Tutorial 6

Pedro Guerra Demingos

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Land Acknowledgment

I wish to acknoledge this land on which the University of Toronto operates. For thousands of years it has been the traditional land of the Huron-Wendat, the Seneca, and most recently the Mississaugas of the Credit River. Today, this meeting place is still the home of many Indigenous people from across Turtle Island and we are grateful to have the opportunity to work on this land.

Anouncements

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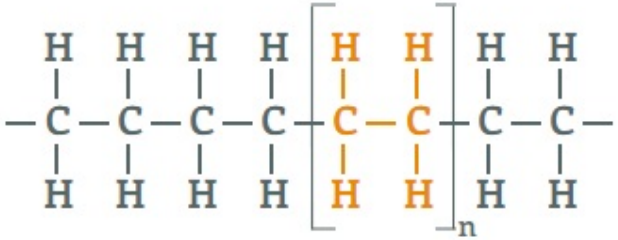
- Midterm
  - You'll have them today, after our Theory Review and Sample Problems.
  - No re-grading today. If you find any wrong grading, make a note and I'll take a look during our next tutorial.
  - Solutions will be posted on Prof. Ramsay's website:
    - https://www.scottramsay.com/home
  - On Quercus, your displayed grade is out of 30, not 34.

- Next week is Reading Week, so no tutorials!

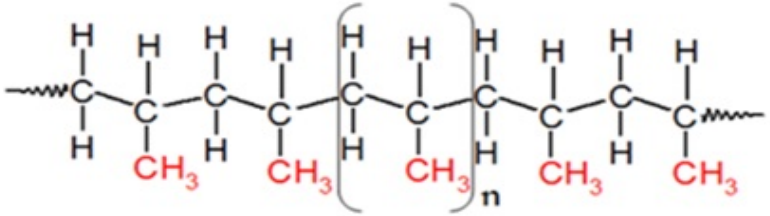
Theory Review

- Polymers
  - *Mer = repeating unit*
  - *Monomer* vs *polymer*

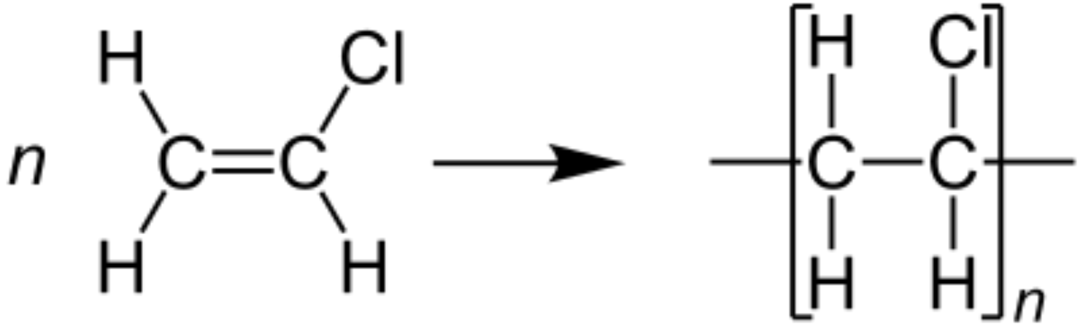
Polyethylene (PE)



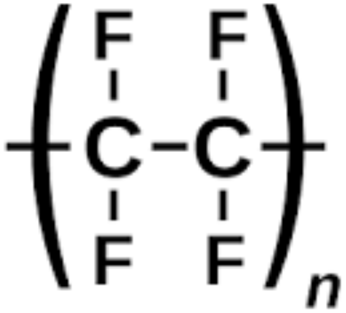
Polypropylene (PP)



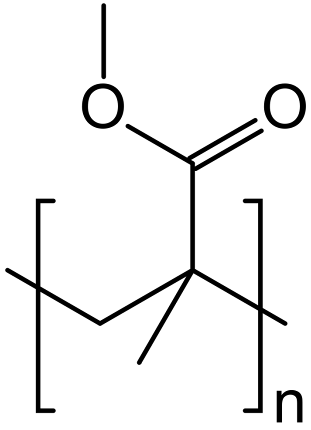
Polyvinylchloride (PVC)



Polytetrafluoroethylene (PTFE)

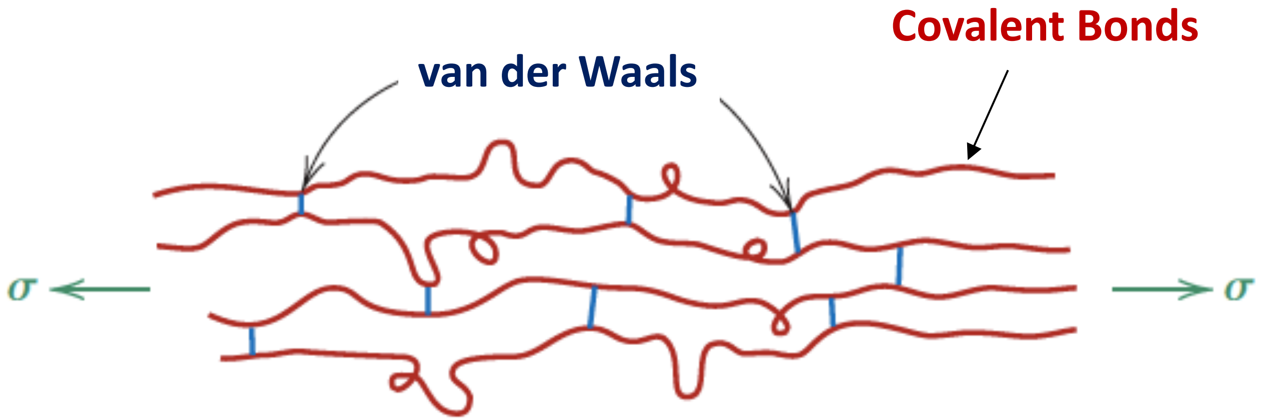


Polymethylmethacrylate (PMMA)



Theory Review

- String Model for Polymers
  - Useful for visualization, for example mechanical deformation:



- Stronger in the alignment direction
- More opaque rather than transparent
  - Because it becomes less amorphous!

Theory Review

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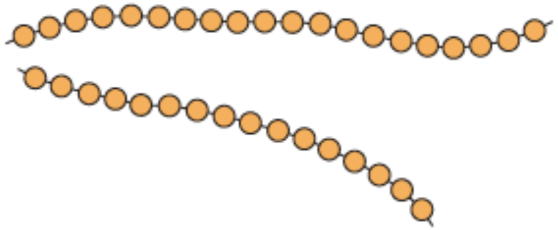
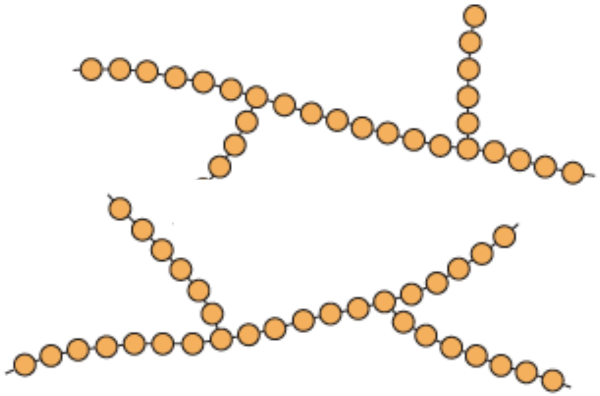
- Structure of Polymers

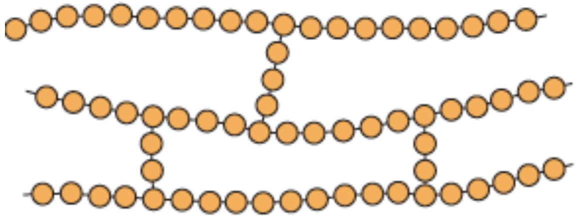
Linear

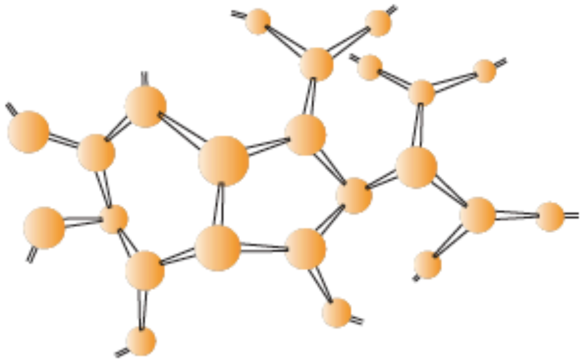




Branched

Cross-Linked

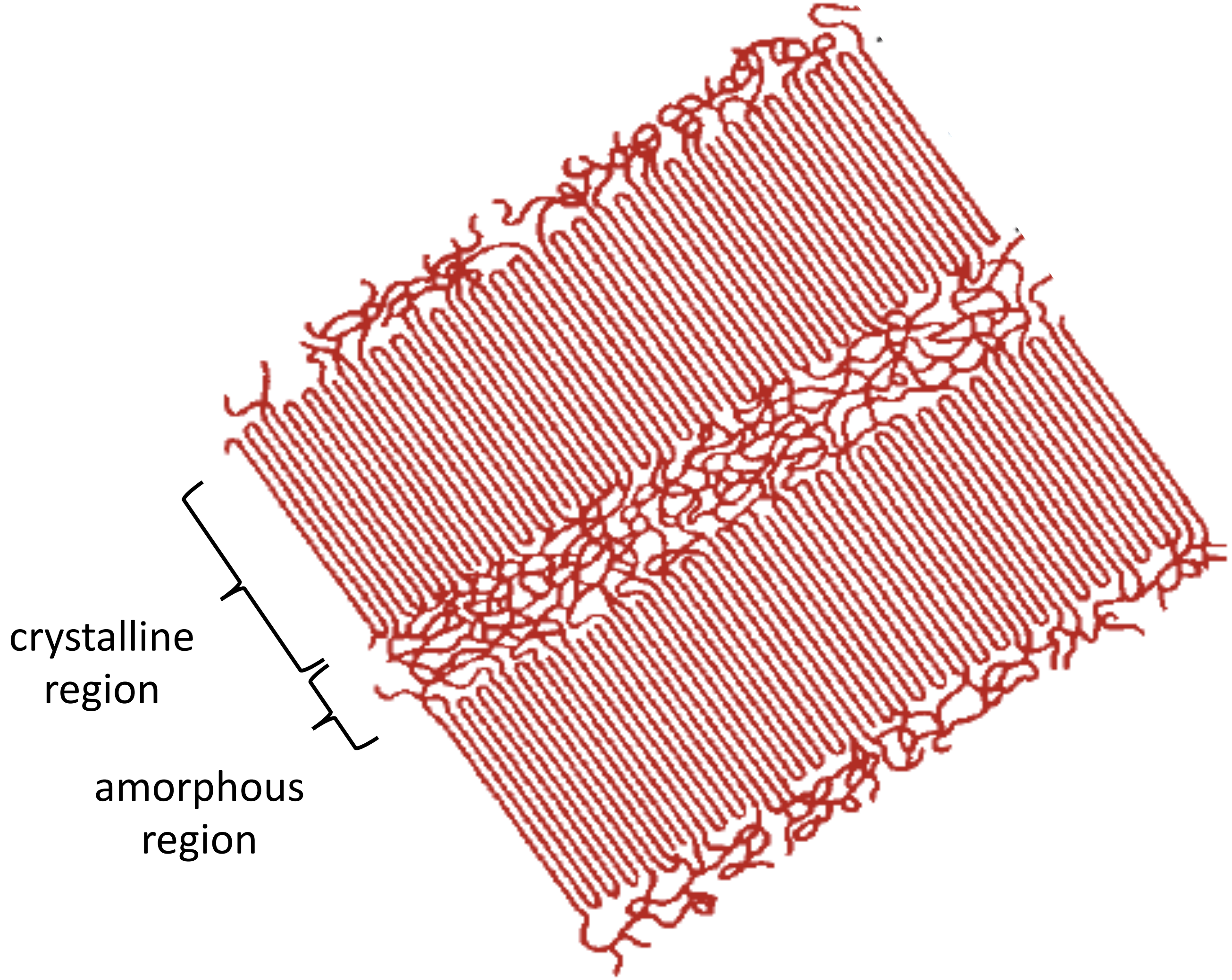




Network (3D)

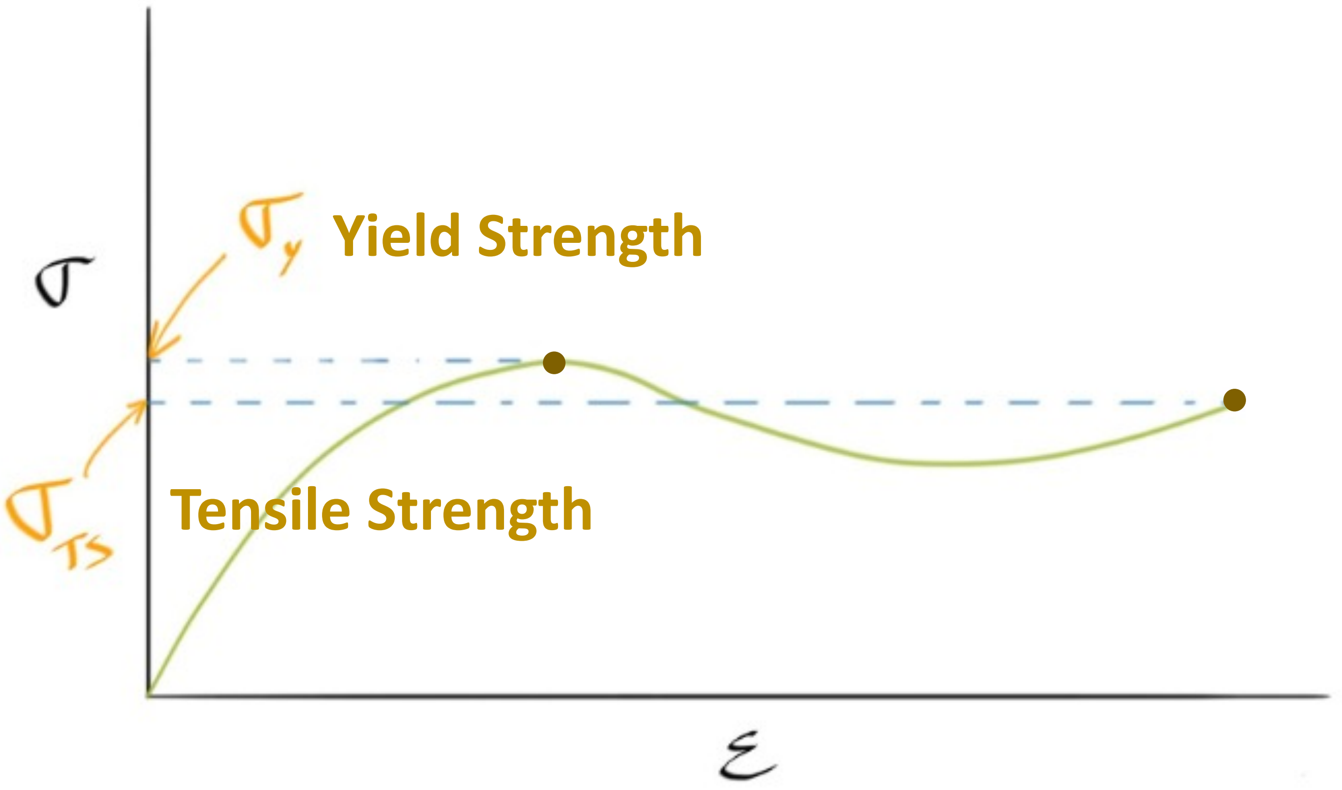
Theory Review

- Structure of Polymers
  - Degree of Crystallinity
    - Amorphous
    - Semicrystalline (fig)
  - What facilitates crystallization?
    - Simple, small mer
    - No branches

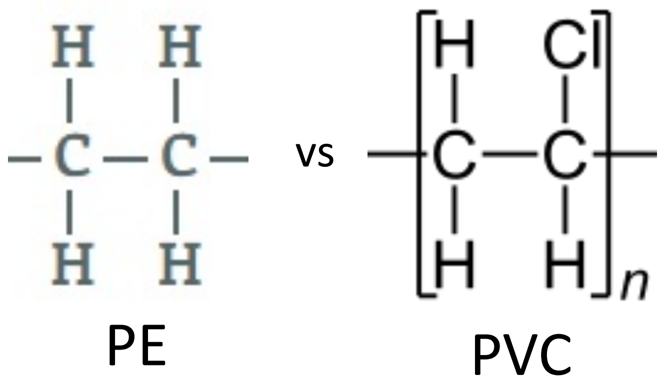


Theory Review

- Mechanical Properties
  - Stress-Strain Curve



- What makes a polymer stronger?
  - Crosslink & Network
  - Stronger van der Waals forces
    - Degree of crystallinity
    - Higher molecular weight
    - Polarized bonds:



Theory Review

- Molecular Weight of Polymers
  - Number Average:

$$\bar{M}_n = \sum_i x_i \bar{M}_i = \frac{\sum_i n_i \bar{M}_i}{N}$$

    - x_i: number fraction in i
    - $\bar{M}_i$: molecular weight of i
    - n_i: number of molecules in i
    - N: total number of molecules:

$$N = \sum_i n_i$$

Obs: $x_i = n_i / N$

  - Weight Average:

$$\bar{M}_w = \sum_i w_i \bar{M}_i = \frac{\sum_i n_i \bar{M}_i^2}{W}$$

    - w_i: weight fraction
    - W: total molecular weight:

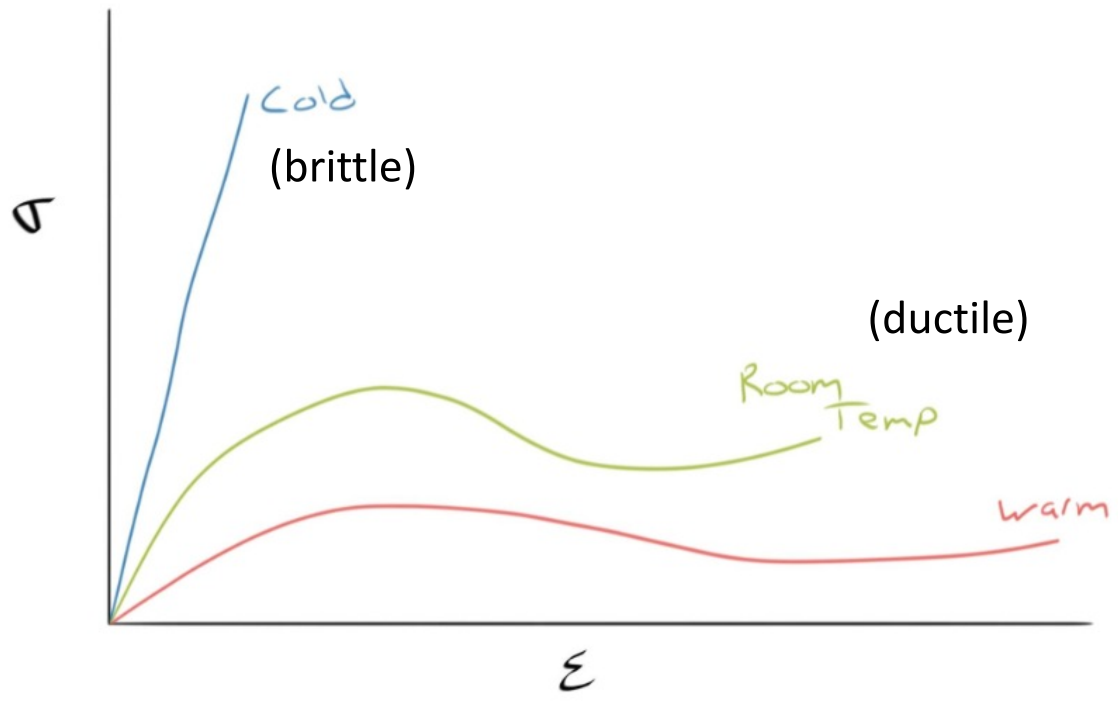
$$W = \sum_i n_i \bar{M}_i$$

Obs: $w_i = n_i \bar{M}_i / W$

Theory Review

- Temperature Changes on Polymers
  - Melting Temperature (T_m):
  when the crystalline parts melt
  - Glass Transition Temperature (T_g):
  when the amorphous part "stops being brittle"
  - Thermoplastic polymers melt
  - Thermoset polymers don't melt
    - Vulcanized (cross-linked)

- SS Curve against T



Theory Review

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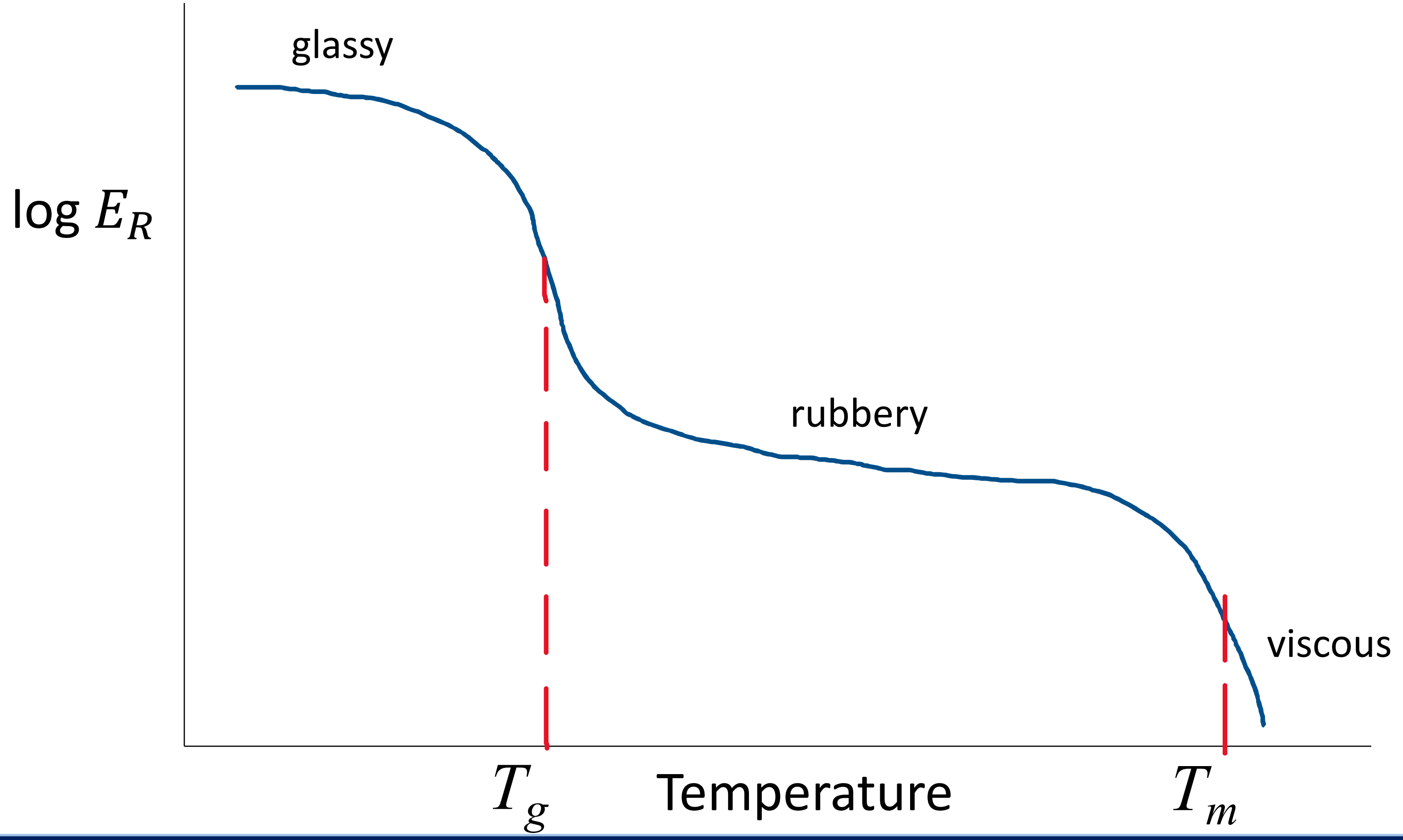
- Viscoelasticity
  - Relaxation Modulus:

$$E_R = \frac{\sigma(t)}{\varepsilon_0}$$

We apply a strain ε_0 and watch the stress $\sigma(t)$ decreasing with time. Then we measure E_R after a certain time to have a standard quantification and…

…plot its log against the temperature:



Sample Problems

Using well organized point form, explain all of the processes or microstructural changes that may be used to increase the strength of a polymer. Only work written on this page will be graded. You may use sketches to support your response.

- increase chain length (molecular weight)
  - ↳ more entanglement
- introduce polar bonds (dipoles) into mer units
  - ↳ stronger 2° bonds
- increase crystallinity
  - ↳ simple, small mer units
  - ↳ regular repeating molecule (stereoisomers - isotactic NOT atactic)

Sample Problems

Using well organized point form, explain all of the processes or microstructural changes that may be used to increase the strength of a polymer. Only work written on this page will be graded. You may use sketches to support your response.

- cross-link
  - ↳ strong 1° bonds b/w chains
  - ↳ prevent / minimize chain sliding.
- use a network polymer
  - ↳ 1° bonds in all directions.
  - ↳ significantly limiting movement of molecules.

Sample Problems

Draw an estimation of the shapes of the relaxation modulus (log scale) versus the temperature curves for the following three polymers. Describe what is unique about each compared to the others, and what occurs during the two transitionary phases on these curves. **[5]**

a) 90% crystalline PE
b) 70% crystalline PE
c) Transparent PMMA

Quizz (not graded)

1. Which of the following is most likely to be correct when comparing the density for samples of polyethylene?
    a. Highly crystalline ≈ low crystallinity, high molecular weight ≈ low molecular weight
    b. Highly crystalline ≈ low crystallinity, high molecular weight > low molecular weight
    c. Highly crystalline > low crystallinity, high molecular weight > low molecular weight
    d. Highly crystalline > low crystallinity, high molecular weight ≈ low molecular weight

2. You are to choose the best material for use as a load bearing hinge surface. Without knowing anything else, how would you rank the following polymers from most appropriate to least appropriate for producing these moulds?
    a. Low molecular weight, highly branched polyethylene
    b. High molecular weight, and lightly branched polyethylene
    c. Ultrahigh molecular weight and highly branched polyethylene
    d. Ultrahigh molecular weight and lightly branched polyethylene

    i. D, C, B, A
    ii. B, C, D, A
    iii. D, B, C, A
    iv. B, C, A, D

Quizz (not graded)

3. A hypothetical polymer has the following molecular weight distribution. Estimate the weight average molecular weight of this polymer
   a. 36246.3 g/mol
   b. 11477.9 g/mol
   c. 32209.0 g/mol
   d. 12587.0 g/mol

Mean Molecular Weight (g/mol)	Number Fraction
7300	0.05
23200	0.17
28000	0.48
48200	0.3

4. Which general class of material has a Young's modulus that is roughly one hundred times less than that of metals?
   a. Polymers
   b. None of the above
   c. Ceramics
   d. Composites

Quizz (not graded)

5. For each of the following polymer pairs, state which you would expect to crystallize to a higher extent compared to the other. Justify your choice.
   a. Syndiotactic linear polyethylene vs. isotactic polystyrene
   b. Linear polyethylene vs. atactic polypropylene

6. An unknown polymer sample is heated and observed to not melt before burning. Which of the following are possible microstructures for this polymer?
   a. Highly branched
   b. Highly cross-linked
   c. Linear
   d. Network
      i. B and C
      ii. B and D
      iii. B only
      iv. C and D

Quizz (not graded) – Solutions

Quiz Answers

1. D
2. A
3. A
4. A
5. Syndiotactic linear polyethylene, linear polyethylene
6. b