

# Structure-Property Relationships in Polymer Systems: Part 2

Updated 26 November, 2011

## Parameters

| Structure and environmental factors  | Properties   |   |
|--|--|---|
| polymer class/structure<br>loading<br>temperature<br>crystallinity<br>molecular weight | strength/hardness<br>elastic modulus (stiffness)<br>ductility<br>toughness | viscoelasticity<br>$T_g$ , $T_m$<br>fatigue |

## General “Useful” Properties of Different Polymer Classes

| Thermoplasts   | Thermosets  | Elastomers  |
|--|---|---|
| can range from soft to hard<br>recyclable<br>often flexible (E), ductile,<br>tough | high strength<br>thermal stability (properties<br>do not change with T) | huge elastic capacity<br>tunable stiffness (crosslinks) |

lightweight, low cost, chemically inert, electrically insulating

## Outline of Structure-Property Relationships Considered

|         | polymer class  |
|---------|--|
| loading | stress-strain as $f(T)$<br>viscoelastic behavior as $f(T)$ |

- effect of crystallinity on mechanical properties
- effect of molecular weight on mechanical properties
- factors affecting  $T_g$ ,  $T_m$
- fatigue characteristics
- design examples given in class

# polymer class

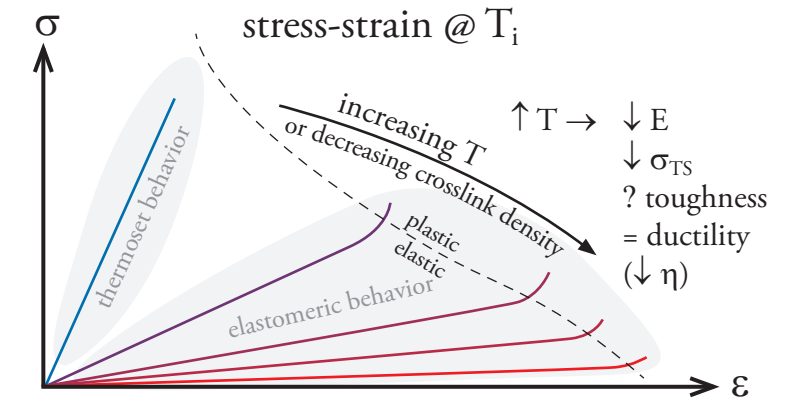
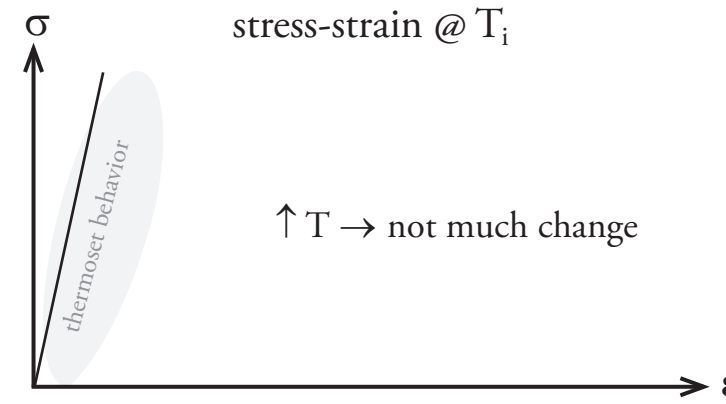
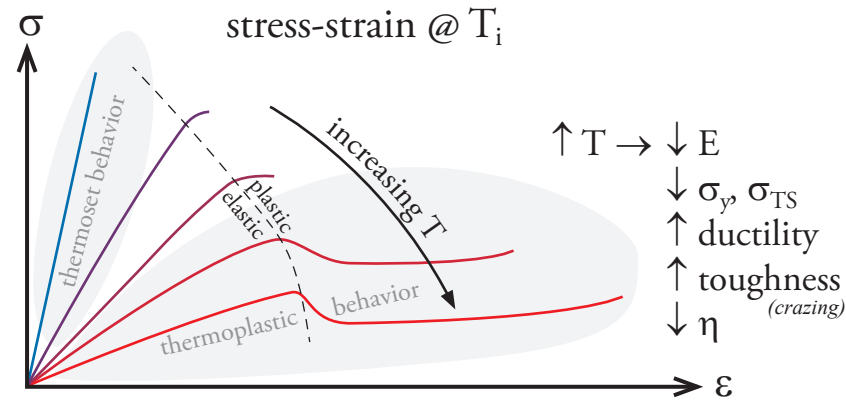
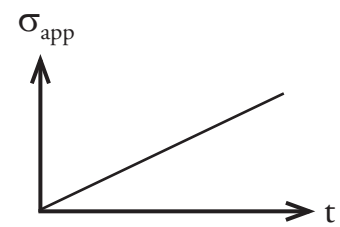
## thermoplasts

## thermosets

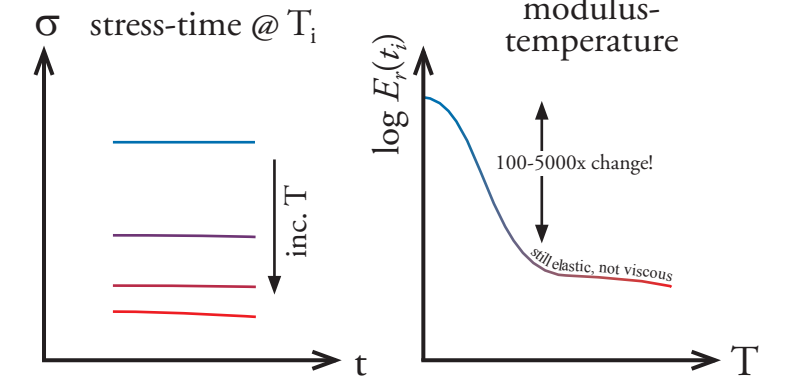
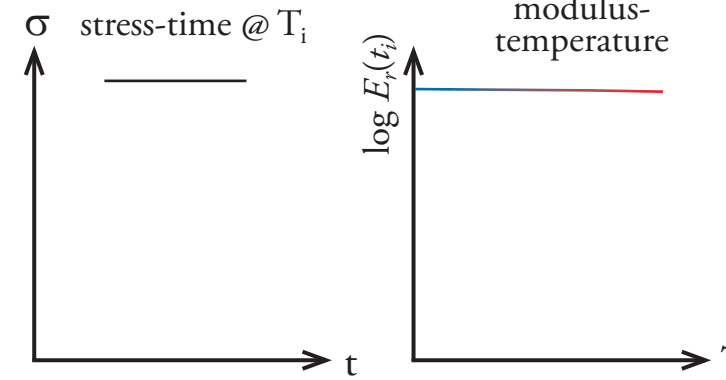
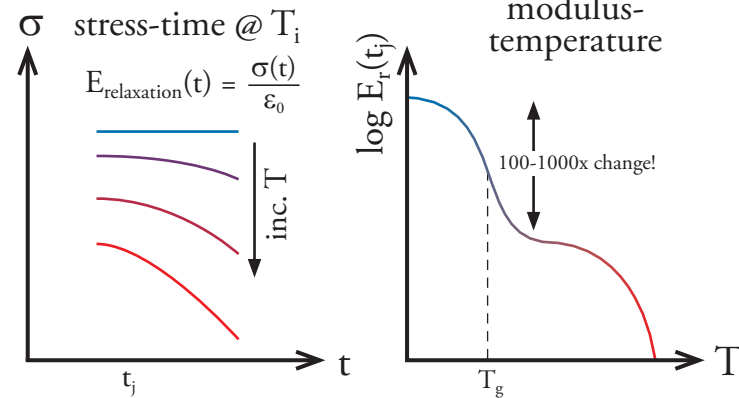
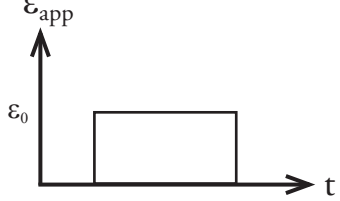
## elastomers

loading

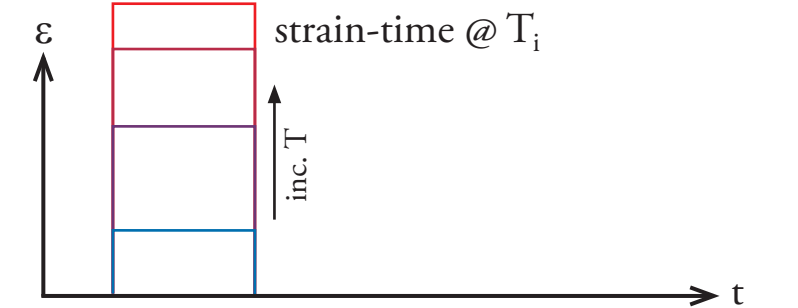
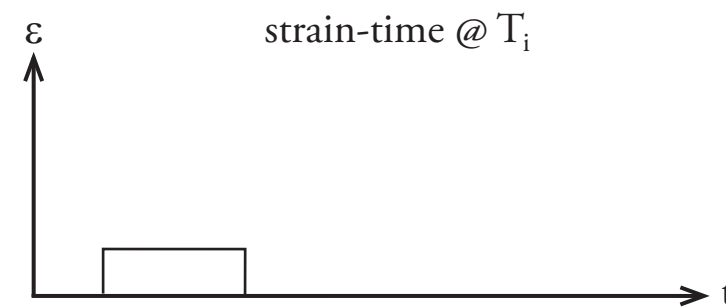
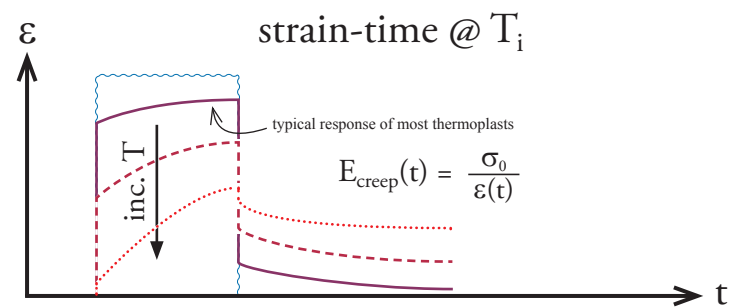
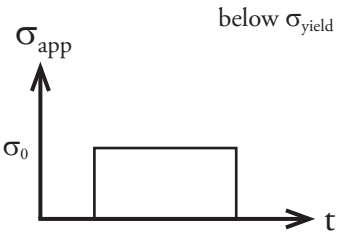
gradual loading  
(tensile testing;  
low  $\dot{\epsilon}$ )



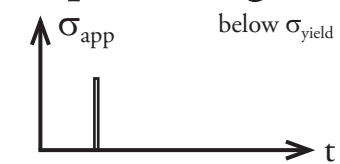
constant strain  
small  $\epsilon$



constant stress  
below  $\sigma_{yield}$



impulse (high  $\dot{\epsilon}$ )



elastic (non-viscous, non-plastic)

elastic (non-viscous, non-plastic)

elastic (non-viscous, non-plastic)

## Effect of Crystallinity on Mechanical Properties

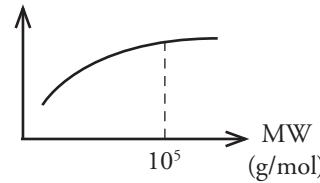
Crystalline polymer regions have increased chain packing and alignment, thus resulting in significantly higher interchain secondary bonding forces compared to those existent in amorphous regions.

$\uparrow$  % crystallinity  $\rightarrow$   $\uparrow$  E  
 $\uparrow$   $\sigma_y, \sigma_{TS}$   
 $\downarrow$  ductility  
 $\downarrow$  toughness  
 $\uparrow$   $\eta$   
 $\uparrow$   $T_g, T_m$

## Effect of Molecular Weight on Mechanical Properties

As polymer chains become longer and longer, there is increased chain entanglement. This causes some reduction in interchain mobility up to a chain weight of about  $10^5$  to  $10^6$  g/mol, where effects level off.

$\uparrow$  molecular weight  $\rightarrow$   $\uparrow$  E  
 $\uparrow$   $\sigma_y, \sigma_{TS}$   
 $\downarrow$  ductility  
 ? toughness  
 $\uparrow$   $\eta$   
 $\uparrow$   $T_g, T_m$



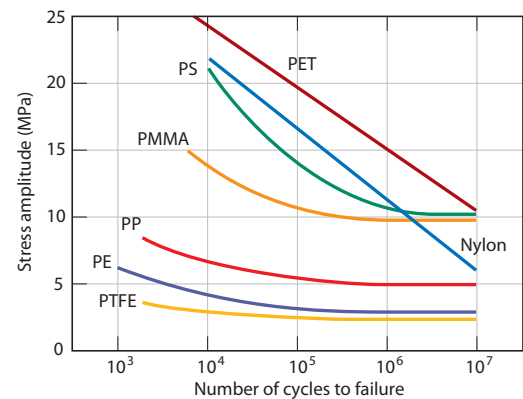
## Factors Affecting $T_g, T_m$

Similar to factors affecting crystallinity of a polymer, structural features that affect interchain mobility will also affect the polymer's glass transition (amorphous regions) and melting (crystalline regions) temperature. Features that hinder interchain mobility will raise the value of these properties:

- crosslinking
- side groups      small H atoms vs. polar or bulky side groups
- branching      small branching "spaces" chains apart,  $\downarrow$  interchain forces,  $\uparrow$  chain mobility, thus  $\downarrow T_g, T_m$  (LDPE melts before HDPE); longer branching hinders mobility
- repeating unit      simple backbone vs. double-bonds or aromatic groups
- molecular weight

## Fatigue Characteristics

Most thermoplastic polymers can survive a large number of cyclic loads before failure. However, the failure stresses (1-10 MPa) are orders of magnitude lower than those of metals (100's of MPa).



## Design examples given in class

- |               |  |
|---------------|--|
| plastic bag   | extremely ductile thermoplast (huge amount of necking); $T_g$ is far below room temperature  |
| ice cube tray | choose thermoplast with $T_g$ far below room temperature to allow for flexibility (low E) and toughness                                    |
| billiard ball | use a network polymer (Bakelite) to maintain high strength and hardness but have good toughness (so it won't shatter)                      |
| coffee cup    | choose a thermoplast with $T_g$ above hot-water temperature to keep it from "flowing" (being viscoelastic) when in contact with hot liquid |
| picnic knife  | flexible thermoplast with viscoelastic response  |
| silly putty   | extremely viscoelastic thermoplast; loading rate affects properties (e.g. modulus) immensely   |