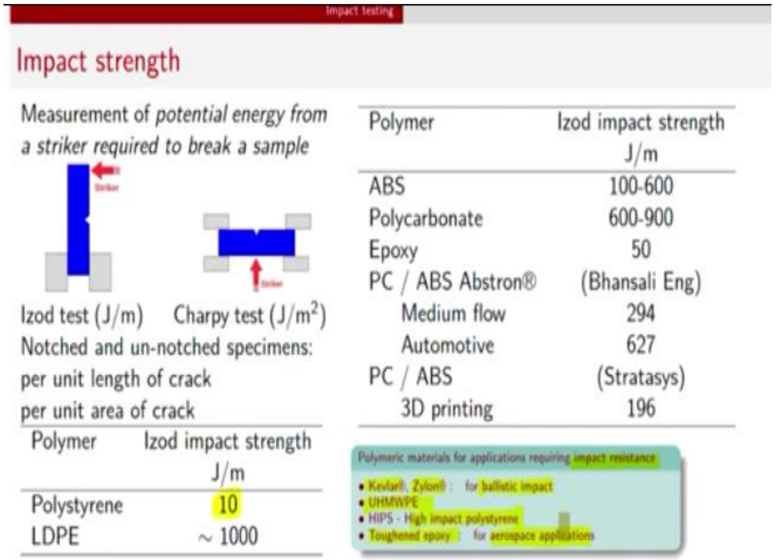
So before we look at impact strength, let us look at an example application material. So the polycarbonate and ABS acrylonitrile butadiene styrene, this blend copolymer system are very popular in terms of application just to highlight the difference, blend is basically a mixture of two polymers. We can have miscible blend, partially miscible, immiscible blend. Generally, we refer to alloy whenever we have an immiscible polymers, but we have done some compatibilization between these two phases. So that is why compatibilized or compatible immiscible polymer blends. So even though the 2 polymers are immiscible at the interface, there is some interaction between the macromolecules of one with macromolecules of another and applications of this polycarbonate ABS alloys are plenty. Whether in automotive or appliances, electronics, fuse deposition, not really molding because molding is a common process to be used for polymers, but this is called fused deposition modeling.

You can search; this is a very popular technique for 3D why would you think that it is called modeling and given that prototyping is a very important manufacturing activity, you will see that this FDM as it is called is used very commonly for prototyping and that will give you a clue as to why this is called modeling. Now if you look at the individual polymers themselves, so polycarbonate has a nice high class transition temperature. So it could be used for a wide variety of temperatures and good mechanical strength. But it is very sensitive to how it fails depending on whether there is a notch. Notch is nothing but a predetermined defect, which is introduced in the material and so for example, if this is a sample a notch sample is basically where we introduce defect like that. So notches can be of several different kinds and practitioners of the measurements of these kinds, we will say that a particular kind of notch gives us much better data which is correlated well with the application that we have. So notch resistance and not sensitivity is a key issue related to assessing how good or bad the material may be for a given application. ABS on the other hand is very nice in terms of processability, the viscosity and how it processes into complex shape is all very reasonably manipulated and you can have a good control over processability of ABS. Its impact strength is also high, though its overall strength in terms of tensile strength or flexural strength may not be high impact properties are very good. And it is also fairly notch insensitive, but of course it has low glass transition temperature and this is how then blending is done. Given that each of them seems to have certain strengths and weaknesses, can we not combine them and get a tunable blend in this case a tunable alloy also because they are compatible at the interface, we can get basically PC ABS blends and alloys and generally we have these abs particles which are distributed in polycarbonate phase.

That is how these blends are arrived at and because there is a favorable interaction between polycarbonate and styrene acrylonitrile part of ABS, this again you can ascertain by just looking at solubility parameters. They are very close to each other. Solubility parameter of polycarbonate is 19.4 and that of ABS is 21.2. So therefore, they are reasonably compatible though immiscible.

So that is why they form an immiscible blend, but they are compatible at the interfaces due to some selective interactions between chains of polycarbonate and chains of styrene acrylonitrile part of the ABS macromolecular system.

(Refer Slide Time: 14:07)



Impact testing

Impact strength

Measurement of *potential energy from a striker required to break a sample*

Izod test (J/m) Charpy test (J/m^2)
Notched and un-notched specimens:
per unit length of crack
per unit area of crack

Polymer	Izod impact strength J/m
Polystyrene	10
LDPE	~ 1000

Polymer	Izod impact strength J/m
ABS	100-600
Polycarbonate	600-900
Epoxy	50
PC / ABS Abstron®	(Bhansali Eng)
Medium flow	294
Automotive	627
PC / ABS	(Stratasys)
3D printing	196

Polymeric materials for applications requiring impact resistance

- Kevlar®, Zylon® : for ballistic impact
- UHMWPE
- HIPS - High impact polystyrene
- Toughened epoxy : for aerospace applications

So let us look at now, how is impact strength measured. Basically what we do is, we take a load and then make it fall, make it impact a sample. So I could keep this as a sample and then I have a load which is let us say tied with a lever and if I leave it is going to come and impact here and that is what is shown here. So it is a striker which is released from a certain height. So we know what is the potential energy that it will gain in terms of arriving at a kinetic energy and therefore we will know what is the velocity of impact?

So impact testers will generally have different types of strikers and from different heights these strikers can be brought down, so that we can vary the impact loading and the striker basically impacts and given that it impacts the sample and we have introduced a notch there will be breakage of the sample and what we try to do is based on the motion of the striker, we can figure out how much of the energy of the striker was absorbed by this material?

And how much of the energy of striker is still remaining with the striker? Because if let us say the sample was not there, then striker will rise all the way to the other side and again potential energy will be equal, when the kinetic energy will go to zero. In this of course the friction due to air is negligible compared to the energy absorbed by the polymer. So therefore, just a very simple method with a dial we can actually ascertain the impact energy or impact strength of the material.

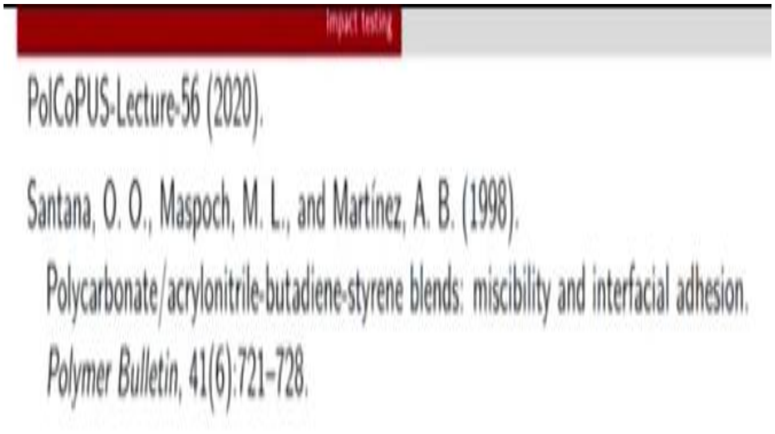
So these are 2 different tests. One is called the Izod. So you can see here in one case one side is clamped; in case of Charpy both the sides are clamped and then the striker hits in the center and generally you can do testing with notched or unnotched specimens and this measures of the impact strength sometimes are based on per unit length or per unit area of the crack. So in case of Izod test, we do per unit length of the crack.

In case of Charpy, it is done over per unit area of the crack and just to give you idea of number the Izod test for polystyrene, the impact strength is 10, but for LDPE which in fact sometimes may not even break the numbers are 1000 or above. So these huge uh three orders of magnitude 2, 3 orders of magnitude difference in terms of impact strength of different materials. Same numbers for ABS are 100 to 600. Polycarbonate also has high impact strength, but it is their blend which can give you processability; it can give you notch insensitivity and all of that combined with high strength and so impact strength can again be optimized based on the blend and these are 2 examples from two different companies and based on the technical data sheet that you can achieve different types. So this is a 3D printing grade which has about 196 impact strength and then there is an automotive or a medium flow grade. You can see that the medium flow grade probably is much easier in terms of processing, but it has lower impact strength. So depending on where this PC ABS blend and alloy is being used you can then make a judgment about what is the impact strength required and what is the processing is that is required. So in general there are several polymeric materials, which are used for impact properties.

In ballistic impact, we have famous example of Kevlar or Zylon which are used, even ultra high molecular weight polyethylene used in extremely demanding applications, because all the polyethylene chains which are completely linear are organized and oriented and crystallites, so that we get very high properties. Similarly, high impact polystyrene, so this is polystyrene as we saw the impact strength is very less, but if we introduce rubber particles in this. So we get high impact polystyrene, because the rubber particles can play the role of being stoppers for the crack growth and similar idea is also exploited in toughened epoxy, where epoxy and rubber particles are put together to increase the toughness or impact strength of epoxy materials, is used in composites in aerospace applications. So there are several examples and you can see that most of these cases it is the rubber particles which are being incorporated into another polymeric material to enhance its impact property.

So it is again rubber. Just the way rubber is a very good damping material; rubber is a very good crack arrester also and it can do this job by having interfaces in the material where crack now has to go longer distance, but it can also absorb the energy itself, because it allows segmental flexibility.

(Refer Slide Time: 19:02)



Impact testing

PolCoPUS-Lecture-56 (2020).

Santana, O. O., Maspoch, M. L., and Martínez, A. B. (1998). Polycarbonate/acrylonitrile-butadiene-styrene blends: miscibility and interfacial adhesion. *Polymer Bulletin*, 41(6):721–728.

So with this we will close the discussion related to the impact testing of polymers. Thank you.