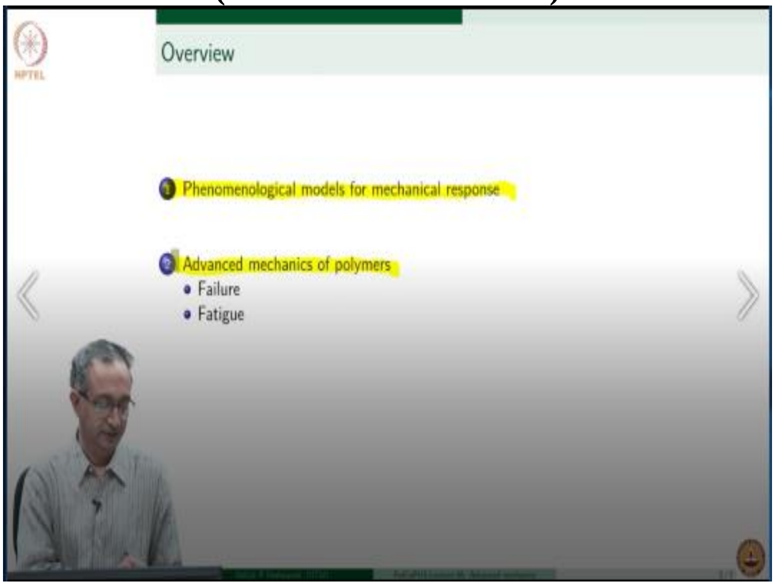
PolCoPUS
Prof. Abhijit P Deshpande
Department of Chemical Engineering
Indian Institute of Technology, Madras

Lecture No -56
Advanced mechanics

Hello, welcome to the course on polymers. In today's lecture we will try to summarize the overall mechanical response of polymers. We have seen that while in this week 8 we are discussing viscoelasticity of polymers the response is quite complex there are several facets of the response. And therefore, we adopt various experimental and theoretical means to try to understand viscoelasticity.

And not only that using these means we actually try to get at some of the information which is relevant for applications of these polymers. And so, in this lecture we will look at couple of advanced mechanical properties which are related to fracture and fatigue. And since this is a introductory course on polymers we will take a brief look at that and advanced students will have to go and do further studies related to these topics.

(Refer Slide Time: 01:09)

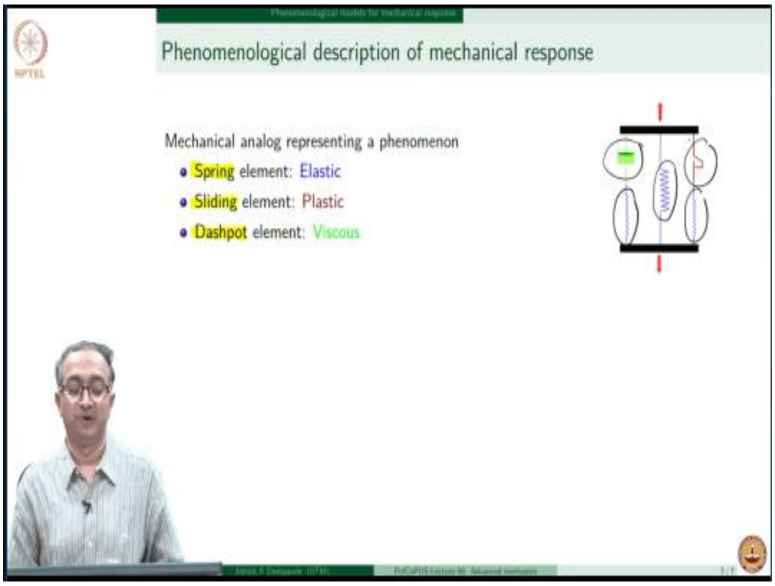


Overview

1. Phenomenological models for mechanical response
2. Advanced mechanics of polymers
   - Failure
   - Fatigue

So, to summarize whatever we have discussed so far we will quickly look at the phenomenological models that are used for mechanical response. And then we will finish the lecture by looking at failure and fatigue.

(Refer Slide Time: 01:25)



Phenomenological description of mechanical response

Mechanical analog representing a phenomenon

- Spring element: Elastic
- Sliding element: Plastic
- Dashpot element: Viscous

So, we have discussed phenomena of elasticity, plasticity and viscoelasticity. Viscoelasticity of course is combination of viscous and elastic. So, therefore from a preliminary analysis point of view and to get handle on you know how are these different phenomena exhibited by polymers. One could think of polymers as being represented by mechanical analogues and this is quite similar to electrical circuits analogy.

So, we have elements instead of resistors, capacitors and inductors. We have these different mechanical analogues which form so to speak a circuit representation of the material and so we have a spring element which represents the elasticity in the material. We have the viscous dashpot which represents the dissipation associated with viscous phenomenon and also, we can make a hypothesis of a sliding element.

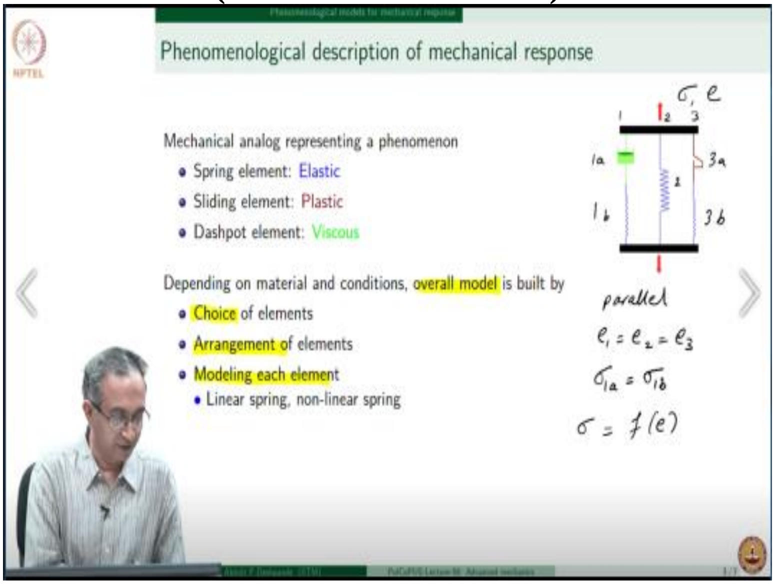
Sliding implies that you know in in plasticity what we saw is there is an yield stress. So, stress goes beyond yield stress then material starts deforming and stress relay remains relatively constant and but strain keeps on increasing. To represent this kind of behavior we can use a sliding element which remains stuck until a certain value of stress is reached. Once that value of stress is exceeded the slider becomes unstuck or slider starts moving and that implies there is deformation in the material.

So, therefore we can have the viscous dashpot, the elastic springs and a slider element. So, all of these can be used to think of phenomena of mechanical response of polymeric materials. Just cautioning you that these are just representations. We know that at the molecular level and microstructural level there are far more complicated mechanisms by which a polymeric material responds to loading stress or strain.

So, therefore these are our way of rationalizing and understanding how the behavior of polymers is. In terms of each of these phenomenon we can relate it back to the mechanistic details on at macromolecular or microstructural scale. For example, elasticity could be related to stretching of macromolecular chains. Sliding could be related to twisting or disentanglement of polymeric chains and so on.

So, therefore we can correlate many of these phenomena to microstructural details. And this is an exercise we must always continue doing if we have to get a better understanding of the viscoelastic response of polymers.

(Refer Slide Time: 04:21)



Phenomenological description of mechanical response

Mechanical analog representing a phenomenon

- Spring element: Elastic
- Sliding element: Plastic
- Dashpot element: Viscous

Depending on material and conditions, overall model is built by

- Choice of elements
- Arrangement of elements
- Modeling each element
  - Linear spring, non-linear spring

parallel

$e_1 = e_2 = e_3$

$\sigma_{1a} = \sigma_{1b}$

$\sigma = f(e)$

And so generally these models are useful and especially in the context of linear viscoelasticity many of these models are used. For non-linear deformation of materials we require much more different machinery, mathematical as well as conceptual to explain the behavior. However these are a good starting point in order to understand the material response. So, therefore the overall model can always be built based on you know choosing different elements.

So, a paint system may incorporate more viscous elements an elastomer may incorporate more spring like elements and so on. And for a semi crystalline polymer we may need a combination of all 3. So, we can choose depending on the material that we are trying to model and our hypothesis regarding what are the mechanisms in the material. And then after choice of elements there could be series, parallel combinations of these elements.

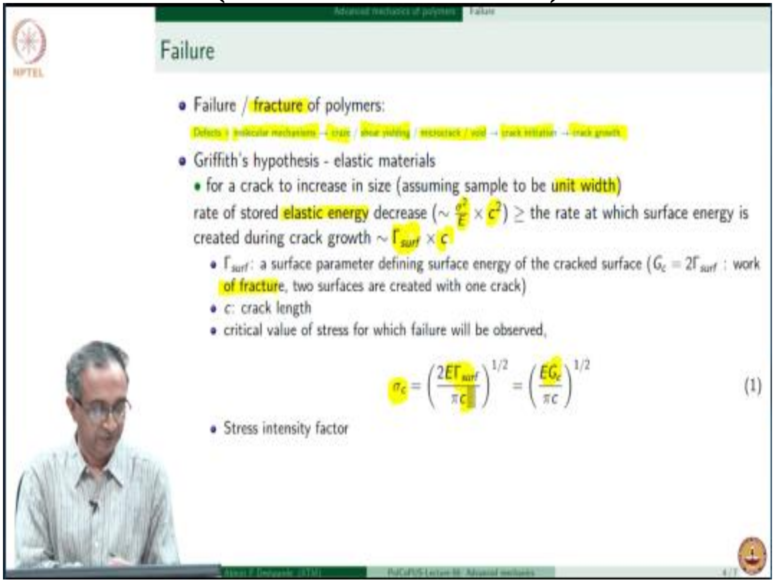
And given that material has multiple processes we saw there are multiple relaxation processes. So, we may need multiple springs and dashpots to represent multiple relaxation processes. Similarly, there may be couple of yielding phenomena each associated with a different mechanism. One associated with the amorphous part one associated with the crystalline part. Then we might have two different sliding elements and so on.

And then of course we have model for each elements. So, this is just like in circuit we know V= IR for a resistor and for a capacitor we have an equation. And then when we combine series parallel we can look at current and voltage across the overall circuit and then simplify it. So, here also for example we can look at the overall stress and strain. So, if let us say there are these different combinations in parallel and then you have 1a and 1b.

And similarly 2 and this is 3a and 3b. We know that stresses. So, when we have a series and parallel combinations of these we know that when they are let us say in parallel then strain is same in all of them. But when they are in series then stress is same in all of them. So, using these criteria we can then try to arrive at what is the relationship between the stress and strain. And of course these will involve derivatives of stress and derivatives of strain and so on.

So, this is as far as overall description of mechanical response is concerned which is related to deformation in the material and looking at stress strain response and stress as a function of time and strain as a function of time.

(Refer Slide Time: 07:05)



Advanced mechanics of polymers | Failure

Failure

- Failure / fracture of polymers:
  Defects → molecular mechanisms → craze / shear yielding / microcrack / void → crack initiation → crack growth
- Griffith's hypothesis - elastic materials
  - for a crack to increase in size (assuming sample to be unit width) rate of stored elastic energy decrease ($\sim \frac{\sigma^2}{E} \times c^2$) $\geq$ the rate at which surface energy is created during crack growth $\sim \Gamma_{surf} \times c$
    - Γ_{surf}: a surface parameter defining surface energy of the cracked surface ($G_c = 2\Gamma_{surf}$: work of fracture, two surfaces are created with one crack)
    - c: crack length
    - critical value of stress for which failure will be observed,

$$\sigma_c = \left(\frac{2E\Gamma_{surf}}{\pi c}\right)^{1/2} = \left(\frac{EG_c}{\pi c}\right)^{1/2} \qquad (1)$$

    - Stress intensity factor

Over and above this there are two important features which are very important from practical points of view are related to failure of the materials. And so, fracture in polymers is basically a phenomenon which happens because there are already defects present in the material. And then we have several molecular mechanisms because of the deformation which is being imposed on the material we can have crazing happening shear yielding happening and which leads to micro cracks and voids.

And eventually this leads to a macro crack which then can start growing and eventually lead to failure. And so, to analyze the overall fracture it is been common to look at this from an elastic point of view because earlier work was done with metals and other structural materials. And the basic idea here is to think in terms of crack which grows creates a new surface. So, there is a surface energy associated with the crack.

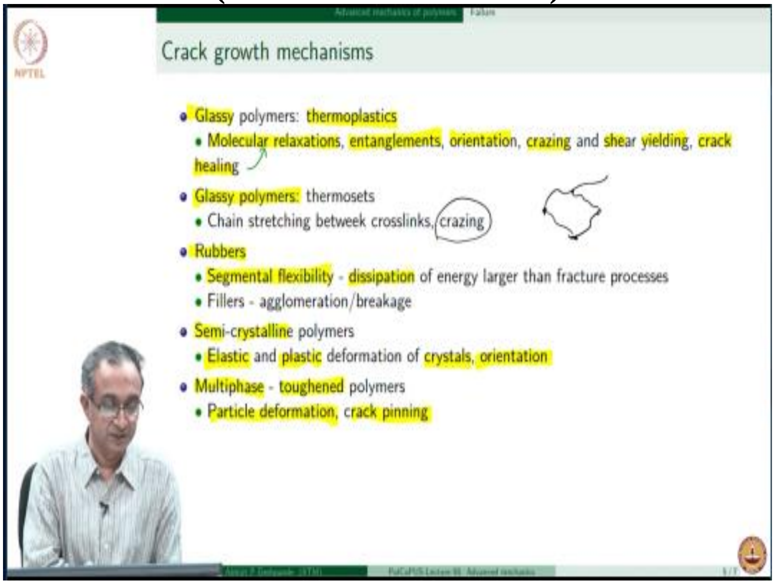
On the other hand there is an elastic material where atoms and molecules are in a minimum energy configuration and when a crack grows it basically separates these atoms and molecules. And so, there is an elastic energy which has which has to be overcome for a crack to proceed, And so, it is a balance of these two sets of energy. So, elastic energy which is related to stress x stain.

And so, I am sure you can rationalize that this is stress x strain for an hooky and elastic material. And so, that into whatever is the area of the crack and we will assume for the time being that you know it is related to a unit width. And this is balanced by the surface energy and whatever is the length of the crack. And so, when you do the balance of these then we can find out the σ_c that is required for crack to be initiated and failure to be observed in material.

And this is usually written in terms of this surface energy or also in terms of G_c, which is called a work of fracture. Because whenever we create a crack in the material we are doing work on the material and causing the failure. And so, this is one way to try to find out what may be the stress required for failure in the material given its modulus of elasticity and given the surface energy associated with the cracked surface.

And in all of this the dimension of the cracks are very crucial also. Other way to think about this is also in terms of a stress intensity factor as we discussed earlier. Where because at the crack tip stresses will be different compared to whatever is applied far away in the sample.

(Refer Slide Time: 09:49)



Crack growth mechanisms

- Glassy polymers: thermoplastics
  - Molecular relaxations, entanglements, orientation, crazing and shear yielding, crack healing
- Glassy polymers: thermosets
  - Chain stretching betweek crosslinks, crazing
- Rubbers
  - Segmental flexibility - dissipation of energy larger than fracture processes
  - Fillers - agglomeration/breakage
- Semi-crystalline polymers
  - Elastic and plastic deformation of crystals, orientation
- Multiphase - toughened polymers
  - Particle deformation, crack pinning

So, in general in polymers given that elasticity is only one type of deformation. There are plastic deformation as well as molecular relaxations and viscoelastic phenomena. We have mechanisms which are different compared to other materials. And in this slide, we will just summarize the mechanisms which are there and all of these mechanisms should be familiar to you. Because we have mentioned all of these while discussion related to solid state of polymeric materials.

So, in case of glassy polymers which are thermoplastics we know that there are linear and branched macromolecules, which are entangled with each other in the amorphous state. And they also have some amount of molecular flexibility though exceedingly small but given the presence of loads some of these molecular relaxations can take place. And we know that orientation can happen.

And because of these processes of relaxation entanglements and orientation crazing and shear yielding in the material can happen when material is being deformed. One other feature which is very significant for thermoplastic materials is the phenomenon of crack healing. And this is related very closely with the fact that there are molecular relaxations possible. So, crack can start growing but then molecules can start fluctuating back and forth slowly but eventually heal the crack.

So, a crack which was created can also heal itself. On the other hand glassy polymers which are thermoplastic have a cross linked network. So, since they have a cross link network the entanglements do not play as bigger role here. It is the chain stretching between crosslinks which initially is the mechanism by which chain start orienting. And then once the orientation starts happening you can form fibrils and therefore crazing can initiate.

And eventually leading to cracks and failure. But because there is a only chain stretching and crazing happening the thermosets give us brittle failure. Rubber on the other hand do have crosslinks but the chain length is very significant and because of the segmental flexibility which is present in the case of rubbers, in addition to the processes of cracking and chain ceassation there are several segmental motions which can dissipate energy.

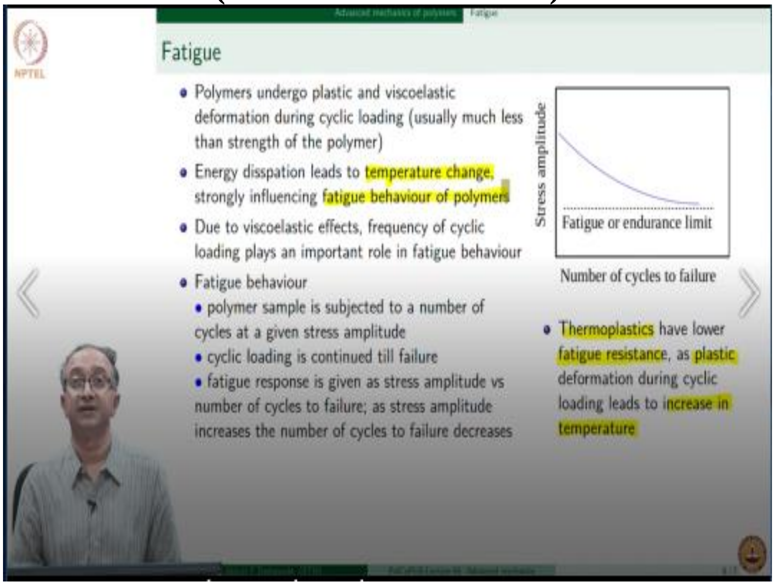
So, therefore fracture process is dominated by dissipative mechanisms of viscous nature which is due to segmental flexibility. The rubbers are quite often used along with fillers. For example, in tyre, carbon black is used. And these fillers are usually in the form of agglomerates. So, during fracture of rubber like materials which are filled there is the additional complication of what are these filler networks doing.

Are they agglomerated or are they getting the fillers are getting broken up into smaller clusters how are these macromolecules interacting with these clusters of particles. So, fracture process is far more complicated in case of filled rubbers. And in case of semi crystalline polymers we have the elastic and plastic deformations of crystal in addition to amorphous chains. And of course, there is orientation of crystals also there.

And so, defect mechanisms in the sense that defect move, defect propagation all of these also contribute to overall fracture phenomena. And lastly one of the important ways in which we create toughened polymers is by incorporating particles quite often rubber particles in otherwise a thermoplastic or a thermoset matrix. And so, these are multiphase toughened polymers. And in this case because the rubber particle which is incorporated can deform easily.

Through particle deformation it can dissipate energy and therefore some of the stresses which are there can get dissipated without leading to a crack formation or crack propagation. Similarly there can be a crack arrested at the interface between a particle and the matrix. So there are several mechanisms because of which high impact polystyrene or PCABS blends or several such blends where there are rubber particles which are improving the strength as well as impact performance as well as fracture behavior of polymeric materials.

(Refer Slide Time: 14:32)



Advanced mechanics of polymers | Fatigue

Fatigue

- Polymers undergo plastic and viscoelastic deformation during cyclic loading (usually much less than strength of the polymer)
- Energy disspation leads to temperature change, strongly influencing fatigue behaviour of polymers
- Due to viscoelastic effects, frequency of cyclic loading plays an important role in fatigue behaviour
- Fatigue behaviour
  - polymer sample is subjected to a number of cycles at a given stress amplitude
  - cyclic loading is continued till failure
  - fatigue response is given as stress amplitude vs number of cycles to failure; as stress amplitude increases the number of cycles to failure decreases

- Thermoplastics have lower fatigue resistance, as plastic deformation during cyclic loading leads to increase in temperature

So, this is a review or related to fracture. Another important mechanism by which materials fail is related to what is called fatigue. And as we know fatigue is basically getting tired in a usual English sense. And in case of mechanical response of fatigue what is very crucial here is that we subject the material to loads which are much less compared to the tensile strength. It could be 20, 30% of the tensile strength.

So, technically material should be able to withstand this kind of a load over very long periods of time. But given that any practical application 20% of load is applied then it is removed then it is applied so there is a cyclic nature to loading in any given application. Any structural or otherwise automotive or any application you think of there is always loading unloading going on. So, even if the loads are small given that there is a periodic loading unloading material starts responding to that.

And so, there is plastic as well as viscoelastic deformations that go on in polymers and these deformations can slowly start leading to some amount of damage in the material. So just the way in case of fracture we saw that when load starts reaching closer to the tensile strength or the flexural strength of the material we have crazing, shear yielding and then eventually forming a crack.

Now here in this case also because of the progressive deformation in the material, progressive changes in the material microstructure crazing, shear yielding and other such phenomena can start taking place only thing is they are much more gradual. And so in case of polymers because of this plastic and viscoelastic deformation during cyclic loading fatigue response is observed.

What that does is if you look at let us say the count the number of cycles to failure. So, we load the stress and keep on changing it as a function of time. And again just reminding you that when we test viscoelasticity of samples we are in the linear regime where there is no damage at all. Where the structure is very close to the equilibrium structure of the material. In this case by definition we are subjecting the loads which are much higher than linear viscoelasticity.

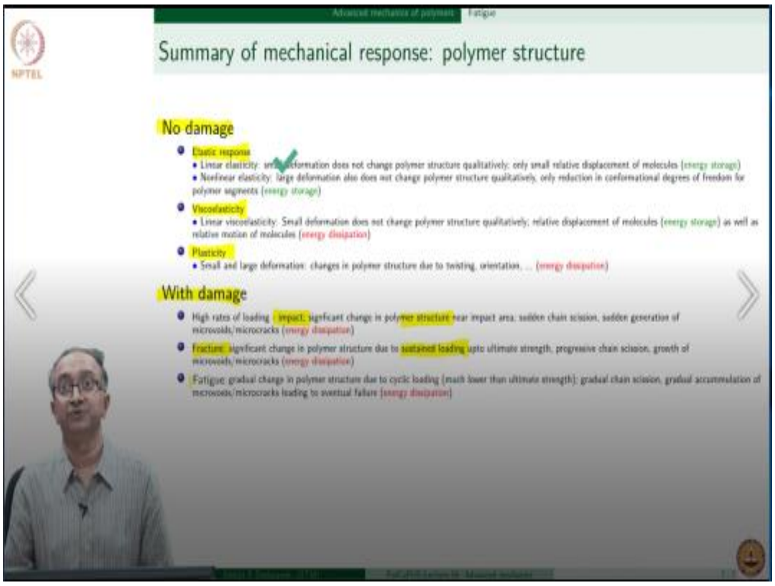
However, they are much lower than the strength of the material. And even then damage happens because of the fatigue that the material undergoes. And so, the stress amplitude we keep on varying and then measure the number of cycle higher the stress we apply it will fail at much less number of cycles. The larger the number of cycles it implies that the stress that is applied on the material is much less.

And so therefore we can see that there is an endurance fatigue limit that we can measure by doing such analysis. In case of polymer there are couple of issues which lead to complicated behavior because there is energy dissipation that can lead to temperature change. And temperature change can change segmental mobility it can change the mechanisms in terms of disentanglement and so on. So that has a very strong influence on fatigue behavior of polymers.

And because of viscoelastic effect the frequency of cyclic loading also plays a very important role in case of polymers. So, generally as I said we can summarize that polymer sample is subjected to a number of cycles at a given amplitude. We measure the number of cycles which lead eventually to failure and then we look at this response of the curve. And this is a fatigue response and we can do this for different materials and try to understand;

Why is it some materials fail at much less number of cycles and some other materials which require much larger number of cycles? So, with this we have completed our overall review of the response of polymeric materials. One other thing for example we can notice, this thermoplastics have lower fatigue resistance because plastic deformation leads to increase in temperature as was mentioned here. Because temperature change strongly influences the fatigue response of polymers.

(Refer Slide Time: 18:56)



Summary of mechanical response: polymer structure

No damage

- Elastic response
  - Linear elasticity: small deformation does not change polymer structure qualitatively: only small relative displacement of molecules (energy storage)
  - Nonlinear elasticity: large deformation also does not change polymer structure qualitatively, only reduction in conformational degrees of freedom for polymer segments (energy storage)
- Viscoelasticity
  - Linear viscoelasticity: Small deformation does not change polymer structure qualitatively; relative displacement of molecules (energy storage) as well as relative motion of molecules (energy dissipation)
- Plasticity
  - Small and large deformation: changes in polymer structure due to twisting, orientation, ... (energy dissipation)

With damage

- High rates of loading : impact: significant change in polymer structure near impact area: sudden chain scission, sudden generation of microvoids/microcracks (energy dissipation)
- Fracture: significant change in polymer structure due to sustained loading upto ultimate strength, progressive chain scission, growth of microvoids/microcracks (energy dissipation)
- Fatigue: gradual change in polymer structure due to cyclic loading (much lower than ultimate strength): gradual chain scission, gradual accumulation of microvoids/microcracks leading to eventual failure (energy dissipation)

So, in this slide I have tried to summarize the overall set of mechanical response that we have discussed. We can classify them in two important ways no damage and with damage. In case of no damage we have elastic response viscoelasticity or plasticity. In case of elasticity we have linear elasticity as well as non-linear elasticity. And in case of viscoelasticity because of our preliminary course we focused only on linear viscoelasticity.

Advanced studies are also there for nonlinear viscoelasticity. Plasticity we have looked at deformation which is accumulated in terms of permanent strain. And changes in structure due to orientation twisting and other mechanisms. So, these are phenomenon which we classify in terms of response of the material in case of plasticity structure may undergo some change. And in case of elasticity the molecular arrangements may change but they recover back.

So, we had a discussion which is not related to damage at all. It is related to response of the material structure to a given mechanical loading. On the other hand now we have damage with damage if we have high rates of loading then we have basically the impact response which is significant change in polymer structure. In all of these cases there is a significant change in polymer structure including initiation of damage and then growth of this damage in terms of crack growth.

Then we looked at fracture which is also again significant change due to sustained loading. And fracture is where we load the sample up to very high stresses up to strength of the material. And then fatigue where we load the material to less extent compared to the whatever is the tensile strength. So, with this we close the lecture related to mechanical response and advanced mechanics I urge you to look at the slide more closely.

And try to understand and rationalize what are all the different mechanisms by which each phenomenon is different compared to the other phenomena. So, with this we will close the lecture. Thank you.