Overview of Polymers

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Polymers

• Where people have, since the industrial revolution, used metals, nature uses polymers. Biological systems such as wood, bone, cartilage, leather perform mechanical functions, others (leaf, veins, cells) contain and regulate chemical reaction.
• Wood and bone are actually composites consisting of strong fibers embedded in soft matrix.
• Usually polymers are less stiff, strong, and tough than metals and ceramics (cement can be considered as a ceramic material).
• Polymers can be classified as
  (1) thermoplastics - soften on heating (polyethylene);
  (2) thermosets or resins - harden when two components (a resin and a hardener) are heated together (epoxy);
  (3) elastomers or rubbers;
  (4) natural polymers - mechanical basis of most plant and animal life (cellulose, lignin, protein…).
Thermoplastics

• Also known as *linear polymers*, which is the chains are not cross-linked (but can branch).
• The secondary bonds that bind the molecules together melt so that it flows like a viscous liquid on heating (formability).
• Some (polystyrene) are amorphous; others (polyethylene) are semi-crystalline.
• Their viscosity falls over a range of temperature, like that of an inorganic glass.
• They are made by adding together (polymerising) sub-units (monomers) to form long chains:
Thermoset Resins

- Thermosets are made by mixing two components (a resin and a hardener) which react and harden, either at room temperature or heating.
- They are heavily cross-linked, also known as network polymers, formed during the polymerisation of the liquid resin and hardener. The structure is almost always amorphous.
- On heating, the stiffness drops due to the melting of the secondary bonds but the cross-links prevent true melting or viscous flow so they cannot be hotworked (it turns into a rubber).
- Further heating just causes it to decompose.
Elastomers

- More commonly known as rubbers.
- They are almost linear polymers with occasional cross-links in which, at room temperature, the secondary bonds have already melted.
- The cross-links provide the "shape memory".

<table>
<thead>
<tr>
<th>Elastomer</th>
<th>Composition</th>
<th>Uses</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyisoprene</td>
<td>( \text{\text{-C-H, CH}_2, H} )</td>
<td>Natural rubber.</td>
</tr>
<tr>
<td>Polybutadiene</td>
<td>( \text{\text{-C-C=-C-C} H} )</td>
<td>Synthetic rubber, car tires.</td>
</tr>
<tr>
<td>Polytetrafluoroene</td>
<td>( \text{\text{-C-C=C-C} H} )</td>
<td>Neoprene, an oil-resistant rubber used for seals.</td>
</tr>
</tbody>
</table>

Natural Polymers

- The rubber polyisoprene, cellulose (paper) and lignin (main components of wood and straw), as well as proteins like wool or silk, are natural polymers.
- Lignin left from wood processing cannot be processed to give a useful polymer. If it could, it would form the base for a vast new industry.

<table>
<thead>
<tr>
<th>Natural polymer</th>
<th>Composition</th>
<th>Uses</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose</td>
<td>( \text{\text{-C-H, CH}_2, H} )</td>
<td>Framework of all plant life, as the main structural component in cell walls.</td>
</tr>
<tr>
<td>Lignin</td>
<td>Amorphous.</td>
<td>The other main component in cell walls of all plant life.</td>
</tr>
<tr>
<td>Protein</td>
<td>( \text{\text{-NH-C-C-H}} )</td>
<td>Gelatin, wool, silk.</td>
</tr>
</tbody>
</table>
## Useful Data

### Properties of Polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Cost (£/t) (EUR/tonne)</th>
<th>Density (g/cm³)</th>
<th>Young's modulus (GPa)</th>
<th>Tensile strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermoplastics</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyethylene, PE (low density)</td>
<td>560 (790)</td>
<td>0.91–0.94</td>
<td>0.15–0.24</td>
<td>7–17</td>
</tr>
<tr>
<td>Polyethylene, PE (high density)</td>
<td>510 (790)</td>
<td>0.95–0.98</td>
<td>0.55–1.3</td>
<td>20–37</td>
</tr>
<tr>
<td>Polypropylene, PP</td>
<td>625 (950)</td>
<td>0.91</td>
<td>1.2–1.7</td>
<td>50–70</td>
</tr>
<tr>
<td>Polyvinylidene fluoride, PVDF</td>
<td>—</td>
<td>2.2</td>
<td>0.55</td>
<td>17–28</td>
</tr>
<tr>
<td>Polyethylene, PS</td>
<td>650 (910)</td>
<td>1.1</td>
<td>3.0–3.3</td>
<td>35–88</td>
</tr>
<tr>
<td>Polyvinyl chloride, PVC (unplasticised)</td>
<td>425 (595)</td>
<td>1.4</td>
<td>2.4–3.0</td>
<td>40–60</td>
</tr>
<tr>
<td>Poly(methyl methacrylate), PMMA</td>
<td>1070 (1550)</td>
<td>1.2</td>
<td>3.3</td>
<td>40–90</td>
</tr>
<tr>
<td>Nylon</td>
<td>2350 (3500)</td>
<td>1.15</td>
<td>2–5.5</td>
<td>60–110</td>
</tr>
<tr>
<td><strong>Birefringence</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polycarbonate</td>
<td>1150 (1600)</td>
<td>1.3–1.4</td>
<td>2.4–5.5</td>
<td>40–85</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>930 (1300)</td>
<td>1.1–1.4</td>
<td>1.3–4.3</td>
<td>45–83</td>
</tr>
<tr>
<td>Polyphenylene oxide</td>
<td>720 (1050)</td>
<td>1.37</td>
<td>1.8</td>
<td>35–65</td>
</tr>
<tr>
<td><strong>Melt shrinkage (underwater)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyethylene</td>
<td>610 (850)</td>
<td>0.91</td>
<td>0.02–0.1</td>
<td>—</td>
</tr>
<tr>
<td>Polyvinyl chloride</td>
<td>619 (850)</td>
<td>1.5</td>
<td>0.04–0.1</td>
<td>—</td>
</tr>
<tr>
<td>Polyethylene terephthalate</td>
<td>1460 (2000)</td>
<td>0.94</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td><strong>Natural polymers</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cellulose fibres</td>
<td>1.5</td>
<td>25–40</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>Lignin</td>
<td>1.6</td>
<td>2.0</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>Protein</td>
<td>1.2–1.4</td>
<td>—</td>
<td>—</td>
<td></td>
</tr>
</tbody>
</table>
Useful Data

- Note that the “same” polymer from different manufacturers can be quite different, since these properties vary with molecular weight that is very sensitive to processing parameters. It is also due to branching, degree of crystallization, degree of alignment, and additives.
- The secondary bonds melt at $T_g$ (glass temperature).
- Below $T_g$ the polymers have a modulus around 3GPa.
- Around $T_g$ polymers are usually fairly tough. $K_{IC}$ decreases rapidly when $T < T_g$.
- However, the secondary bonds can melt under loads and therefore polymers soften after long time loading.
- The ductility of polymer is much better than most of metals and ceramics.

Structures of Polymers

- The structure of polymers is exotic. Even the macromolecules in crystalline polymers are not well ordered. They are more like the poorly oriented woven threads in a horse blanket.
- Note that there is no “fully” crystallized polymers. The crystalline phase is always $< 70-80\%$.
- For amorphous polymers, the chains twine around like a bag full of sticky, tangled rope.
- On heating, linear polymer chains slither past each other and the polymer softens and melts. The viscous flow always tends to straighten and align the chains (fibers).
- Cross-linked polymers behave as networks: each chain is cross-linked in many places, so that if stretched out the array would look like a piece of Belgian lace, somehow woven in three dimensions.
Molecular Length

- Ethylene, C₂H₄, is a molecule (monomer).
- Polymerisation breaks the double bond, allowing it to link to others.

Many activated monomers form polymer.
- The ends of the chain can either link to other macromolecules (or monomers) so the chain grows, or link to a terminator (such as a -OH group) so that the chain growth stops (if both ends are terminated).
- To form useful polymers, the number of the repeat unit must be > 500.
- The molecular length spectrum is usually referred as degree of polymerisation (DP): the number of repeat units (~10³ - 10⁵).
- The molecular weight = DP × weight of monomer (28 for ethylene).
Molecular Length

- For polyethylene, DP < 300 gives no strength (short chains slip too easily).
- Strength rises with DP, but so does viscosity (hard to mold if DP > 10^3).

Molecular Architecture

- Thermoplastics are the largest class of engineering polymer. They have linear molecule and not cross-linked.
- Monomers have two active bonds (*bifunctional* monomers) form linear chains.
- Small molecules with only one active bond act as terminators.
- Monomers with three or more active sites (*polyfunctional* monomers) form networks, which are basis of thermoset resins.
- The simplest linear-chain polymer is polyethylene.
- By replacing on H atom by a *side-group*, we obtain the *vinyl group* of polymers: polyvinyl chloride (Cl), polypropylene (CH₃), polystyrene (C₆H₅).
Molecular Architecture

- Since the zig-zag nature of the backbone causes asymmetry, there are three possible structures to arrange the side groups: *isotactic* (same side); *sindiotactic* (altered regularly); and *atactic* (altered randomly).

Molecular Architecture

- The tacticity affects polymer properties significantly.
- The regular molecules (first three) can stack side-by-side to form crystals (side group can nestle into concavities of the next molecule).
- The atactic molecules cannot. Their side-groups clash. Thus the polymers are of low density and non-crystalline structure.
- The isotatic (one-sided) molecules carry a net electric dipole and can be electroactive, e.g. piezoelectric effects.
- If another macromolecule instead of a side-group is attached, *branching* occurs. It hinders crystallization, just as acteticty does.
Molecular Architecture

- If two H atoms are replaced by radicals, we have vinylidene group polymers.
- E.g., polymethylmethacrylate (PMMA). The two radicals are -CH₃ and -COOCH₃.
- Obviously it is more difficult for them to get crystalline structure (though they are still linear chains).
- When linear chains are drawn into fibers, the chains are aligned, leading to much higher modulus and strength (nylon, Dacron, Kevlar fibers reflect the near-perfect lining up of the macromolecules).

Molecular Architecture

- Thermosets start from large polyfunctional monomers. They react with each other or with small, linking molecules in a condensation reaction (one which plucks an -OH from one molecule and an -H from the other to given H₂O, a by-product, welding the two molecules together).
- Since one of the two molecules is polyfunctional, random three-dimensional networks are possible.
- They do not soften upon heating, and do no dissolve in solvents.
- They cannot be formed after polymerisation.
- They are stiffer, chemically more stable, an useful under high temperature.
- They are used as coating, adhesives, and the matrix of composites.
Molecular Architecture

- Elastomers are special sort of cross-linked polymer.
- They are really linear polymers with just a few cross-links (one every hundred or more repeat units). E.g. a molecular with a DP of 500 have fewer than 5 cross-links along its length.
- The elastomer has a glass temperature well below room temperature, so that at room temperature the secondary bonds have melted.

Chain Packing

- Usually a polymer chain has a contoured configuration since each C-C joint in their backbone has rotational freedom. In melts, the chain-links bend in a random way.
- The end-to-end distance is most likely to be $n^{1/2}\lambda$. 
Chain Packing

• When the melt is cooled (becomes a solid), the “spaghetti tangle” may simply freeze without rearranging, which leads to an amorphous polymer.

• In some cases, part of the chain can move and may partly line up to form crystallites, with the chain-folded structure, due to the lower potential (the charged side groups pull the molecules together into parallel bundles).

Chain Packing

• The chain folding can never be perfect. Note that the cell is much smaller than the molecule itself.

• The semi-crystalline (crystallinity is always < 80%) looks like bundle chain-folded segments, forming the crystallites separated by amorphous phase (matrix, glass region).
Chain Packing

- Often the crystalline platelets organize themselves into spherulites.
- Bundles of crystals growing radically trap amorphous chains between them, wedging them apart. Thus more crystallites nucleated on the bundle. They splaying continuous until the crystallite bend back on themselves and touch.
- The sperulites grow as a sphere until it impinges on others, forming a grain-like structure.

Chain Packing

- When a liquid crystallizes to a solid, there is a sharp, sudden decrease of volume at the melting point.
- The random arrangement of the molecules changes rapidly to the locally ordered, nearly packed crystal grains.
- Other properties, e.g. viscosity, also changes dramatically.
- The transition of polymers is usually blunt since the imperfect packing and the molecular weight distribution.
Chain Packing

- For amorphous polymers that cannot crystallize (side-groups, atacticity, branching, cross-linking), the random arrangement of chains in melts remains in solids.
- In melts, the thermal motion of the chains makes the volume larger, with the extra volume known as free volume. It is the free volume, together with the thermal energy, that allows the molecules to move relative to each other, giving viscous flow.
- When $T$ decreases, the free volume is lost gradually, and the viscosity increases. When all the free volume is lost, glass transition occurs.
- Below $T_g$, the polymer is a glass. Secondary bonds bind the molecules into an amorphous, brittle solid (rubber below -70°C is like PMMA ($T_g = 100°C$) at room temperature).
- Above $T_g$, the polymer becomes first leathery, then rubbery, capable of large elastic extensions without brittle fracture.

Mechanical Behavior

- All polymers are brittle elastic at low $T$. As $T$ increases, they will become plastic, viscoelastic (leathery), rubbery, and finally viscous.
- The mechanical properties of the polymers depend on their molecular weight and temperature (how close is $T$ to $T_g$).
Mechanical Behavior

- The stiffness is defined as $E = \sigma / \varepsilon(t, T)$. It is not a constant for polymers. It changes with time and temperature (by as much as a factor of 1000!).
- Linear-amorphous polymers (PMMA, PS…) show 5 regimes:
  1. the glassy regime. $E \sim 3$GPa.
  2. the glass-transition region. $E$ drops to $\sim 3$MPa.
  3. the rubbery regime. $E \sim 3$MPa.
  4. the viscous region. Polymers start to flow.
  5. the regime of decomposition. Chemical breakdown starts.
- **Glassy region**: when $T < T_g$, the secondary bonds are relatively stable. Chains pack closely together, either in an amorphous tangle or in poorly crystallized phase embedded in amorphous matrix.

Mechanical Behavior

- The covalent bonds that form the backbone are always strong (pure C-C bond $\rightarrow$ diamond).
- The secondary bonds bringing the chains together are flabby and soft.
- The overall modulus is the average of the two bonds:
  \[
  \varepsilon = f \frac{\sigma}{E_1} + (1-f) \frac{\sigma}{E_2} = \sigma \left( \frac{f}{E_1} + \frac{(1-f)}{E_2} \right).
  \]
  \[
  \sigma = \frac{\varepsilon}{f} = \left[ \frac{f}{E_1} + \frac{(1-f)}{E_2} \right]^{-1}.
  \]
  $f$: fraction of covalent bonds ($E_1$);
Mechanical Behavior

- When $f = 1$, it is diamond. $E_1 \sim 10^3 \text{GPa}$.
- If $f = 0$, it hydrocarbon like paraffin wax, $E_2 \sim 1 \text{GPa}$.
- Thus, we have
  $$E = \left(\frac{f}{10^3} + \frac{(1-f)}{1}\right)^n \text{GPa}.$$ 
- At low $T$, $E$ is temperature insensitive, while secondary relaxations can occur due to the adjustment of the loose sites (side groups) to give a little extra strain.

Glass Transition: As $T$ rises, the secondary bonds melt. Then segments of the chains can slip relative to each other like bits of greasy string, and $E$ falls steeply.
- It is helpful to imagine that each chain is restrained by surrounding nest of molecules. The effect can be represented by a "tube" (free volume).
- The chain can slide in the tube (reptation) giving extra strain and dissipating energy, but can not move out of the tube.
Mechanical Behavior

- As \( T \) rises, the polymer expands and the extra free volume lowers the packing density, allowing more region to slide, and give a lower apparent modulus.
- However, there are still non-sliding (elastic) part. When unloading, the elastic part push the polymer back to the original shape (it must do so against the reverse viscous sliding). Thus, the material becomes leathery.
- Within this regime, \( E \) is both temperature and strain rate dependent. Increasing \( T \) is equivalent to lowering strain rate.

\[ a_T \approx \frac{C_1(T_1 - T_0)}{C_2 + (T_1 - T_0)} \]

where \( a_T = t_0/t_1 \). \((t_0, T_0)\) and \((t_1, T_1)\) give the same \( E \).

- \( C_1 \) and \( C_2 \) are material constants. For all amorphous polymers \( C_1 \sim 17.5; C_2 \sim 52^\circ\text{K} \).
Mechanical Behavior

- As $T > T_g$, the flow becomes easier and easier. Eventually the thermoplastics turns into a sticky liquid. But before that, due to the difficulty of chain slip, polymers with long chains (DP > $10^4$) will go through a rubbery state.
- The chains interpercolate each other and form entanglements (knots), which act like chemical cross-links.

Mechanical Behavior

- The entanglements give the material a shape memory: load it, and the segments between entanglements straighten out; remove the load and the wriggling of the molecules (being above $T_g$) draws them back to their original configuration, and thus shape.
- The rubbery is only 0.1% of the glassy modulus. But it is there nevertheless, giving the rubbery plateau.
- More pronounced rubbery behavior is obtained if the chance entanglements are replaced by deliberate cross-links. The number of cross links is only one per several hundred repeat units. But, being strong, the covalent cross links do not melt, and the material is capable of elastic expansion of ~300%.
- The the cross-link density is too high, the flexibility is lost.
Mechanical Behavior

- When $T > \sim 1.4T_g$, even the entanglement points slip. Thus, the thermoplastics can be molded. They become **viscous flow**.
- The viscosity is always defined in shear (ratio of shear stress to shear strain rate)
  $$\eta = \frac{\tau}{10\gamma}$$
  The unit is poise (P) or $10^{-1}\text{Pa}\cdot\text{sec}$.
- In $1.3-1.5T_g$, the viscosity still follows WLF equation. This is called rubbery flow.
- For higher temperature, Arrhenius law dominates (like inorganic glass). This is called Arrhenius flow.
- If the viscosity at $T_0$ is $\eta_0$, at a higher $T_1$,
  $$\eta_t = \eta_0 \exp\left(\frac{C_2(T_1 - T_0)}{C_3 + T_1 - T_0}\right)$$

Mechanical Behavior

- Cross-linked polymers never melt. But all polymers **decompose** if $T$ is high enough, since the thermal energy exceeds the energy of some part of the molecular chain.
- Some (PMMA) decompose into monomers; some (PE) randomly degrade into many products.
- Usually the molding temperature does not exceed $1.5T_g$. 
Mechanical Behavior

- The temperature/time dependence of modulus can be reflected by the modulus diagram.
- The diagram is divided into five areas corresponding to the five regimes.

Mechanical Behavior

- If we increase the cross-link density, the contours of the modulus diagram are pushed up (the rubbery plateau is extended).
- Crystallization increases the modulus too (crystallite is stiffer than the amorphous matrix) but it does not suppress melting. So crystallized polymers can still be molded.
Mechanical Behavior

- Polymers can fail through
  1. brittle fracture, like that in ordinary glass
  2. cold drawing, the drawing-out of the molecules in the solid state, giving a large shape change
  3. shear banding, giving slip bands rather like those in metal crystals
  4. crazing, a kind of microcracking, associated with local cold drawing
  5. viscous flow, when the secondary bonds have melted
- These five mechanisms occur roughly in order in increasing $T$.

Brittle fracture: below $\sim 0.75T_g$.
- The failure stress is
  $$\sigma = \frac{K_{IC}}{\sqrt{\pi c}}$$
- The initial flaw can be caused by abrasion or environmental attack.
- $K_{IC} \sim 1\text{MPa} \cdot \text{m}^{1/2}$
  - $c \sim \text{a few mm}$
  - $\sigma \sim 100\text{MPa}$
Mechanical Behavior

- **Cold drawing**: at ~50°C below $T_g$, thermoplastics become plastic (hence the name).
- At low strain: linear elastic.
- At a strain ~0.1, the material yields and then draws. The chains unfold (if semi-crystalline) or draw out of the amorphous tangle (if glassy), and straighten and align.
- The drawing starts from a weak portion with the formation of the neck. The neck spreads out (the material in the neck is stronger, so the neck will not fail).

Mechanical Behavior

- **Crazing**: PE, PP and nylon draw at room temperature. Others (PS) with a higher $T_g$ do not (but they draw well at higher $T$), instead, they craze.
- Small crack shaped region draw down, but being constrained by the surrounding, ending up as ligaments that link the craze surfaces.
- Also known as “whitening”.
- Eventually, crazing leads to fracture.
Mechanical Behavior

- **Shear banding**: while crazing limits the ductility in tension, large plastic strains may still be possible in compression shear banding.
- Within each band a finite shear has taken place.
- As the number of the bands increases, the total overall strain accumulates.

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Mechanical Behavior

- Most of the information can be summarized in a **strength diagram**.
- The temperature/time-dependence of the strength, as well as the area of the failure mode, are shown.
- The strength always decreases with increasing *T* and time scale (reciprocal of loading rate).
- Note that the **toughness** can increase with *T* and time scale! (more energy dissipated)
Synthesis

- Natural polymers (wood, cotton, leather, etc.) are useful and plentiful.
- Synthetic polymers are cheaper, stronger, and suitable for mass production.
- Plastics are made by a chemical reaction in which monomers add (addition reaction, with nothing left over) or condense (condensation reaction, with H₂O left over) to give a high polymer.
- For example, for polyethylene, the initiator (H₂O₂) with very reactive –OH radicals breaks the double-bond of an ethylene monomer, creating an aggressively reactive end that continues to attack other monomers.

\[
\text{HO} + \text{C} = \text{C} \rightarrow \text{HO} - \text{C} - \text{C} \cdot \cdot \\
\text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H}
\]

- Note that the initiator can also act as terminator if it occupies the reactive end.
- DP depends on the amount of initiator, temperature, and pressure.
- For nylon, two different kinds of molecules react to give a larger and larger molecule, and a by-product (H₂O).
- The reaction gives symmetric large molecules that can crystallize easily. The reaction does not rely on the initiator.

\[
\text{HO} - \text{C} \cdot \cdot \cdot (\text{CH}_2)_n - \text{C} - \text{OH} + \text{H} - \text{N} - (\text{CH}_2)_m - \text{N} - \text{H}.
\]

- Most of the network polymers are synthesized through the condensation reactions.
Synthesis

• If two monomers are mixed, the chain (copolymcr) which forms contains both units (copolymcrization).
• The units add randomly, so the chain structure is less regular, and, therefore, favor an amorphous structure (low density, low $T_g$).
• PVC, when pure, is brittle; but copolymerizing it with vinyl acetate (with –COOCH$_3$ radical) gives the flexible copolymer.
• The copolymer can have either random structure or regular structure (block copolymer).

Synthesis

• A plasticiser, oily organic liquid with relatively low molecular weight (MW) 100-1000 that dissolve in large quantities (up to 35%) in solid polymers, can force apart and lubricate the large chains, making it easier for them to slide, and thus become more flexible.
• It lowers Tg, but also reduces strength.
• The surface feel slightly oily,
• It must have a low vapor pressure or it will evaporate and leave the polymer brittle.
Synthesis

• When styrene and butadiene are polymerized, the result is the mixture of distinct molecules of PS and a rubbery copolymer of styrene and butadiene.
• Upon cooling, the rubbery copolymer precipitates out.
• The resulting structure is the matrix of glassy PS contains rubbery particles of S-B copolymer particles, which stop cracks and thus increase the toughness. This is called **two-phase polymer alloy** or **toughened polymer**.
• This is called high-impact polystyrene (HIPS).

Synthesis

• Polymers (paints) are damaged by radiation, particularly by the ultraviolet in sunlight. UV photon can break the C-C bond and split the chain into short ones.
• Pigment or carbon can be added to absorb the radiation. E.g. car tires contain ~30wt% of carbon to stabilize the polymer.
• Oxygen can also attack polymers by creating –o– cross-links between polymer chains (unwanted vulcanization), which raises $T_g$ and makes the polymer brittle.
• The way to avoid this is to avoid using polymers with double bonds.
Forming

- Thermoplastics soften when heated, allowing them to be formed by injection molding, vacuum forming, blow molding, or compression molding.
- Thermosets and rubbers must be heated, formed, and cured simultaneously, usually by compression molding.
- Polymer coating can be done by using a evaporable polymer as solvent or applying the liquid mixture of the polymer and hardener (thermoset) at the same time.
- Polymer fibers are produced by forcing molten polymer or polymer in solution through fine nozzles (spinnerettes).
- Polymers can be expanded into foams by mixing in chemicals that release CO₂ bubbles into the molten polymer or the curing resin.

Forming

- **Extrusion**: A polymer extruder is like a giant cake-icer. It is a cheap continuous process for producing shapes of constant section (semi-finished products, or “semis”).
- Granules of polymers are fed into a screw turning in a heated barrel, where they are melted, compacted and mixed, and then forced through the die and cooled.
- The shear flow in the die orients the molecules in the extrusion direction.
- Considerable transverse expansion can occur when cooled, due to the recovery of the amorphous phase. Thus, the final shape can be somewhat different from the die shape.
Forming

- **Injection molding**: polymer granules are compressed by a ram or screw, heated until molten and squirted into a cold, split-mold under pressure.
  - The polymer is cooled to $< T_g$ in the mold, thus the shape is quite precise. But it is slow (1-5 minutes) and the mold is expensive.
  - The molecules are oriented parallel to the flow direction.

Forming

- **Vacuum and blow forming of sheet**: sheet produced by extrusion are heat softened and shaped by vacuum or pressure forming.
  - Cheap and quick, and fairly accurate.
  - Plastic bottles are made by blowing heated tubes in a split mold.
Forming

- Both thermosets and thermoplastics can be formed through **compression molding**.
  - The polymer, or the mixture of resin and hardener, is heated and compressed between dies.
  - The products can be removed when they are hot, so the cycle time can be ~10sec. for small components and ~10min for large parts.
  - Pressures are lower than for injection moldings.

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Forming

- Thin sheets and fine fibers of polymers are extruded, using a narrow slit or a die with many small holes.
  - The molten polymer cools very fast when it is extruded that is solidifies in the amorphous state.
  - If the sheets or the fibers are drawn off through a tensioning device which stretches them, unravelling the tangled molecules and aligning them, they can be strengthened.
  - Films have to be stretched in two directions at once: blow an enormous thin-walled bag which is then cut, opened out flat, and rolled onto a drum.

The bubble is split, flattened, and rolled onto a drum.
Joining

- Polymers are joined by cementing, welding, or various sorts of fasteners.
- A polymer is joined to itself by cementing with a solution of the same polymer in a volatile solvent.
- Polymers can be stuck to other materials with adhesives, usually epoxies.
- Polymers can be attached to a variety of fasteners that should be appropriately designed to give uniform fastening load.
- Ingenious splined or split fasteners can be molded onto polymers, allowing the parts to be snapped together.
- Threads can be molded onto parts to allow them to be screwed together.
- Polymers can be friction-welded to bring the parts, rotating or oscillating, into contact; frictional heat melts the surfaces that are held under static load until they resolidify.

Homework

- Discuss how the modulus of elasticity of a polymer is affected by
  (1) temperature
  (2) loading rate
  (3) fraction of covalent cross-link
  (4) molecular orientation
  (5) crystallinity
  (6) degree of polymerization
- (10.1) A polyethylene has an average molecular weight of 410,000 g/mol. What is its average degree of polymerization (i.e. what is average number of repeat units in one macromolecule)? Give the references of the data that you use.
  (Answer: 14,643)
- (10.7) An ABS copolymer consists of 25 wt% polyacrylonitrile, 30 wt.% polybutadiene, and 45% polystyrene. Calculate the mole fraction of each component. Give the references of the data that you use.
  (Answer: 0.324: 0.382: 0.294)