Mechanical Properties of Polymers

Kamyar Davoudi

October, 2013

Materials Science Seminar
Definition of Polymers

- Polymers are materials consisting of very long molecules, made up of hundreds or thousands repeating chemical units (the monomer units), covalently bonded together.
- Organic glasses
- The long molecules are bonded together by
  - Van der Waals
  - Hydrogen bonds
  - Covalent cross-links
Degree of Polymerization (DP):
the number of monomer units in a molecule.

Amorphous & Crystalline
Classes of Polymers

- **Thermoplastics**: such as PE. soften on heating
- **Thermosets**: such as epoxy. Harden when two components are heated together
- **Elastomers or rubbers**
- **Natural polymers**: such as cellulose, lignin, and protein
Thermoplastics

• Commonest: Polyethylene (PE)
• Often described as **linear polymers** (chains are not cross linked)
• \( T \uparrow \) secondary bonds melt, flow like viscous liquid
• Polystyrene (PS): amorphous
  PE: partly crystalline
• Sub-units (monomers) of most of them
Thermosets

• Are made by mixing two components (resin and hardener) → react and harden at RT or on heating

• Heavily cross-linked → also called network polymers

• T † secondary bonds melt, E drops → rubber

• T †† †† decomposes
Elastomers

- Almost linear polymers with *occasional cross-links*
- only in noncrystalline
- the backbone of the chain must be very long and have many kinks and bends.

\[
\begin{array}{c}
\text{H} \\
\text{C} & \text{C} & \text{C} & \text{C} & \text{C}
\end{array}
\]

- At RT, secondary bonds have already melted
- **Vulcanization**
- Cross-links provide the *memory* of the material so that it returns to its original shape
Elastomers

- Helical pattern to the chain because of carbon-carbon double bonds

- Mechanical Model: a highly coiled skeleton of primary bonds (including cross-links) immersed in a viscous like medium.

- During application of a tensile load: coils are unwound to an extent

- Upon unloading, the cross-linking atoms act to restore the original dimensions.

- No links, no restoration
Elastomers

- Elastic behavior of rubbers is different from that of crystalline material

- Only at extensions where the chains approximately fully extended does the force begin to stretch primary bonds

- Decrease in $S$ $\rightarrow$ Increase in $F$ (free energy)

- Potential energy is unchanged

- No primary bond stretching $\rightarrow$ small modulus

Source: Courtney, Mechanical Behavior of Materials, 2000
Elastomers

• Akin to ideal gases (no change in potential energy) but ...

• Incompressible

• Neo-Hookean \( \mu = N k_B T \)

\( N \) : no. polymer chains/\( V \)

\[ \sigma = \mu \left( \lambda^2 - \lambda^{-1} \right) \]

Source: Courtney, Mechanical Behavior of Materials, 2000
Glass Transition Temperature

(a) Perfect crystallisation

(b) Imperfect crystallisation

(c) Glass formation

Volume

Melting point
Expansion coefficient

Temperature

Glass transition
“Free” volume
Deformation of Polymers

- Elastomers $\rightarrow$ Always elastic response
- Thermosets $\rightarrow$ viscoelastic response
- Thermoplastics $\rightarrow$ elastic or plastic
Change of Young’s modulus for linear polymers

Linear-amorphous polymers (like PMMA & PS) show five regimes of deformation

In general

\[ E = \frac{\sigma}{\varepsilon(t, T)} \]

Glassy Regime and secondary relaxations

- $T \ll T_g$

\[
\varepsilon = f \frac{\sigma}{E_1} + (1 - f) \frac{\sigma}{E_2} = \sigma \left[ \frac{f}{E_1} + \frac{1 - f}{E_2} \right]
\]

$E_1 \sim 10^3$ GPa

$E_2 \sim 1$ GPa

Glass or visco-elastic transition

- $T > T_g$ Extra free volume lowers the packing density
- Still there are some non-sliding parts
- On unloading the elastic regions pull the polymer to its original shape
- Modeled by springs and dashpots

Higher Temperatures

- **Rubber behavior**
  - $\text{DP}<10^3 \rightarrow$ polymer becomes sticky liquid
  - $\text{DP}>10^4 \rightarrow$ long molecules intertwined like a jar of very long worms $\rightarrow$ rubbery behavior

- **Viscous flow**
  \[ \tau = \eta \dot{\gamma} \]

- **Decomposition**
  - The thermal energy exceeds the cohesive energy of some parts of the molecular chain, causing degradation or depolymerization.
  - PMMA $\rightarrow$ decomposes into monomer units
  - PE $\rightarrow$ randomly degrade into many products
Modulus Diagram for Polymers

The influence of Cross-linking on a contour of the modulus diagram for polyisoprene

The effect of Temperature on Deformation

PMMA
Strength decreases and elongation increases with higher temperature

Source: Carswell & Nason, ASTM Symposium on Plastics, Philadelphia, 1944

Brittle Fracture

- Polymers are brittle at $T < \approx 0.75 \ T_g$
- Pre-existing cracks left by machining or abrasion or caused by environmental attack

$$\sigma = \frac{K_{IC}}{\sqrt{\pi a}}$$

- Fracture toughness $K_{IC} \sim 1 \ \text{MPa m}^{\frac{1}{2}}$
- Crack size $a \sim O(\mu m)$
- $\sigma \sim 1 \ \text{MPa}$

Cold Drawing

At $\varepsilon \sim 0.1$

The chains unfold (if folded) or draw out of the amorphous tangle (if glassy)

For $\lambda$ sufficient enough (2-4) ($\varepsilon=100-300\%$) : alignment of molecules $\rightarrow$ neck propagates until it is all drawn

Crazing

- Craze $||$ maximum stress
- Propagates along a direction perpendicular to the principle axis
- Depends on $T$ (PE & PP draw at RT, PS does not, but it crazes)
- No crazing in compression
- Precursor to fracture
Shear Banding

Highly localized

In the direction of maximum shear stresses

More easily formed in tension

Crazing and shear banding compete with each other

Source: McClintock & Ashby, Mechanical Behavior of Materials, 1966
Glassy Polymers: Thermoplastics

Micro-shear bands
At-Polystyrene at 22° C under compression
(Optical Microscopy w/ Polarized Light)

Crazes
At-Polystyrene in tension
(TEM)

Source: http://www.files.chem.vt.edu/chem-dept/marand/Lecture23.pdf
Deformation of Crystalline Polymers

- Crystalline polymers always contain some remnant non-crystalline material.
Crystallization

Crystallization increases the modulus too

Source: Courtney, Mechanical Behavior of Materials, 1998
Summary

• Polymers may be amorphous or semi-crystalline
• Deformation of polymers is highly affected by temperature, time, DP, etc.
• Elastomers deform elastically over a long range of temperature
• Linear polymers may be glassy, leathery, rubbery or viscous flow
• Plastic behavior of linear polymers may cause by cold drawing, crazing or shear banding
• Crystalline polymers always have remnants of amorphous polymers
• The tension and compression behavior of polymers can be quite different
Glass Transition Temperature

Figure 8.2
Molar volume-temperature curves on cooling from above $T_m$ to below it. If the material crystallizes (curve (a)), a discontinuity in molar volume occurs at $T_m$. If it does not (curve (b)), the thermal expansion coefficient ($\sim dV_m/dT$) is unchanged at $T_m$ and the liquid structure remains below $T_m$. At $T_g$ — the glass transition temperature — there is a discontinuity in the thermal expansion coefficient. Below $T_g$, the material demonstrates mechanical characteristics of a solid rather than a supercooled liquid. Some materials partially crystallize at $T_m$ and their molar volume-temperature behavior on cooling is illustrated by curve (c). In certain materials (e.g., long-chain polymers) crystallization is easily avoided on cooling; in others (e.g., metals) very rapid cooling is required to prevent crystallization.