

# Structure-Property Relationships in Polymer Systems: Part 2

Updated 26 November, 2011

## Parameters

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

## General “Useful” Properties of Different Polymer Classes

Thermoplasts	Thermosets	Elastomers

Generally:

## Outline of Structure-Property Relationships Considered

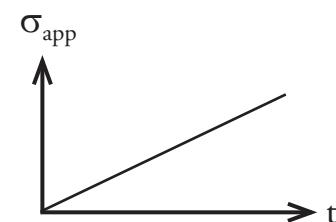
	polymer class
loading	stress-strain as $f(T)$ viscoelastic behavior as $f(T)$

- 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

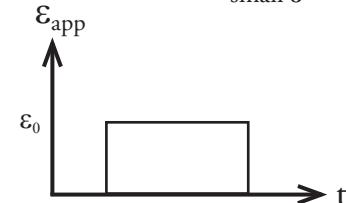
# polymer class

## thermoplasts

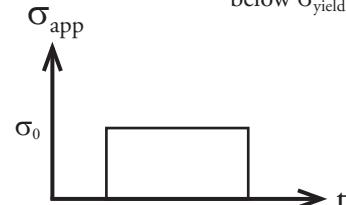
gradual loading  
(tensile testing;  
low  $\dot{\varepsilon}$ )



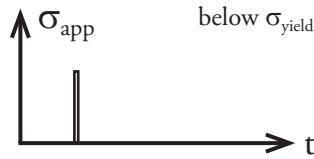
constant strain  
small  $\varepsilon$



constant stress  
below  $\sigma_{yield}$



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



## thermosets

stress-strain @  $T_i$



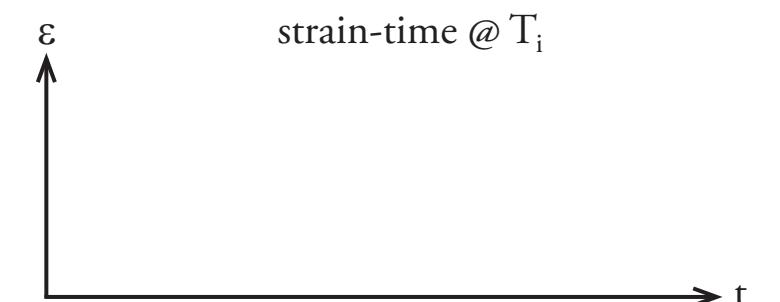
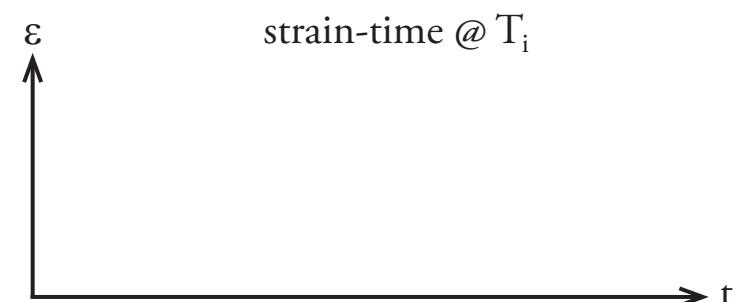
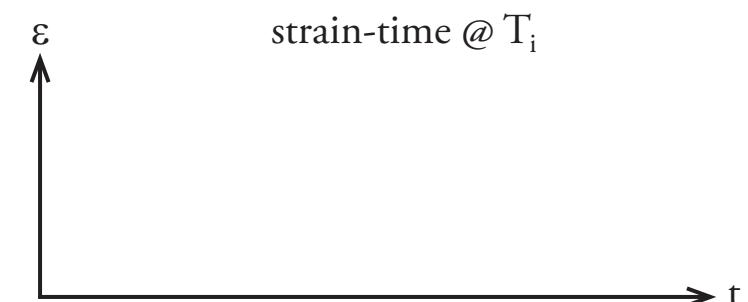
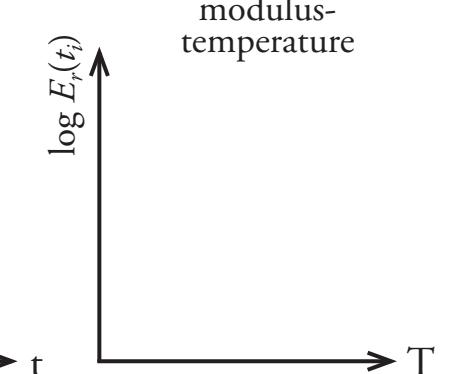
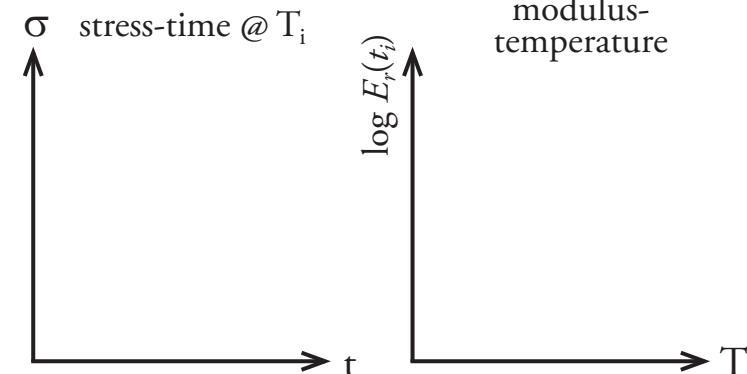
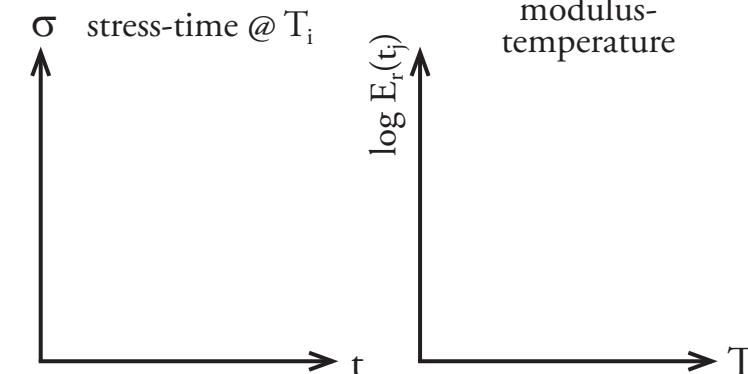
stress-strain @  $T_i$



stress-strain @  $T_i$



stress-strain @  $T_i$



loading

## 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.

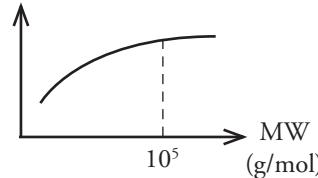
$\uparrow$  % crystallinity  $\rightarrow$

E  
 $\sigma_y$ ,  $\sigma_{TS}$   
 ductility  
 toughness  
 $\eta$   
 $T_g$ ,  $T_m$

## Effect of Molecular Weight on Mechanical Properties

As polymer chains become longer and longer, there is increased chain [redacted]. 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  $\rightarrow$



E  
 $\sigma_y$ ,  $\sigma_{TS}$   
 ductility  
 toughness  
 $\eta$   
 $T_g$ ,  $T_m$

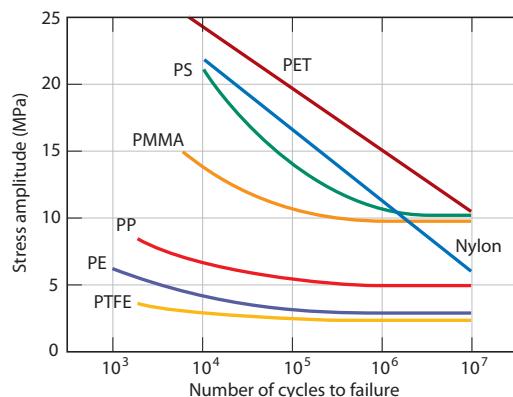
## Factors Affecting $T_g$ , $T_m$

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 [redacted] 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