Lecture 4

Pushing chains around

Temperature strongly influences the mechanical response of a polymeric materials– wood is composed of macromolecules.

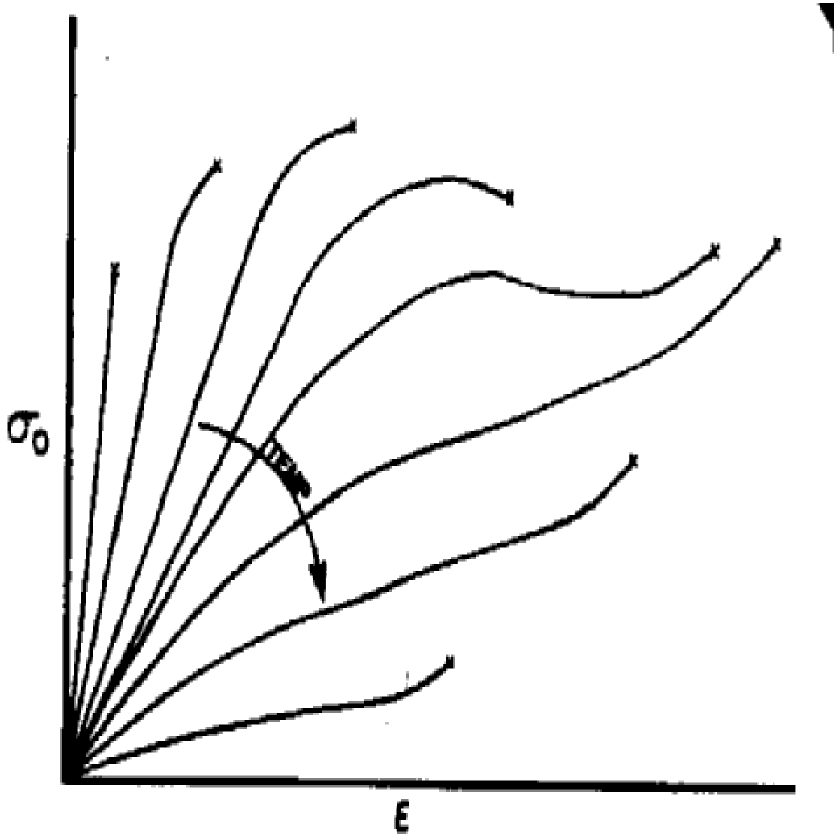
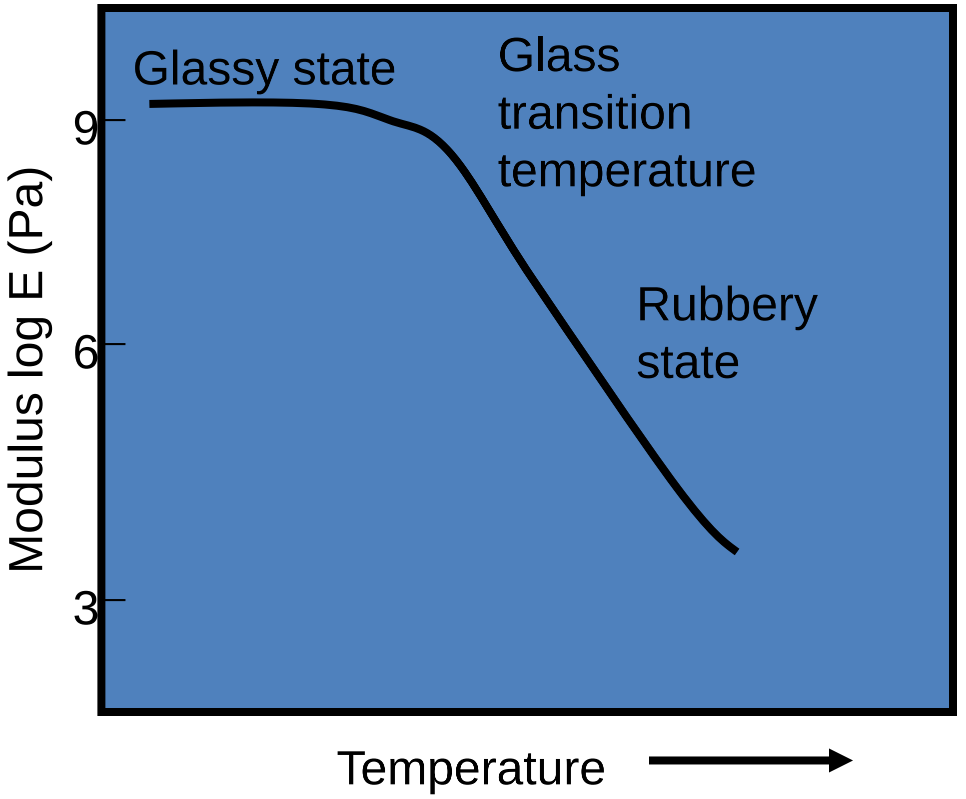


FIGURE 10 Generalized stress–strain curves showing the effect of temperature.

G. Wilkes

Data from the last graph



Moving polymer chains

- Glass transition- temperature where large segmental motion occurs related to the movement of polymeric chains. Input of thermal energy causes segmental motion.
- Another method to change the temperature at which large segmental motion occurs is to add plasticizer to "loosen" intermolecular interactions amongst chains, and change packing of chains.

Why does water lower the glass transition of wood?
Answer- water is a plasticizer of wood.

Polymer materials are influenced by bond type

Thermal Energy (KT) at 25C (J)	4.1E-21

Bond type	Bond energy J/bond (examples)	bond energy/ KT
covalent	3.321E-19	81.00
dipole	2.491E-20	6.08
disper	6.642E-21	1.62

Bond strengths, in part relate to the Tg of polymers and resulting properties. Typically CH polymers have Tg below 0˚ C while CO polymers have Tg (PVA, PET, PVC) above 0˚ C.

What happens to polymers when you heat them?

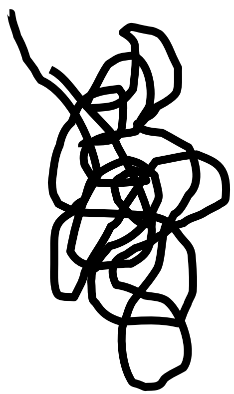
- It depends upon the polymer…but if they behave as thermoplastics then the following occurs:
  - Heating the polymer adds thermal energy to the system
  - This energy allows thermal motion of chain segments to occur
  - Concerted motion increases and there is collective movement of chain segments
    - When this occurs the materials soften moving from a glassy material response to rubbery material response.
    - The temperature that this occurs is known as a glass transition ($\mathbf{T_g}$) temperature of the material
    - The rate at which the specific volume changes of the material changes at this temperature and this is because of a change in free volume.

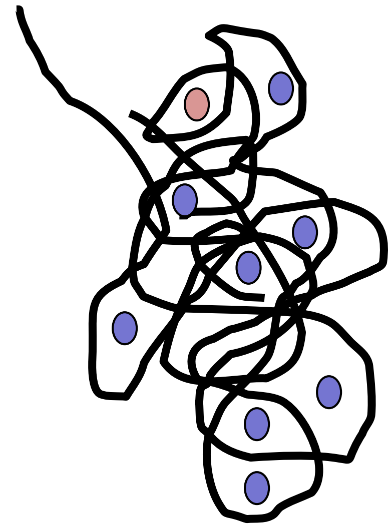
What dictates Tg of a polymer?

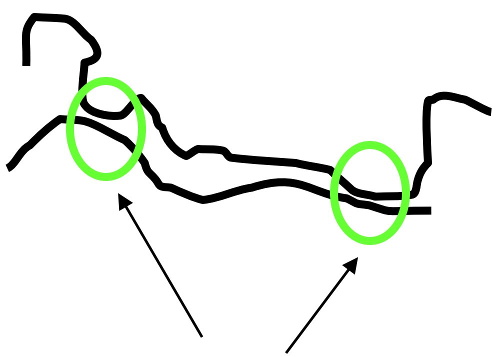
- Chemistry of the backbone (rigidity and functionality)
  - Polyethylene -125 to -20°C
  - Polyvinyl chloride 80 °C
  - Polyvinyl alcohol 85 °C
  - Polycarbonate 149 °C
- Pendant groups (size)
  - Polypropylene 0 °C
  - Polystyrene 100-115°C
- Presence of a **plasticizer**
  - Changes free volume
  - Disrupts interactions between chains

So how can shopping bags hold our groceries? They are made from polyethylene.

Schematic of polymer chain interactions



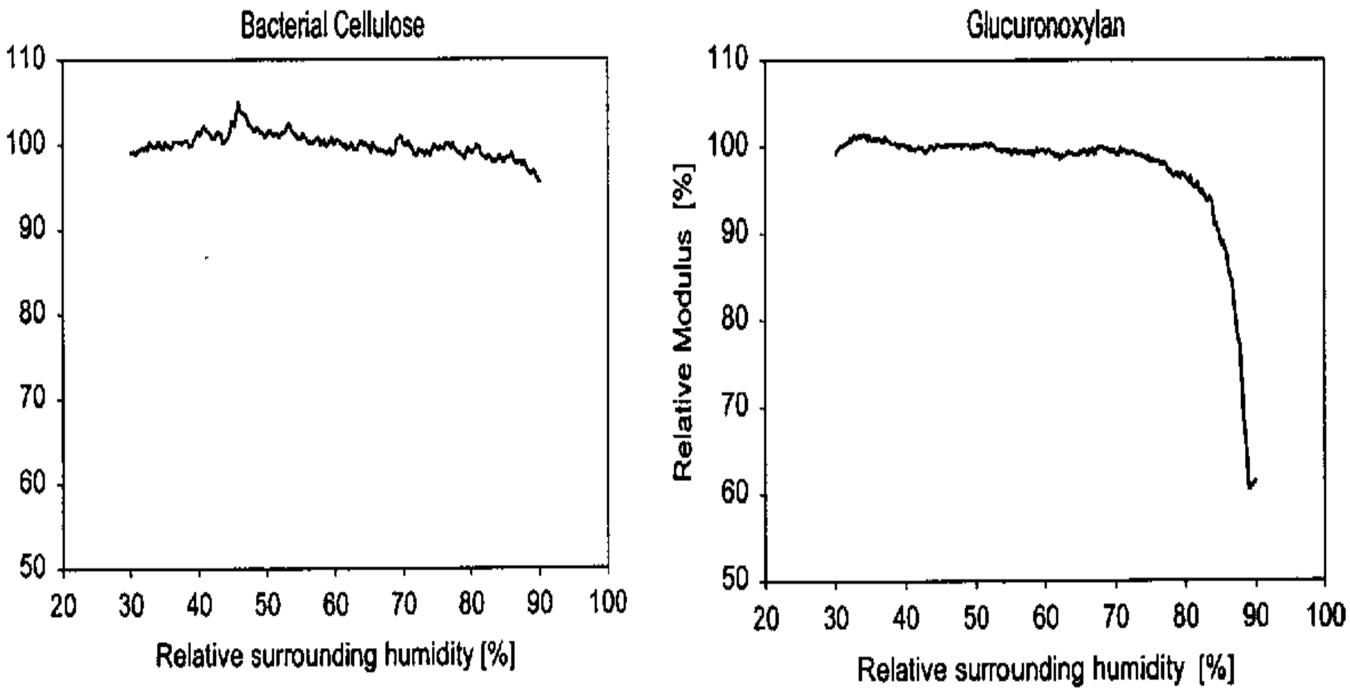




Intermolecular bonds preventing large scale motion

Thermal energy (known as KT) or presence of plasticizer influences the ability for polymer chains to undergo motion

Change in plasticizer content impacts glass transition temperature



Dammstrom et al.

Temperature influences the stress strain curve making it possible for the same materials to show both brittle and ductile behavior when tested at different conditions (i.e. above and below the glass transition and/or melting temperatures)

What happens when you keep heating the polymer past it's T_g

- For amorphous polymers it continues to be transformed into a liquid like state.
- For a semicrystalline polymer there is a second phase that must transform
  - The crystalline phase must be disrupted and it is phase transition refers to the "melting" of the polymers T_m
  - Some polymers have a T_m that is greater than T_d, the thermal decomposition temperature.

So why can’t cellulose/starch flow like other polymers when heated?

- **Thermoplastics** “flow” when heated and can be dissolved in some solvent*
- **Thermosets** “are cured” and do not flow when heated because each chain is linked with another forming a network.

as a linear or branched polymer is not crosslinked, it can usually be manipulated to behave as a thermoplastic.