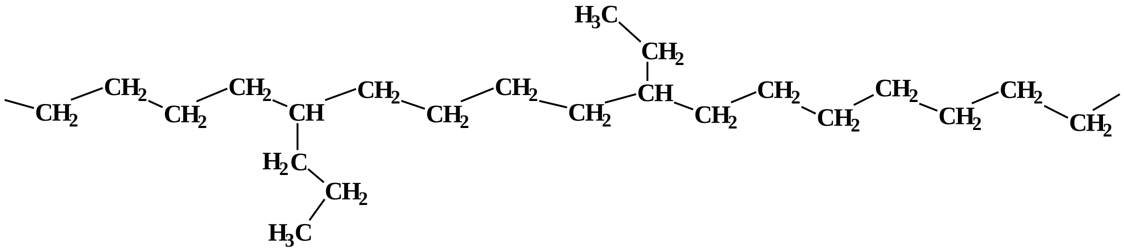
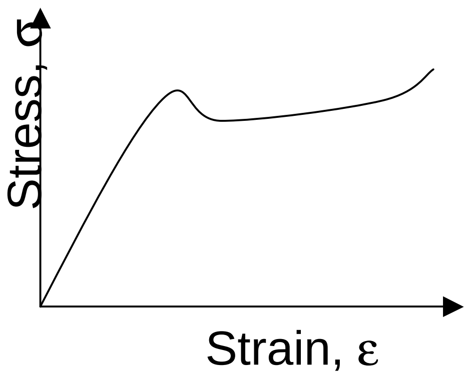
In the following slides, you will be introduced to

polymers and plastics,



the mechanical properties of plastics,



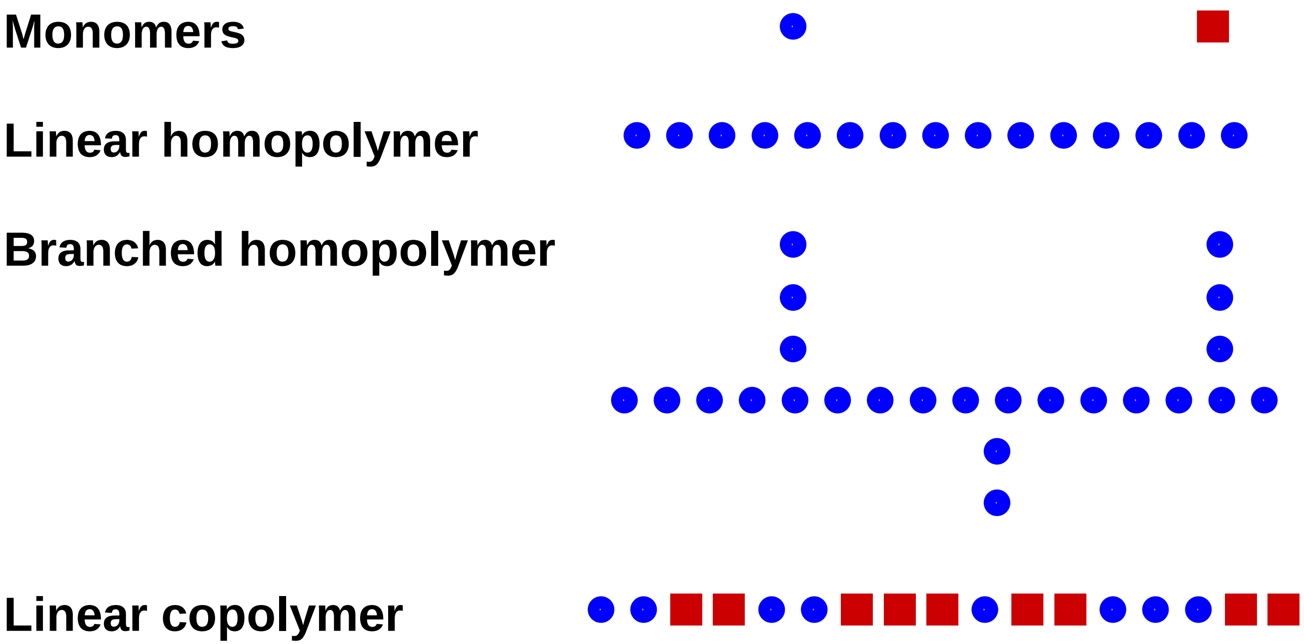
and the environmental degradability of plastics.

Polymers

A **polymer** is a substance consisting of molecules characterized by the repetition of one or more types of monomeric unit.

A polymer can contain a single type of monomer (homopolymer) or more than one type of monomer (copolymer).

Polymer molecules are described as chain-like, and can have linear or branched chains.



From little molecules to big molecules --$[CH_2]_n$--

Large molecular weights affect the nature of the material.

Number (n) of Carbons in Chain	State and Properties of Material	Application
1-4	Simple gas	Gas
5-11	Simple liquid	Gasoline
9-16	Medium viscosity liquid	Kerosene
16-25	High viscosity liquid	Oil & grease
25-50	Crystalline solid	Paraffin wax
50-1000	Semicrystalline solid	Milk carton adhesives, coatings
1000-5000	Tough **plastic** solid	Poly(ethylene) bottles
$3 – 6 \times 10^5$	Fibers	Fabrics

Gas

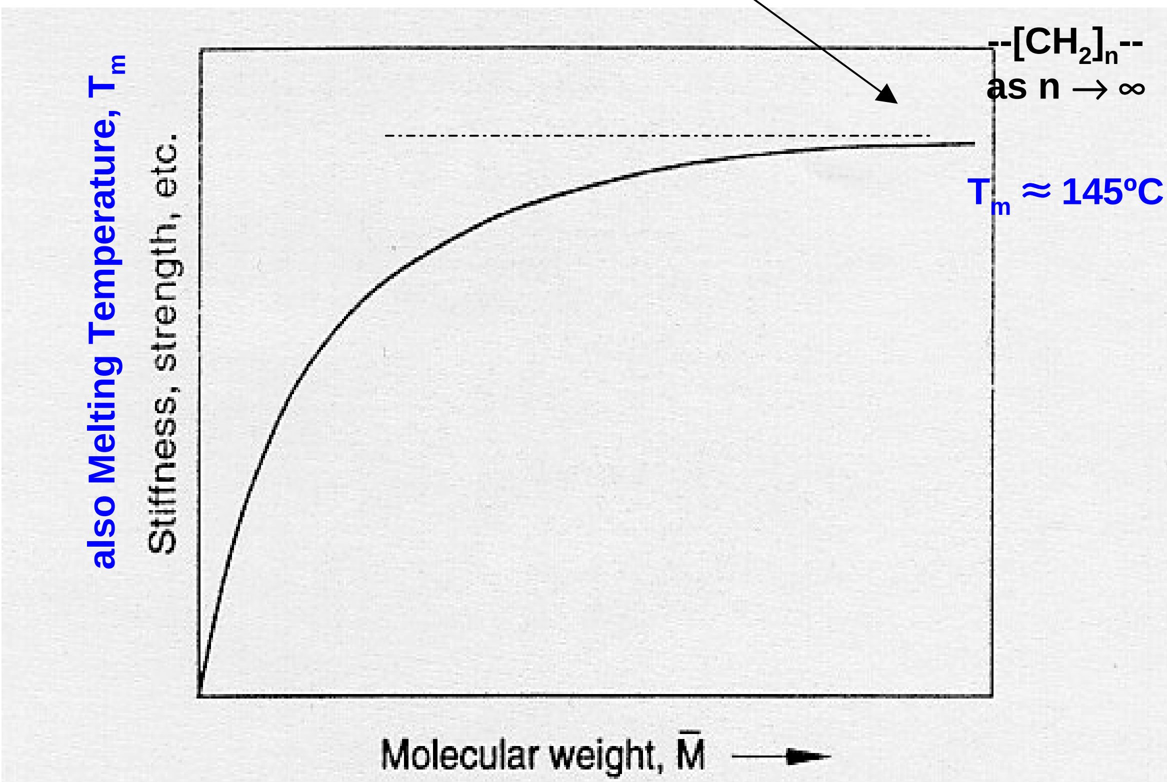
Liquid

Solid

From L. H. Sperling, “Introduction to Physical Polymer Science”

Molecular weight affects properties

Properties plateau with Increasing MW.



Long chain molecules have entanglements -- like a bowl of spaghetti

Properties plateau at a chain length of about 8 entanglements

The polymeric nature of the molecules makes polymers distinct from other materials groups, such as metals.

Example:

Density of metals	**7-10 g/ml**
Density of polymers	**0.9-1.5 g/ml**

Most commercial polymers are synthetic.

Polyolefins

The most abundant and cheapest synthetic polymers are polyolefins. Polyolefins are synthesized from olefins (the common name for alkenes). Olefins are obtained from petroleum.

An olefin is a hydrocarbon that contains at least one carbon-carbon double bond.

The simplest olefin is ethylene,

$$CH_2{=}CH_2$$

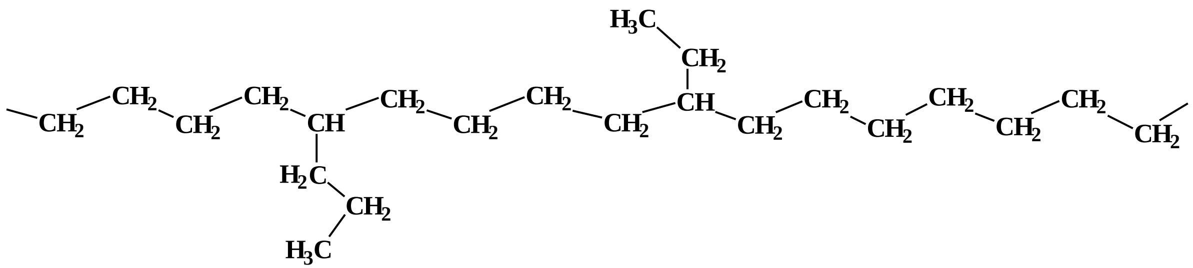
The simplest polyolefin is polyethylene (PE). A simple representation of polyethylene is

$$-\left[CH_2-CH_2\right]_n-$$

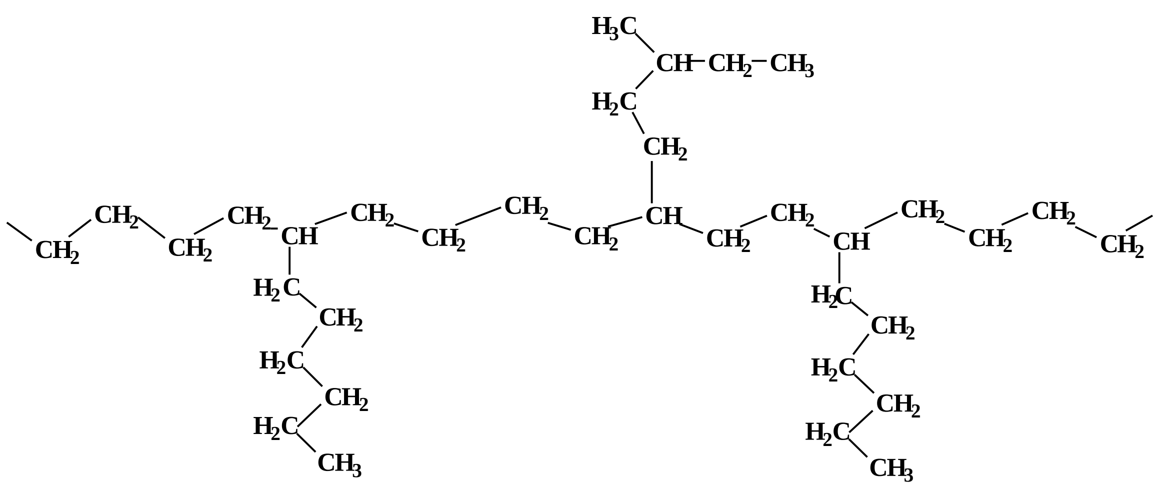
where the n is the number of monomer units.

In the polymerization, the double bond is lost.

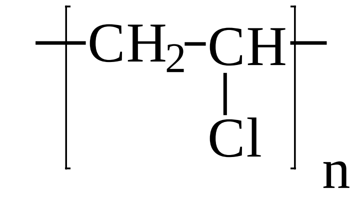
If the polyethylene chain is produced to have few and short branches (side chains) the result is high-density PE (HDPE).



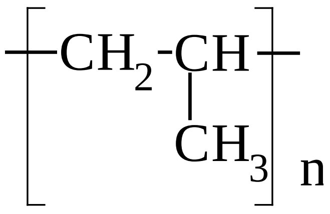
If the chain is produced to have many, longer branches, the result is low-density PE (LDPE).



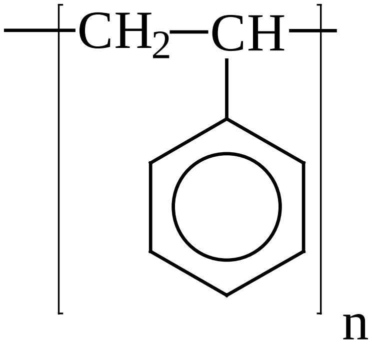
Other polyolefins



poly(vinyl chloride) (PVC) (from ethylene chloride)



polypropylene (PP) (from propylene)

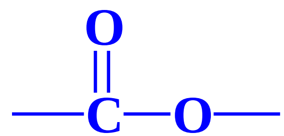


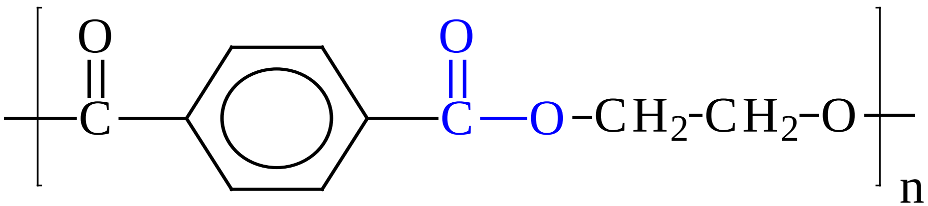
polystyrene (PS) (from styrene)

Polyolefins are very stable. Oxidative degradation is extremely slow. If not recycled, they are landfilled or incinerated. They are not biodegradable or compostable.

The single most important reason for their stability is that they have carbon-carbon single bonds in their backbone.

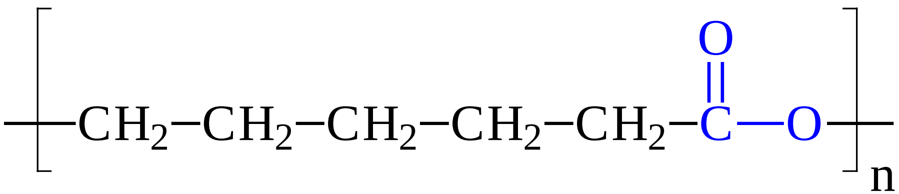
Polyesters

Polyesters contain the **ester** group, 

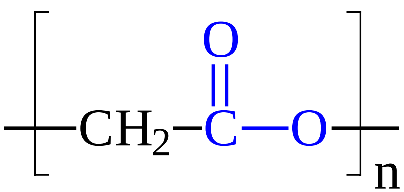


poly(ethylene terephthalate) (PET)

PETE



poly(ε-caprolactone) (PCL)

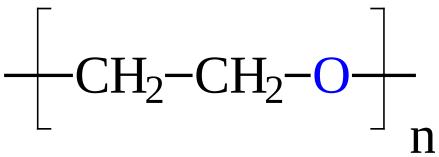


polyglycolic acid (PGA)

PGA and PCL are biodegradable.
The heteroatom (an atom other than carbon) in the backbone leads to environmental degradation by hydrolysis.

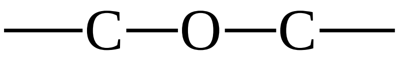
PET is not biodegradable in spite of the oxygen in the backbone, because its high crystallinity impedes access of water molecules. Most recycled plastic is PET.

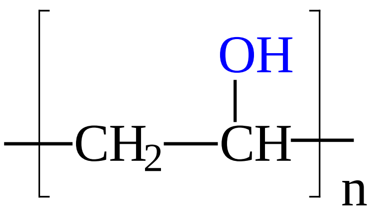
Other polymers synthesized from petroleum:



poly(ethylene glycol) (PEG)

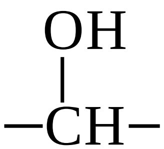
(a polyether)





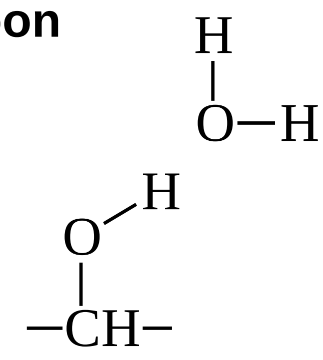
poly(vinyl alcohol) (PVA)

(a polyalcohol)



Both are environmentally degradable. PEG has a heteroatom in its backbone and environmentally degrades by hydrolysis.

PVA also degrades by hydrolysis, in spite of its -C-C- backbone, because the hydroxyl group on alternate carbon atoms leads to strong interactions with water.



Other synthetic polymers are:

poly(vinyl acetate), acrylics, polyamides (like nylon), polybutylene, polycarbonate, polyimides, polyurethanes, and epoxy resins.

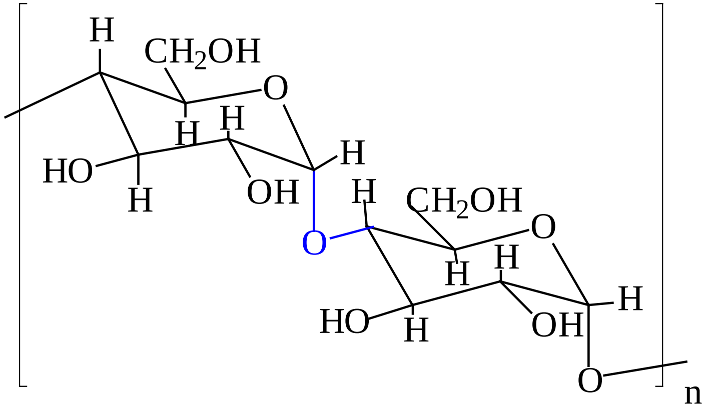
Giving polymers standardized names (polymer nomenclature) is important so that everyone understands the structure when discussing a polymer.

Not all polymers are synthetic.

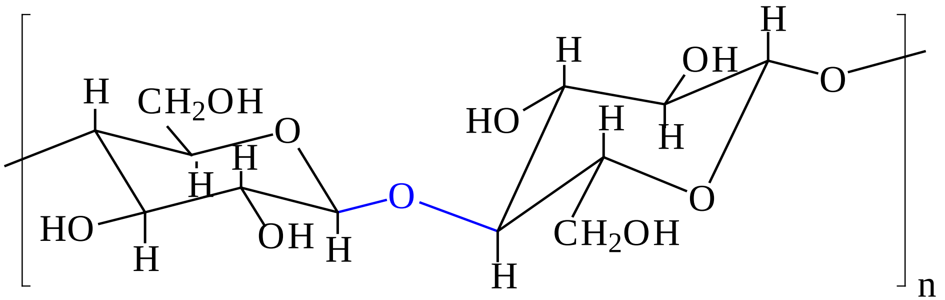
Biological polymers (biopolymers) are found in nature.

Commercially important polysaccharides include starch, cellulose, chitin, agar, carrageenan, and pectin.

amylose, a major component of starch



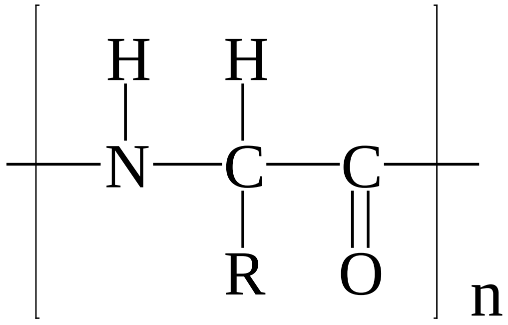
cellulose, a major component of woody plants



Biopolymers are intrinsically biodegradable.

The two structures differ only in the geometric arrangement about the linkage.

Commercially important proteins include gelatin(denatured collagen), casein, whey protein, and soy protein. Silk is also a protein.



A generic protein monomeric unit

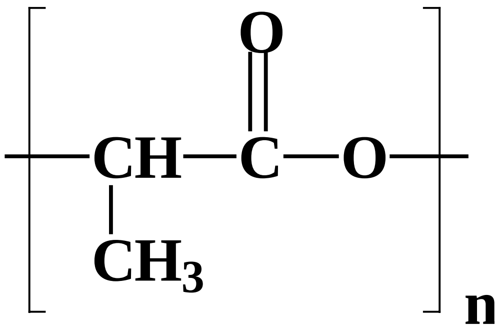
The **R** in the structure represents the side chain of an amino acid.

There are twenty common amino acids. Examples are glycine (R= H), alanine (R=CH_3) and glutamic acid (R= $CH_2CH_2COO^-$).

Any particular protein is identified by its specific sequence of amino acids.

Some polymers are synthesized, but from biomolecules found in nature. Perhaps the most important example is poly(lactic acid).

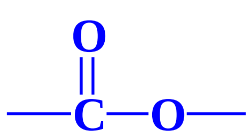
Lactic acid, ($CH_3CHOHCOOH$), the monomer, is now produced on large scales in biorefineries from the fermentation of sugars or hydrolyzed starch.



Poly(L-lactic acid) (PLA) is synthesized from lactic acid.

PLA is a polyester.

Polyesters contain the ester group



PLA is biodegradable; the heteroatom in the backbone leads to environmental degradation by hydrolysis.

From Polymers to Plastics

A **plastic** is a material that contains as an essential ingredient one or more organic polymer substance of large molecular weight.

Additives. In addition to the polymeric component, almost all plastics contain chemical additives to facilitate processing and/or improve properties.

For example, **plasticizers** are softening agents that are added to a polymer to facilitate processing or to enhance properties.

Process engineering. The bulk polymer material, called resin, is processed into three-dimensional shapes or film.

Various types of engineering processes are used, including **extrusion, molding, or film casting.**

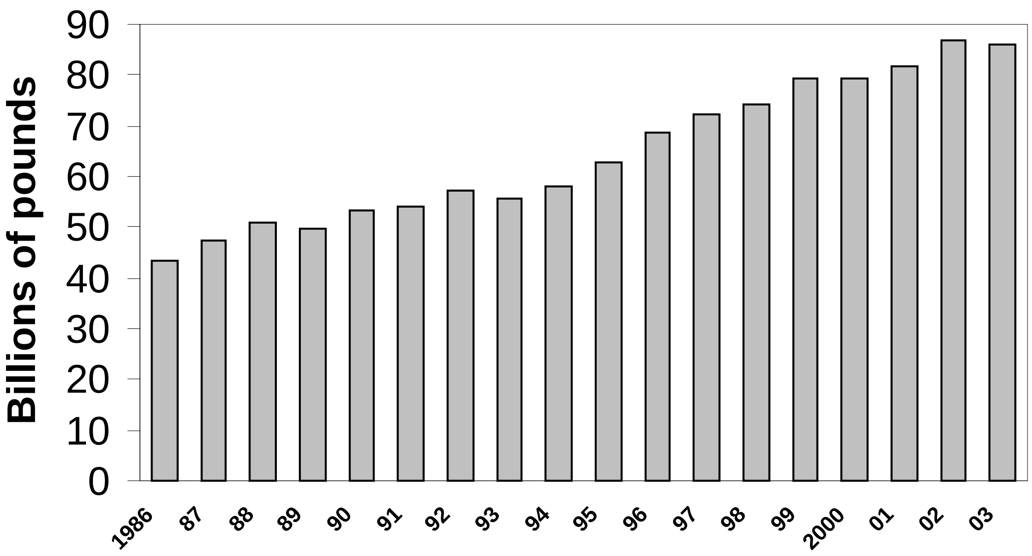
A Brabender extruder

A **thermoplastic** is a plastic that can be heat-softened and shaped. (PE, PVC, PEG, PLA are all thermoplastics.)

A **thermoset** is highly cross-linked; once it is formed it cannot be heat-softened. (Phenolic plastics and epoxy resins are thermosets.)

Plastics Production

Scope



U. S. plastics production

Worldwide production exceeds 200 billions pounds. By volume, plastics production exceeds steel production.

Properties are Important

Mechanical Properties of Plastics

Mechanical Properties:

tensile properties,* compressive properties, bending, flexural, and shear properties;

impact resistance, crack resistance, tear and tear-propagation resistance; fracture toughness.

*This introduction to polymers and plastics focuses on tensile properties of plastic film.

Properties other than mechanical properties:

density, viscosity, coefficient of linear thermal expansion,

glass transition temperature, softening temperature, ignition temperature,

water absorption, permeabilities (barrier properties), adhesion properties,

loss of volatiles, resistance to chemical reagents, aging properties,

outdoor weathering, biodegradability.

ASTM Test Methods

In the United States it is the American Society of Testing and Materials (ASTM) that is responsible for developing test methods for materials, including plastics.

Standard test methods are important for comparing products across the industry.

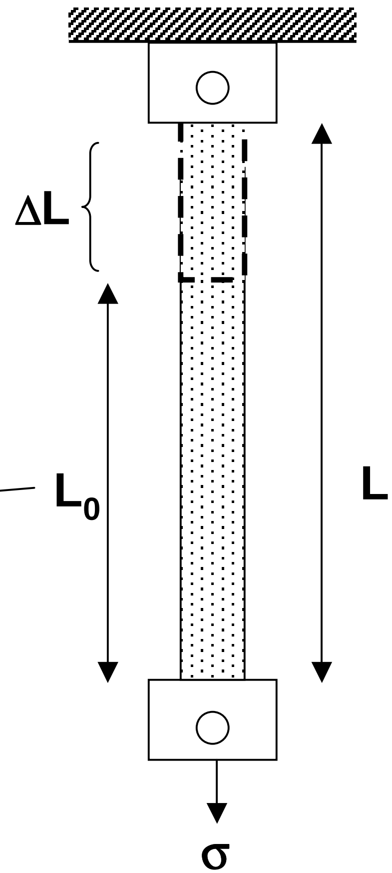
ASTM has developed over 500 test methods for plastics alone.

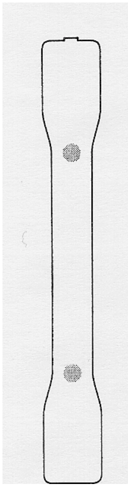
The international counterpart organization is the International Standards Organization (ISO).

Measurement of tensile properties of plastic film.

Experimental setup

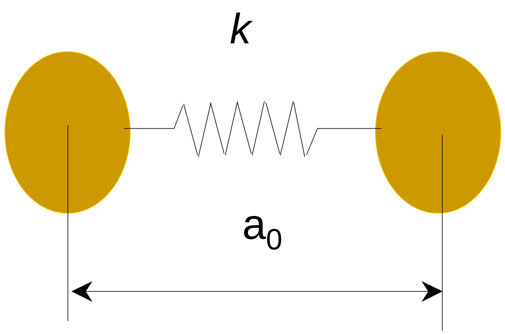
A sample is clamped in tension. A force is applied and the sample stress and strain are recorded.





a typical “dogbone” sample

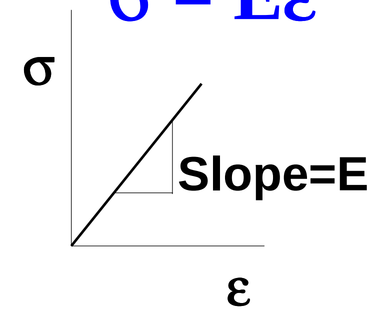
The initial film deformation is elastic.



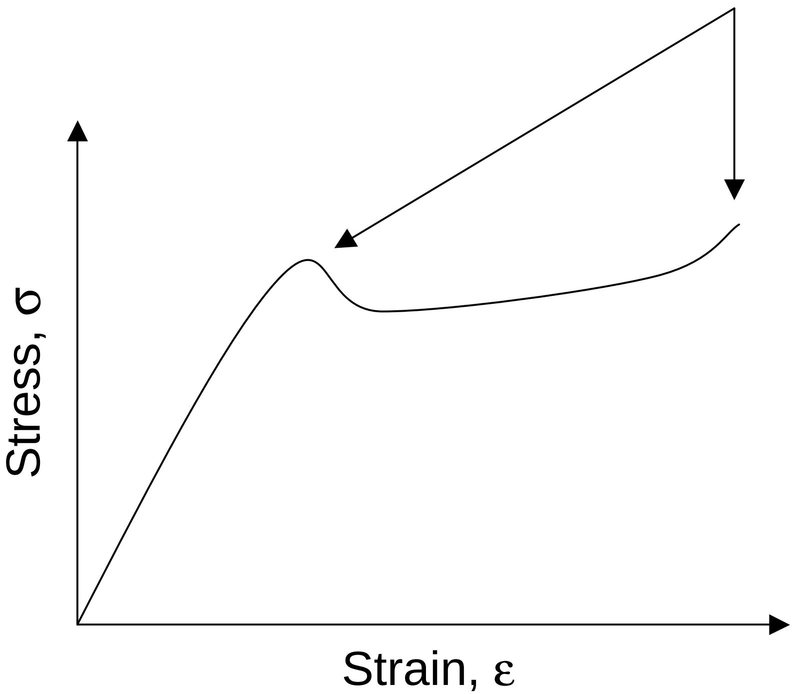
E (Young's modulus) is equivalent to the spring constant k.

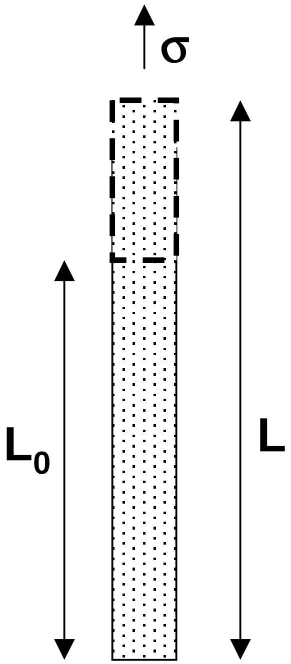
Hooke's law

$$\sigma = E\varepsilon$$



But most plastics show viscoelastic behavior





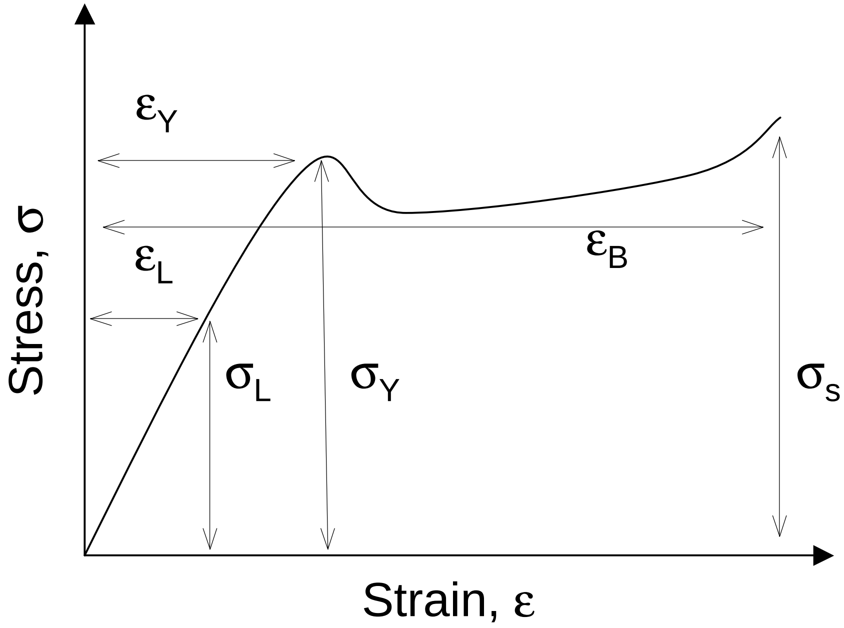
Stress, σ = force per unit area

Strain, $\varepsilon = (L-L_0)/L_0$

where L_0 is the sample's initial length and L is the final length.

The result is a stress-strain curve.

Tensile properties are obtained from features in the curve.



$d\sigma / d\varepsilon = \sigma_L / \varepsilon_L$ (L in linear range)=E tensile (Young's) modulus

σ_Y = yield stress

ε_Y = elongation at yield

σ_S = ultimate tensile strength (tensile strength at break)

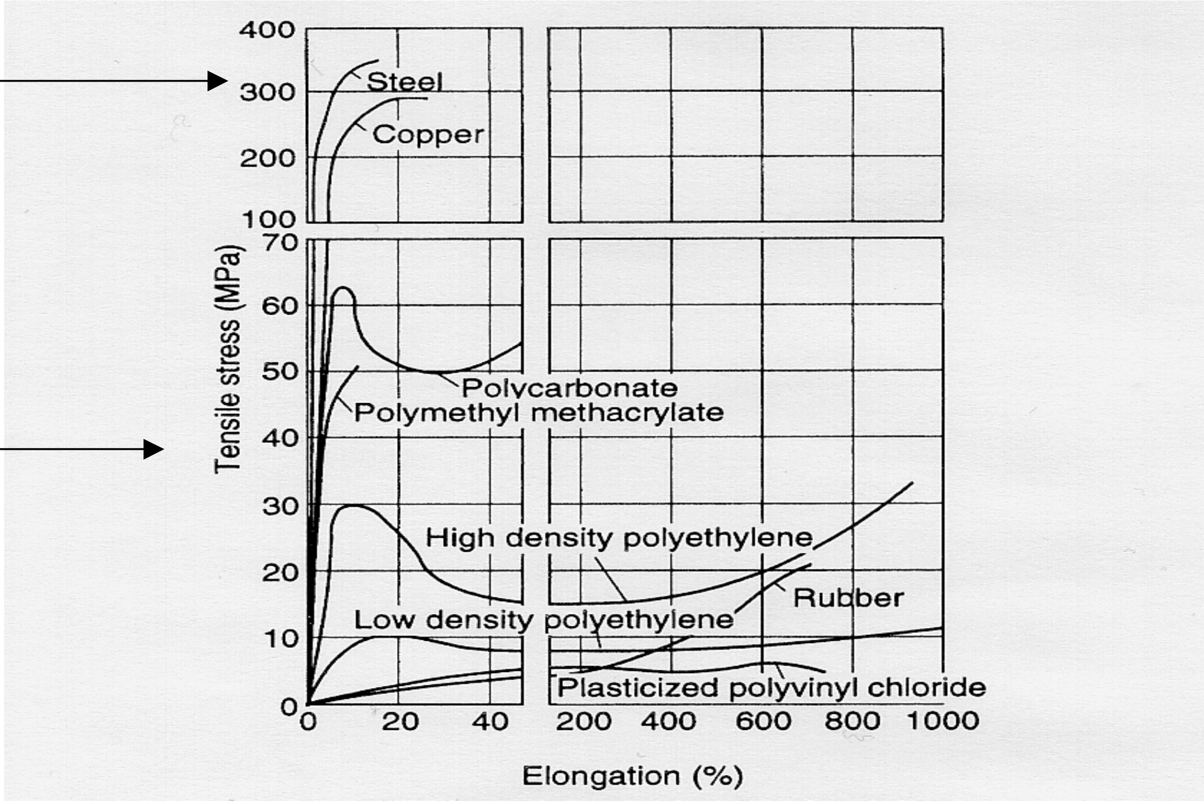
ε_B = elongation at break

The shape of the curve depends on the material.

Metals have high modulus and low elongation.
Plastics have a high or low modulus, and larger elongation than metals.

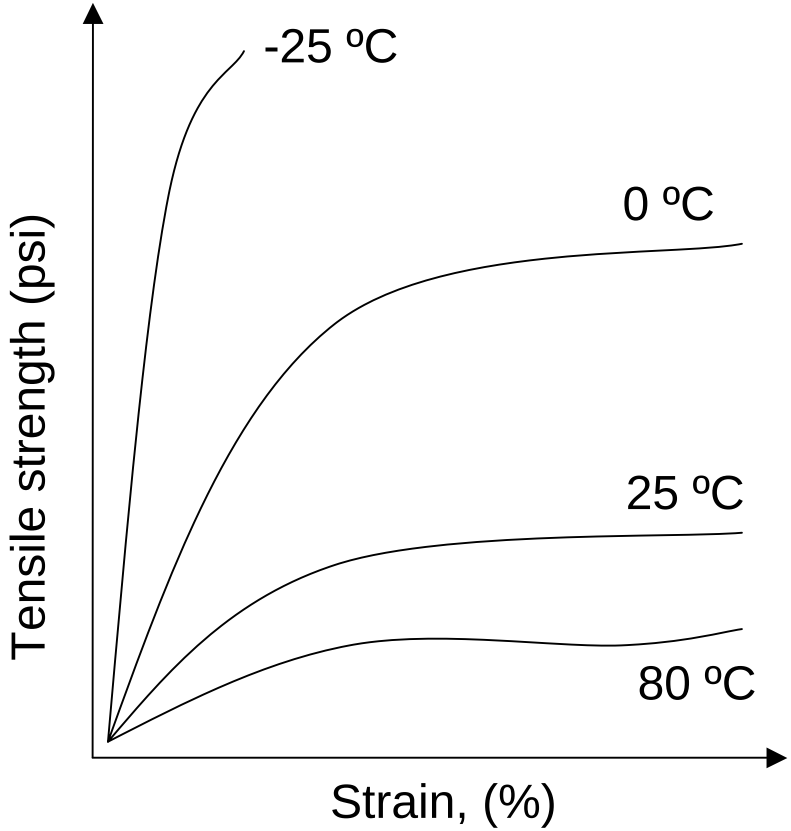
Metals

Plastics



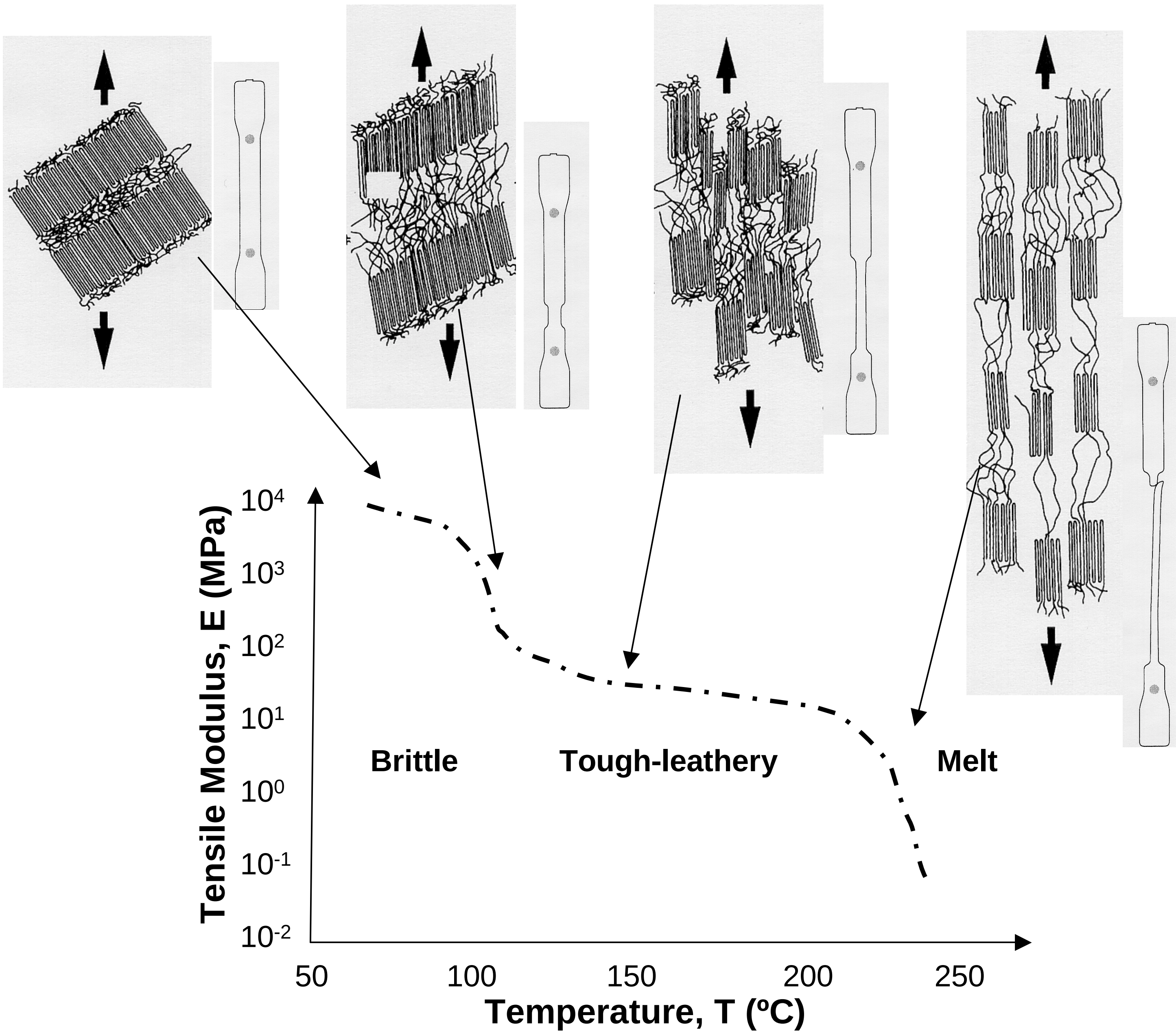
Plastics vary from soft and weak to hard and brittle.

For polymers, tensile properties are a function of temperature.



Stress-strain curves for cellulose acetate at various temperatures *(schematic)*

Tensile Modulus (E) versus temperature for a semicrystalline polymer



Environmental concerns

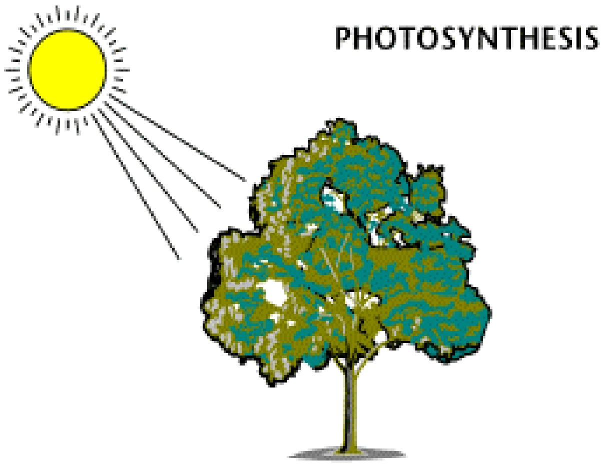
Plastics are made from non-renewable petroleum. Production is not sustainable in the long run.

6-8% of petroleum use is for plastics, contributing to U.S. reliance on imports.

Current plastics are not biodegradable or compostable. They must be landfilled, incinerated or recycled.

In spite of efforts to recycle, over 90% of waste plastic is incinerated or landfilled. Less than 10% is recycled.

Partly for environmental reasons, there is growing interest in biomaterials, including bioplastics, made from molecules found naturally in the biomass (mainly biopolymers).



Their raw materials (called feedstocks in industry) are renewable, biodegradable, and compostable.

Biomaterials are becoming more and more important in areas like polymer chemistry, biomedical science, and bioengineering.

Biomaterials can be commodity materials or specialty biomedical materials.

Commodity materials (produced on a large scale and cheap) have applications in

- disposable packaging
- disposable food service items
- agricultural products, and
- disposable consumer products.

Feedstocks and processing must be very inexpensive.

Biomaterials conserve fossil resources (petroleum) and aid waste management (they are compostable).

Biomedical materials are specialty materials that have applications in

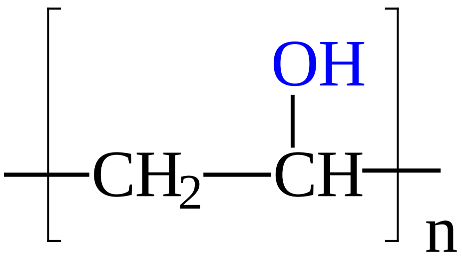
- drug-delivery systems
- wound treatment applications, and
- implants.

Biomedical materials can be biodegradable as well as biocompatible.

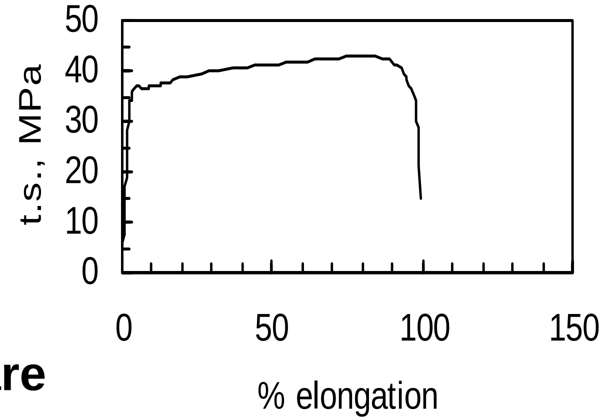
Cost is not an important factor.

In developing new bioplastics, what is kept in mind is that the properties of plastics materials are ultimately determined by chemical structure.

The backbone and side-chains determine where a polymer lies on the related scales of stiffness versus flexibility, amorphous versus crystalline, and degree of cross-linking.



These factors determine strength, elongation, toughness, and other polymer properties.



Even degradability and biodegradability are determined by chemical structure.

The development of new plastics is interdisciplinary.

Chemists formulate new materials and characterize them chemically.

Biochemists work to optimize biopolymer properties, sometimes through genetic engineering.

Engineers and physicists measure the physical properties of newly formulated materials, or develop processes for manufacturing materials so that they possess particular properties.

The growing importance of biomaterials makes it useful for students majoring in these areas to become acquainted with biomaterials.