Physico - Chemical, Mechanical and Electrical Properties of Polymers

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Lecture – 36
Mechanical Properties I

Hello, as we are discussing properties of polymeric systems, the focus of this lecture will be on mechanical properties, we have already looked at the stress strain curves and preliminary quantities which are defined based on such stress strain curves. In this lecture, let us look at the elastic behaviour, which is at small deformation for all materials. But we have also seen that for rubber like materials, elastic deformation can be present for very large deformations.

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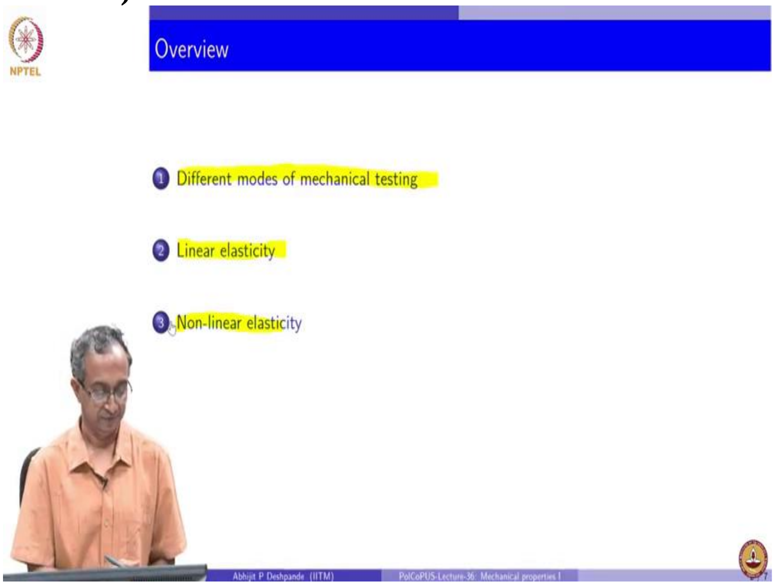

Overview

1. Different modes of mechanical testing
2. Linear elasticity
3. Non-linear elasticity

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So, we will look at both of these from the point of view of properties of polymeric materials. And this will be done by first quickly summarizing different modes of mechanical characterization that we can do and then we will look at small deformation, elastic behaviour, or large deformation elastic behaviour. You can notice here the word linear and nonlinear. And so small deformation behaviour in most materials is where linear elastic behaviour is observed while materials which generally show elasticity under large deformation such as 100% and 500%. In that case, it is the relationship between stress and strain is nonlinear.

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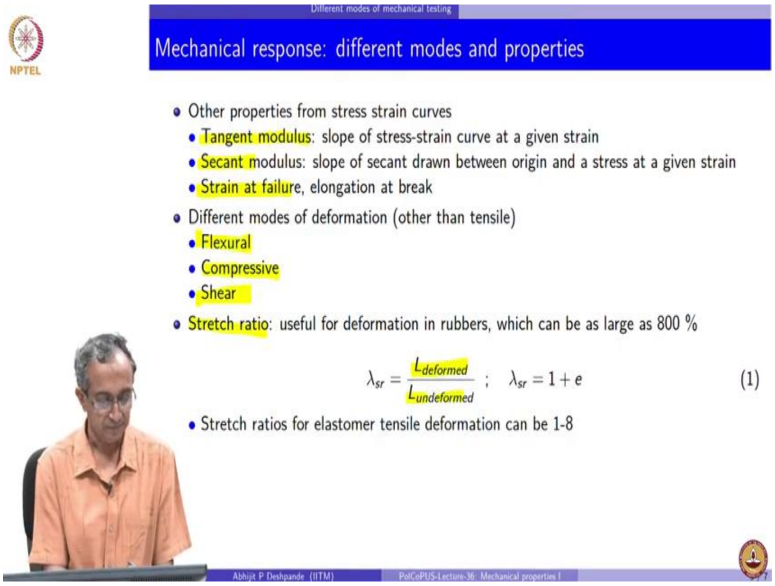

Different modes of mechanical testing

Mechanical response: different modes and properties

- Other properties from stress strain curves
  - Tangent modulus: slope of stress-strain curve at a given strain
  - Secant modulus: slope of secant drawn between origin and a stress at a given strain
  - Strain at failure, elongation at break
- Different modes of deformation (other than tensile)
  - Flexural
  - Compressive
  - Shear
- Stretch ratio: useful for deformation in rubbers, which can be as large as 800 %

$$\lambda_{sr} = \frac{L_{deformed}}{L_{undeformed}} \; ; \quad \lambda_{sr} = 1 + e \qquad (1)$$

  - Stretch ratios for elastomer tensile deformation can be 1-8

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So, let us quickly recap the different modes or properties which are possible to be described in the lecture on stress strain curves, we looked at extensional behaviour or uniaxial tension behaviour. However, we can also have flexural or compressive, or shear deformation. And so the same stress strain curves that we talked about could also be generated in any of these different modes.

And the challenge in mechanics of materials is that sometimes it is not easy to correlate the behaviour of tension and flexural mode or flexural and compression mode, because of the underlying mechanisms and interactions, which are present in the material. With the same stress strain curves that we had looked at earlier, we could also define in addition to the modulus, which was defined, we could also define modulus, which is tangent modulus or a secant modulus, I suggest you just go and look up these definitions.

These are very standard definitions, especially when linear region is very small, then these are very useful quantitative measures for engineering decision making. We can also look at strain at failure or elongation at break to quantify the nature of mechanical response of the material. Since In this lecture, we will also discuss very large deformation, one useful quantity, in addition to strain is called the stretch ratio.

In this case, we look at the ratio of the deformed length versus undeformed length. And the stretch ratio in case of rubber band, for example, can be 3 or 4, or even 5, so, we can stretch the rubber band to 5 or 6 times its original length. And so rather than saying 600% strain, we say 6 as the stretch ratio.

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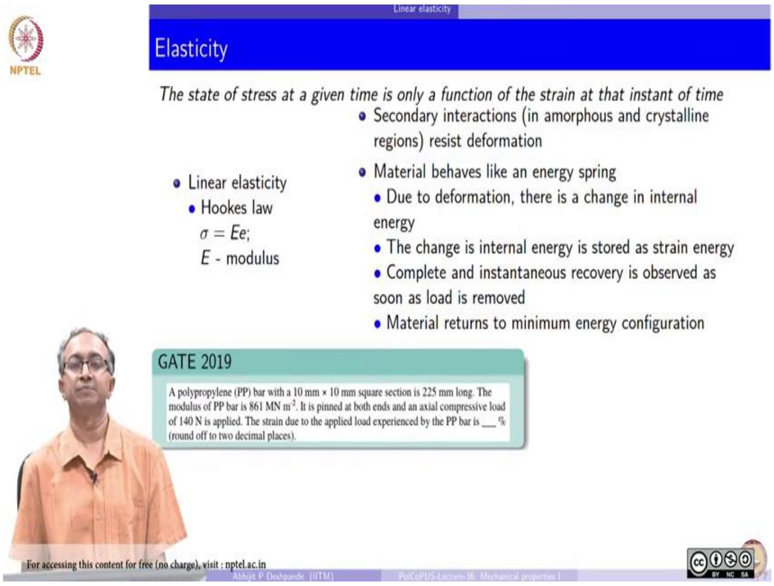

Elasticity

The state of stress at a given time is only a function of the strain at that instant of time

- Linear elasticity
  - Hookes law
    $\sigma = Ee$;
    E - modulus

- Secondary interactions (in amorphous and crystalline regions) resist deformation
- Material behaves like an energy spring
  - Due to deformation, there is a change in internal energy
  - The change is internal energy is stored as strain energy
  - Complete and instantaneous recovery is observed as soon as load is removed
  - Material returns to minimum energy configuration

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A polypropylene (PP) bar with a 10 mm × 10 mm square section is 225 mm long. The modulus of PP bar is 861 MN m^{-2}. It is pinned at both ends and an axial compressive load of 140 N is applied. The strain due to the applied load experienced by the PP bar is ___ % (round off to two decimal places).

And so, let us start with the elasticity and defining it. So, elastic materials are those materials where stress at any given instant of time is related to the strain at that instant of time. So, this implies that whatever was the history in terms of the deformation or no deformation is irrelevant. If I know the stress in the material, I immediately know the strain in the material. If I specify the strain in the material, I immediately know the stress in the material.

It does not matter how fast the stress is being applied, it does not matter how fast the strain is being applied, it does not matter whether the material was undeformed earlier or deformed earlier, it does not matter that I apply 10% strain and come back to 5% strain, the stress will be dependent on 5% current strain if the material is subjected to 5% strain currently, and so, this is the definition of elasticity.

And for linear elasticity, this can be represented where there is a linear relationship between stress and strain. And this all of you are familiar with in terms of Hookes law. And if you look at macromolecular systems and how this Young’s modulus or the Hookean modulus depends on the nature of macromolecules in amorphous and crystalline materials, it is the secondary interactions, which lead to the material being deformed or the chains themselves also cannot be deformed, because of the covalent bonds.

And so, secondary interactions are the ones which can allow some amount of displacement of molecules. And similarly, in case of a crystal, which is well ordered system can get stretched. So, if I just depict it using a 2 dimensional and if there is a force like this being applied, then because of the force, the crystal can get stretched in this direction and it can without changing the order of the atoms and molecules.

So therefore, in these cases, what happens is, there is an energy associated with interaction of atoms and molecules. And when we apply deformation we have to basically work against this energy. So therefore, material in such cases behaves like an energy spring. So as soon as we release, it comes back. So that is why it is an energetic spring and the minimum energy configuration is always reached.

So, therefore, sample will always come back from the default state to undeformed state in exactly identical way. And that is why the current state of strain is only important whatever is the deformation that is applied in the material gets stored in the material as strain energy, when we release it the strain energy is released back material comes back to original state. And just to highlight the application of Hookes law is quite common for engineering materials.

So, you can look at this question where there is a cross sectional area is given and the modulus of the material is given and based on Hookes law, you can actually then find out what is the strain that is being applied on the material.

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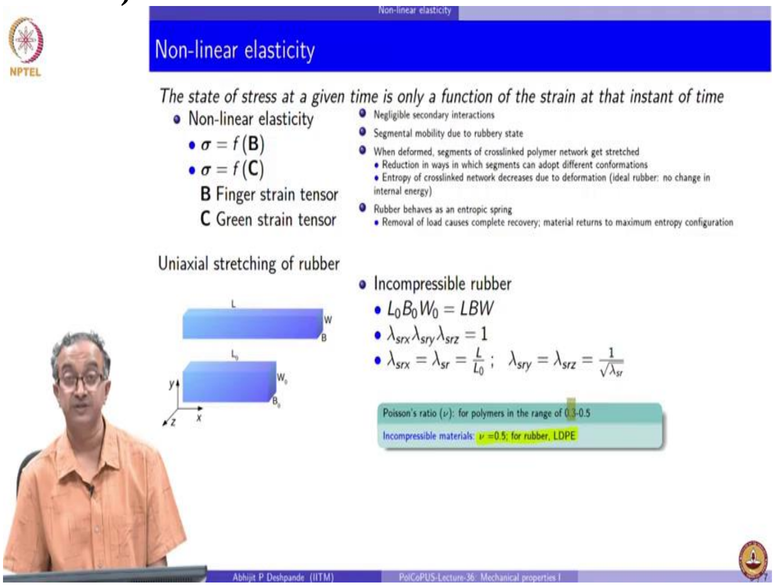

Non-linear elasticity

Non-linear elasticity

The state of stress at a given time is only a function of the strain at that instant of time

- Non-linear elasticity
  - $\sigma = f(\mathbf{B})$
  - $\sigma = f(\mathbf{C})$

  B Finger strain tensor

  C Green strain tensor

- Negligible secondary interactions
- Segmental mobility due to rubbery state
- When deformed, segments of crosslinked polymer network get stretched
  - Reduction in ways in which segments can adopt different conformations
  - Entropy of crosslinked network decreases due to deformation (ideal rubber: no change in internal energy)
- Rubber behaves as an entropic spring
  - Removal of load causes complete recovery; material returns to maximum entropy configuration

Uniaxial stretching of rubber

- Incompressible rubber
  - $L_0 B_0 W_0 = LBW$
  - $\lambda_{srx}\lambda_{sry}\lambda_{srz} = 1$
  - $\lambda_{srx} = \lambda_{sr} = \frac{L}{L_0}$; $\lambda_{sry} = \lambda_{srz} = \frac{1}{\sqrt{\lambda_{sr}}}$

Poisson's ratio (ν): for polymers in the range of 0.3-0.5

Incompressible materials: ν =0.5; for rubber, LDPE

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Now, when we go to large deformations and material is still elastic, I hope you remember from our discussions of stress strain curves in the lecture 32 that many materials will deform plastically and in that case at large deformations elasticity will not be observed. And so, in case of rubber like materials, where this is most relevant, what we have is again state of stress is dependent only on the instantaneous strain in the material or the instantaneous value of strain depends on the instantaneous value of stress.

And the discussion that I had about you know, strain rates being irrelevant all of that is equally applicable here, except for the fact that now, deformations can be very large. And because of these large deformations, the strain that we use to quantify deformation in Hooke's law kind of applications is no longer valid and we define what are called either finger strain tensor or Green strain tensor.

And the statement of nonlinear elasticity is that the stress is dependent on the value of strain and because of the large deformation, these strain measures have multiple possibilities in terms of which strain measure can be used. So, depending on historical applications or depending on the scientists who have developed and engineers who have worked on these concepts, there are various options present to describe the stress strain behaviour of these nonlinear materials.

And in this case, the idea for rubber like materials is that there are negligible secondary interactions, the macromolecules are not interacting with each other the only bonded interactions, which lead to the stretching and flexibility of macromolecule are relevant, however, a coarse grained picture of in terms of ideal chain or an expanded chain is sufficient for us to look at the elasticity of the macro molecular system.

And because we are looking at temperatures where segmental mobility is feasible, because of the rubbery state, this is crucial in terms of macromolecular stretching. And so, when deformed segment of the crosslink polymer network gets stretched. And this is possible because of the segmental mobility. And this is again, has been highlighted few times, but maybe I will just repeat it once more.

So, if let us say this is a polymer chain, which is dangling between 2 crosslink points, and if this is being stretched, what happens is if you stretch it, then the chain has much less freedom and the number of ways in this conformation can change for a stretch chain is very less compared to an undeformed chain. And so, therefore, different conformations become less and less if you do stretch and therefore, the entropy of crosslink network decreases.
And as soon as you release the extension, the material comes back because of maximization of entropy. So, therefore, rubber behaves like an entropic spring, the internal energy changes in neglected in case of deformation of rubber because of negligible secondary interactions. And so, material returns to maximum entropy configuration. And so, just to talk about the rubber stretching given that very large deformations are possible, and also we know that rubbers are incompressible.

So, quite often, there will be questions related to how does a rubber deform and how do its dimensions changed. So, for example, if we have a rubber with L_0 length and it is stretched to L, what happens is even its width and breadth also change, but because it is incompressible, the volume will remain the same whether it is deformed or undeformed. And therefore, the volumes can be related to each other and the stretch ratios which are defined as the ratio of lengths can also be related to each other.

And if we assume that it is stretching in x direction in this case and the y and z direction, the response is equivalent then the reduction in y and z will be similar, while x axis the elongation is there. And so, you can just read about in the Poisson's ratio for polymeric materials, for rubber, Poisson's ratio is 0.5, but for many polymeric material the ratio is 0.3 to 0.5.
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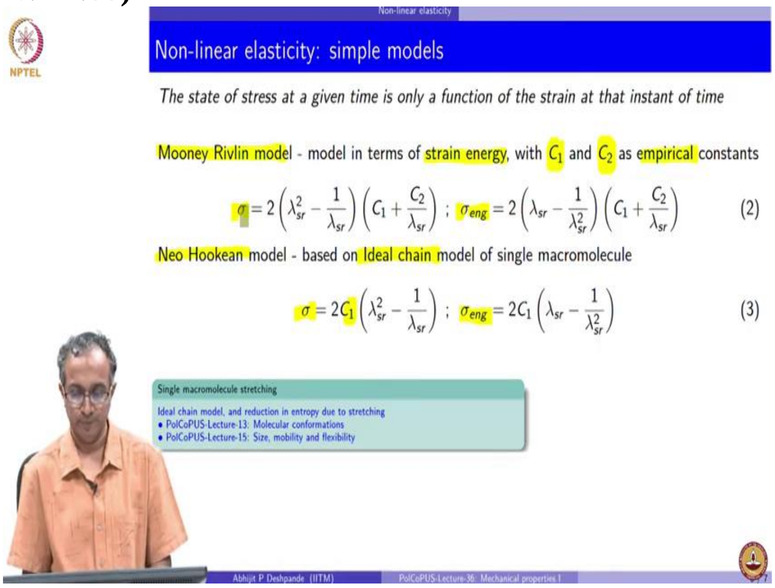

Non-linear elasticity

Non-linear elasticity: simple models

The state of stress at a given time is only a function of the strain at that instant of time

Mooney Rivlin model - model in terms of strain energy, with C_1 and C_2 as empirical constants

$$\sigma = 2\left(\lambda_{sr}^2 - \frac{1}{\lambda_{sr}}\right)\left(C_1 + \frac{C_2}{\lambda_{sr}}\right) \; ; \; \sigma_{eng} = 2\left(\lambda_{sr} - \frac{1}{\lambda_{sr}^2}\right)\left(C_1 + \frac{C_2}{\lambda_{sr}}\right) \qquad (2)$$

Neo Hookean model - based on Ideal chain model of single macromolecule

$$\sigma = 2C_1\left(\lambda_{sr}^2 - \frac{1}{\lambda_{sr}}\right) \; ; \; \sigma_{eng} = 2C_1\left(\lambda_{sr} - \frac{1}{\lambda_{sr}^2}\right) \qquad (3)$$

Single macromolecule stretching

Ideal chain model, and reduction in entropy due to stretching
- PolCoPUS-Lecture-13: Molecular conformations
- PolCoPUS-Lecture-15: Size, mobility and flexibility

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So, it is on the side of incompressibility in case of polymeric materials. Now, we will close this lecture by just quickly looking at 2 different models for describing the nonlinear elasticity. You can as a first exercise to get familiar with these equations; you can ask the question what happens if the deformation is small. So, if deformation is small, then λ_{sr} which is the stretch ratio will be basically $1+\varepsilon$ and ε is a very small quantity.

So, you can substitute 1+ε for λ_{sr} in these equations and try to simplify and convince yourself that both of these will reduce to Hookes law. So, these are equations which are valid for arbitrarily large deformations, because they are describing the rubber behaviour, but if you look at exceedingly small deformation at very small deformation, again Hooke's law will be valid. And so, these are 2 different models.

Mooney Rivlin is a phenomenological model, which is arrived by specifying a specific strain energy and it has 2 constants, which are empirical. And we will solve problems related to both of these models to give us an idea, how linear and nonlinear elasticity is very different, where some of the macromolecular picture and a single macro molecule that we discuss during second week is important is in terms of the ideal chain model directly giving us a Neo Hookean model.

So, in this case, there is one coefficient C_1 and you can see the similarity between Neo Hookean and Mooney Rivlin model. So, when we look at practical applications of rubber, Neo Hookean works for a much smaller class of materials while Mooney Rivlin is applicable for a larger class of materials, but both of these again have been modified to a significant extent to look at variety of rubbers which are present.

So, these are the simplistic models which are present as in terms of stress, because the cross sectional area keeps on changing we can define engineering stress or the true stress and properties change just a little bit based on what the definitions are.

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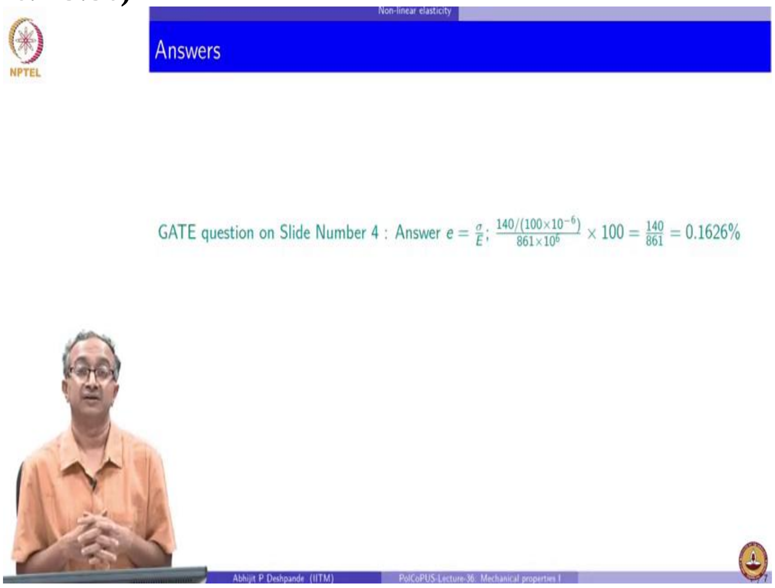

Non-linear elasticity

Answers

GATE question on Slide Number 4 : Answer $e = \frac{\sigma}{E}$; $\frac{140/(100\times10^{-6})}{861\times10^{6}} \times 100 = \frac{140}{861} = 0.1626\%$

So, in terms of the question related to Hooke's law, the answers are straightforward in terms of the ratio of stress to the modulus. So, with this, we will close this discussion on mechanical properties of elastic like response of polymers, what remains is to look at plastic deformation in many of these polymers. And there are also advanced mechanical responses in terms of what happens when it is extremely high deformation rate, which is called impact or what happens when material is failing.

Why and how the cracks propagate in the material. So, some of that we will quickly recap in one of the future lectures and aside from all of this, viscoelasticity of polymers is also a broad mechanical property, which we will discuss later on in the course. Thank you.