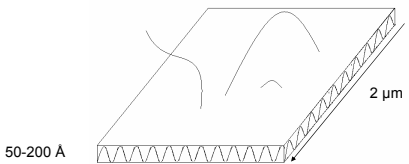


Class 4: Polymer Crystallinity



PRIME Modules
Project-based Resources for Introduction to Materials Engineering

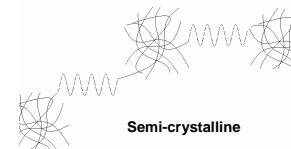
Polymers can have a crystal structure (arrangement) to the chains

In polymers, samples can be amorphous, crystalline, or semi crystalline.

Crystalline and semi-crystalline polymers have an arrangement of their chains that comes from packing.



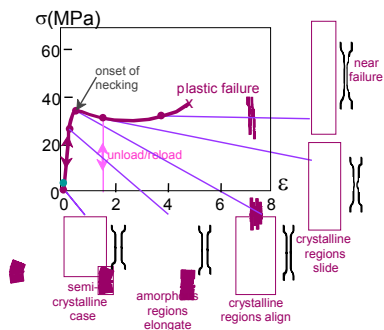
Amorphous



Semi-crystalline

Crystalline polymers are stronger

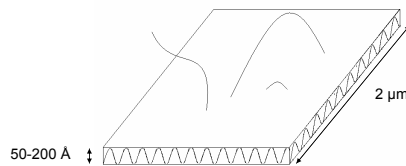
Crystal regions require a greater force to deform them than amorphous regions



Stress-strain curves adapted from Fig. 15.1, Callister 6e. Inset figures along plastic response curve (purple)

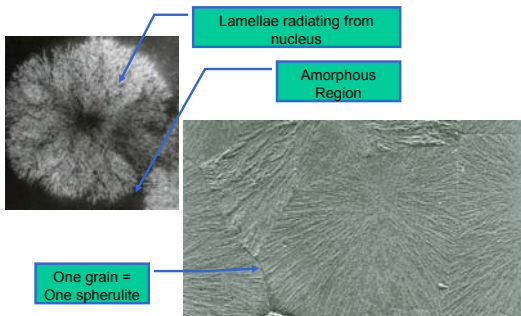
Chains fold back on each other in crystal regions

Lamellar crystals are regions of a polymer where the chains fold back on each other in tight packing



Polymers can crystallize in spheres

Spherulites are crystalline regions of a polymer that form from chain folded lamellae radiating out in 3-D from a nucleus



Left: William D. Callister, Jr. "Materials Science and Engineering an Introduction - 6th Edition"
Right: R.J. Young - "Introduction to Polymers - 2nd Edition"

The degree of crystallinity is quantified based on the density

Volume % crystallinity

$$\frac{\rho_s - \rho_a}{\rho_c - \rho_a} \cdot 100$$

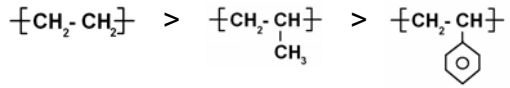
Density of semi-crystalline sample (points to ρ_s)
Density if all crystalline (points to ρ_c)
Density if all amorphous (points to ρ_a)

Weight % crystallinity

$$\frac{\rho_c (\rho_s - \rho_a)}{\rho_s (\rho_c - \rho_a)} \cdot 100$$

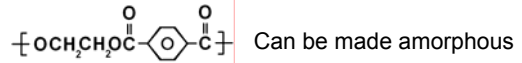
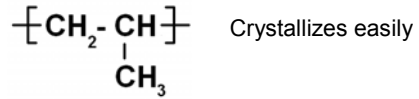
Bigger side groups are less crystalline

Bulky side groups make it harder for chains to pack



Bigger = Harder for chains to pack

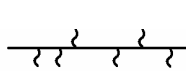
Chain complexity decreases crystallinity



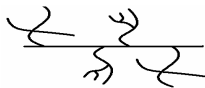
A more complex chain is harder to pack into crystal

Branching reduces crystallinity

Branching makes it harder for the chains to pack



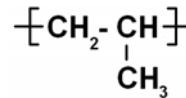
HDPE
>90% crystalline



LDPE
40% 60% crystalline

Branches are harder to pack

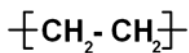
Ordered tacticity increases crystallinity



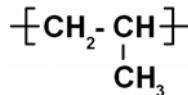
Atactic: amorphous, gummy
Isotactic: semicrystalline, rigid (yogurt cup)

A regular structure is easier to crystallize

Randomness decreases crystallinity



semicrystalline +
= 50/50 random copolymer



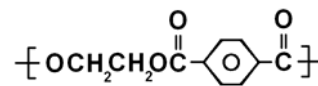
semicrystalline

→ AMORPHOUS

Random copolymers are less regular

Rapid temperature changes decreases crystallinity

Thermal history is the processing steps a polymer has gone through involving temperature changes.



Melt and rapid cool: amorphous

Melt and hold at 150°C: ~40% crystalline

Slow phase transformation allows for crystal regions to form

In summary, a polymer can form crystalline regions that affect the mechanical properties

Polymers can be amorphous, crystalline, or semi-crystalline

Crystal regions strengthen a polymer

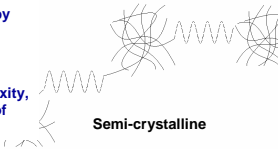
Crystal regions are formed through packing when chains folded back over each other

The degree of crystallinity is quantified by the densities

Factors affecting degree of crystallinity include bulky side groups, chain complexity, chain branching, tacticity, randomness of copolymers, and thermal history.



Amorphous



Semi-crystalline