

Objective

The primary objective of this study is to gain an understanding of the mechanical properties, and underlying atomic structures that cause the properties, for the three major classifications of polymers: thermoplastics, thermosets and elastomers. An evaluation and understanding of stress relaxation in polymers, which is directly related to their creep behavior, will also be pursued.

Abstract

The mechanical properties of polymers vary significantly from polymer to polymer as a result of atomic structure and bond strength. Thermoplastic polymers are generally composed of long coiling carbon chains that are primary bonded along the chains, but are secondarily bonded between chains. Thermoplastics tend to either contain crosslinks (primary bonds between chains) or are composed of three-dimensional space networks, but thermosets tend to be comparatively expensive and can't be recycled. The tensile properties of representative samples from the three primary polymer types (thermoplastics, thermosets and elastomers) will be tested and evaluated. When a polymer is subjected to a constant strain yet realizes a decrease in stress as a function of time, it is said to be undergoing Stress Relaxation. Two experiments will be conducted on polymeric samples to investigate their stress relaxation behavior. The quantifying parameter, Relaxation Time Constant, will be determined for the two samples tested.

Background

Polymers ("Plastics") are high molecular weight materials that are synthesized from simple organic compounds. The simplest of these is polyethylene, $-(CH_2)-$, which is obtained by polymerizing ethylene, C_2H_4 . Ethylene is an example of a monomer (single mer); monomers are usually unsaturated with higher order covalent bonds between the carbon atoms in the molecule. In the polymerization process, the higher order bond is broken leaving a single bond that takes its' place and frees an electron for further bonding. The polymerization process generally continues rapidly until the chain ends are terminated; in the case of polyethylene, OH molecules terminate the growth of the chains.

Characteristic properties of polymers include low density, low strength and high mechanical damping ability. They are generally unable to withstand low or high temperatures and are therefore used primarily at ambient temperatures.

Vinyl compounds are formed when one of the hydrogen atoms is replaced by another atom. If in C_2H_4 one of the hydrogen atoms is replaced by a chlorine atom, the polymer is termed polyvinyl chloride (PVC). Similarly, when a hydrogen atom is replaced by a benzene ring (C_6H_6), polystyrene is formed.

In an engineering context, the combination of two or more monomeric compounds yield copolymers which can be very important. Consider the combination of vinyl chloride and vinyl acetate alternating along the carbon chains. Different proportions of these compounds can be mixed and polymerized to yield different copolymers with different properties. Similarly, polymer properties can also be modified by grafting, branching, cross-linking etc. and by the addition of suitable additives.

Engineering polymers generally fall into one of three important categories:

- **Thermoplastics** which are generally are generally low-strength, low-modulus polymers which soften when heated and harden when cooled in a reversible manner.
- **Thermosetting** Polymers form permanent crosslinks between chains when cured and are comparatively strong and stiff but can't be recycled.
- **Elastomers** (Rubbers) form the third category and include polymers which can forego a significant amount or reversible plastic deformation.

Teflon is a commercially valuable polymer that is quite similar to ethylene where all of the hydrogen atoms are replaced by fluorine atoms (C₂F₄ monomers). Teflon withstands elevated temperatures up to 350°C and has good flow and sealing characteristics. C₂F₃Cl and its derivatives are fluoro-chloro equivalents that have similar properties to Teflon. These polymers, as well as rubbers, are linear chain-type compounds that are highly stretchable due to the comparatively weak secondary bonding between chains.

Polymer cost based on McMaster-Carr 1/8" thick nominal 12"X24" sheets (1998):

- Acrylic (\$3.14/ft²)
- HDPE (\$2.10/ft²)
- Nylon 6/6 (\$8.99/ft²)
- Phenolic (\$4.26/ft²)
- Polycarbonate (\$3.43/ft²)
- PVC (\$2.42/ft²)
- Natural Rubber (\$3.36/ft²)

Mechanical Behavior of Polymers

Many of the properties of polymers are measured and recorded in the same manner as metallic materials.

Stress-Strain, Modulus of Elasticity, Strength, Creep, Fracture, Hardness, etc. have the same meaning for polymers as they do for metals.

Polymer responses are more temperature dependent than metals and some polymers have unique viscoelastic (elastic flow) properties.

Simple linear chain polymers → generally relatively soft and ductile.

Complex network polymers → generally relatively hard and brittle.

Rigidity and Melting Point increase with the degree of polymerization.

Stress-Strain Behavior

Simple Stress-Strain tests in polymers generally result in one of three types of behavior:

A → Brittle (low temperature thermosetting)

B → Ductile (high temperature thermoplastics)

C → Highly Elastic (elastomers)

Temperature can drastically effect a polymer's stress-strain characteristics!

The influence of temperature on the stress-strain behavior of plexiglass is shown to the right. *Note the transformation from brittle to ductile behavior.

Many polymers are Viscoelastic where deformation is also a function of time.

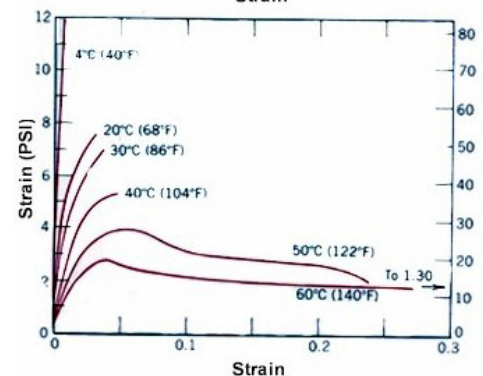
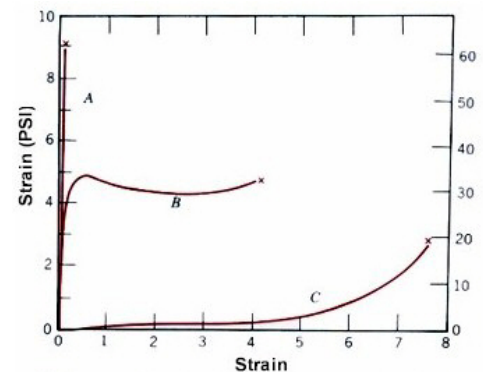


Figure 1 – Typical polymer stress-strain behavior (upper), Polymer stress-strain as a function of temperature (lower). [Callister, 1991]

1. **Creep** often occurs in polymers where deformation continues to occur under conditions of constant stress.
2. **Stress Relaxation** refers to the decrease in the amount of stress required to maintain a specific strain.

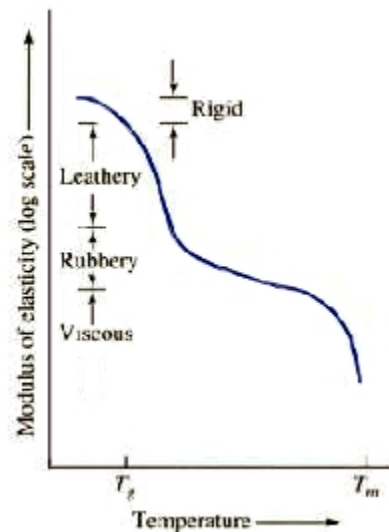
Creep and Stress Relaxation occur as a result of the relatively gradual sliding of polymer chains with respect to each other when loaded.

The **Modulus of Elasticity (E)** is also highly dependent on temperature.

The curve to the left shows how the Modulus of Elasticity varies as a function of temperature for a thermoplastic polymer. There are four distinct regions of viscoelastic behavior:

- | | |
|------------|-------------|
| 1) Rigid | 2) Leathery |
| 3) Rubbery | 4) Viscous |

Figure 2 – Polymer Modulus versus Temperature. [Shackelford, 1996]



Melting and Glass Transition Temperature

At relatively high temperatures, polymers become liquid like and deform viscously where segments of the long polymer molecules vibrate, rotate and translate.

At relatively low temperatures, polymers are rigid solids which generally deform elastically: rotational and translational motion cease.

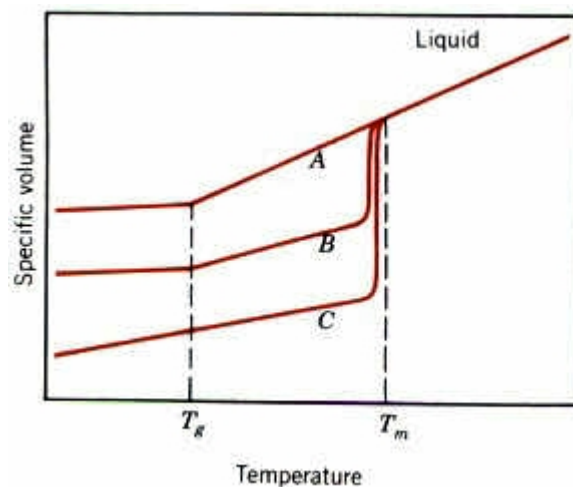


Figure 3 – Glass Transition Temperature. [Callister, 1991]

The boundary between Elastic and Viscous behavior is known as the **Glass Transition Temperature (T_g)**.

For semicrystalline materials there is a sudden change in specific volume due to the collapse of the crystalline structure when the temperature is above the **Melting Temperature (T_m)**.

Elastomers are used well above their Glass Transition Temperature (T_g) in order to retain the molecular mobility necessary for elastic behavior.

Thermoplastics are generally utilized at temperatures above T_g due to their toughness and ductility.

Thermosets are often used at temperatures below T_g to take advantage of their structural rigidity.

Deformation

Many semicrystalline polymers exhibit a unique deformation process. Deformation proceeds above and below the necked region of a specimen when loaded in tension. This phenomenon is a result of the alignment and straightening of the chains in the necked region; further deformation requires the breaking of bonds.

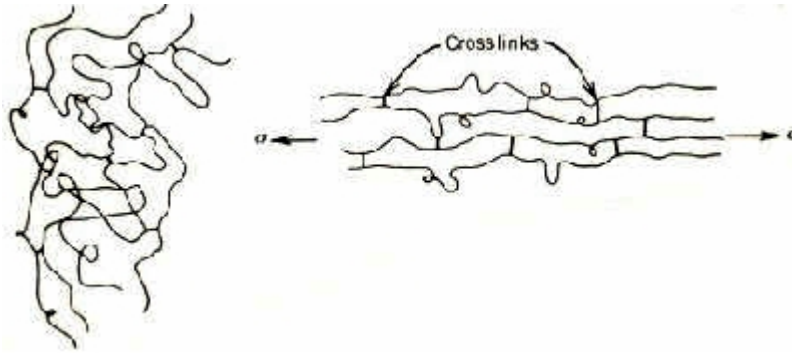


Figure 4 – Alignment of polymer chains. [Callister, 1991]

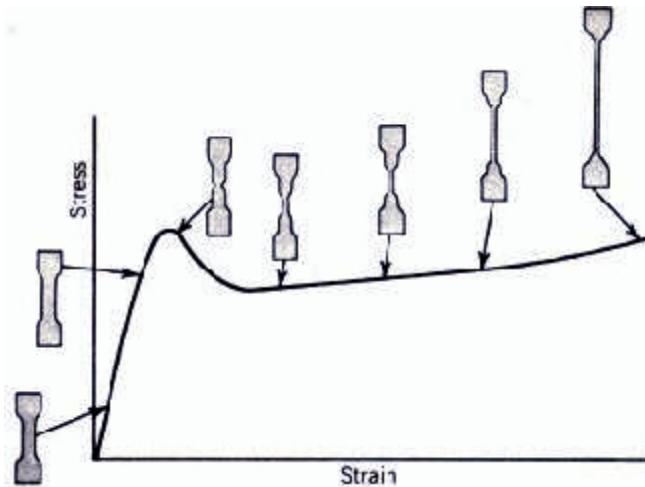


Figure 5 – Alignment of chains in a polymeric tensile test. [Callister, 1991]

Stress Relaxation

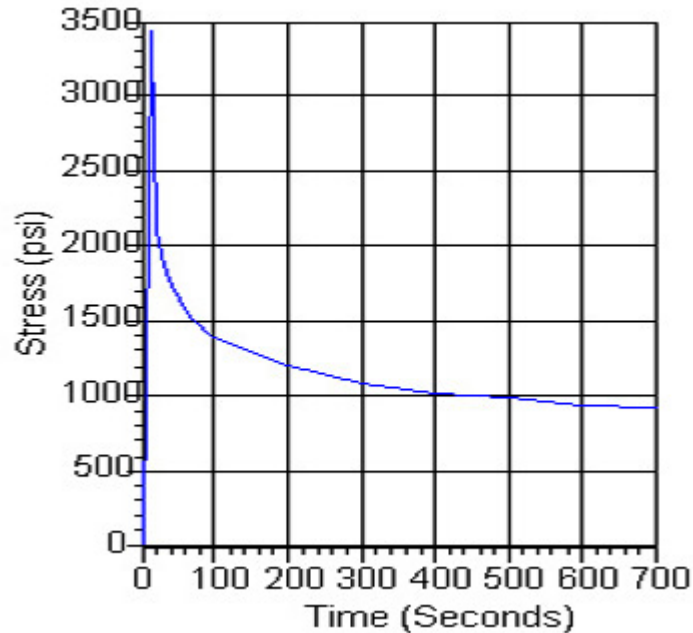
Loaded materials that are subjected to constant strain sometimes realize a decrease in stress as a function of time; this is referred to as Stress Relaxation. The cause of Stress Relaxation is that viscous flow in the polymeric material's internal structure occurs by the polymer chains slowly sliding by each other, by the breaking and reforming of secondary bonds between the chains, and by mechanical untangling and recoiling of the chains. The amount of Stress Relaxation that occurs within a material is highly dependent on Temperature.

The rate at which stress relaxation occurs depends on the Relaxation Time Constant (τ) which is a material property and is defined as the time needed for the instantaneous stress (σ) to decrease to 0.37 ($1/e$) of the initial stress (σ_0). The decrease in stress as a function of time is given by-

$$\sigma = \sigma_0 \exp(-t/\tau)$$

where σ = stress after time t (near study state), σ_0 = peak stress and τ = relaxation time constant.

Example - The figure shown below presents the stress versus time results for a Acrylic sample that was loaded to 450 pounds then stopped (stroke held constant). Determine the relaxation time constant for the Acrylic sample.



Solution:

$$\sigma = \sigma_0 \exp(-t/\tau)$$

$\sigma_0 = 3450$ psi (at peak),

$\sigma = 900$ psi (at end),

and $t = 690$ seconds (peak to end)

Substitution $\rightarrow 900$ psi = 3450 psi $\exp(-690 \text{ sec}/\tau)$

Solving for τ : $\tau = 513.5$ seconds

Polymerization

Polymerization involves the joining together of many monomers by chemical reaction.

Addition Polymerization starts with the creation of an active initiation site. This active site is produced by the addition of an initiator or catalyst to the monomer which supplies atoms with "free" electrons. The initiator may be an active radical (R) or an ionized group; the free electrons act on the double carbon bond by breaking the chain. The reaction proceeds by successive addition of the monomers to the active site in a chain reaction. The reaction ends when the active ends of two rapidly growing chains collide or by their collision with a terminator radical.

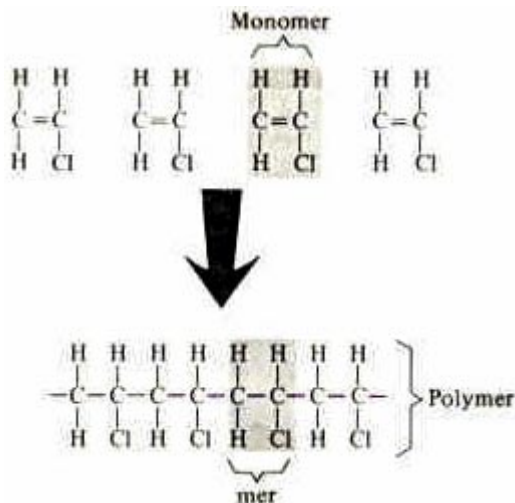


Figure 6 – Schematic representation of Polymerization. [Shackelford, 1992]

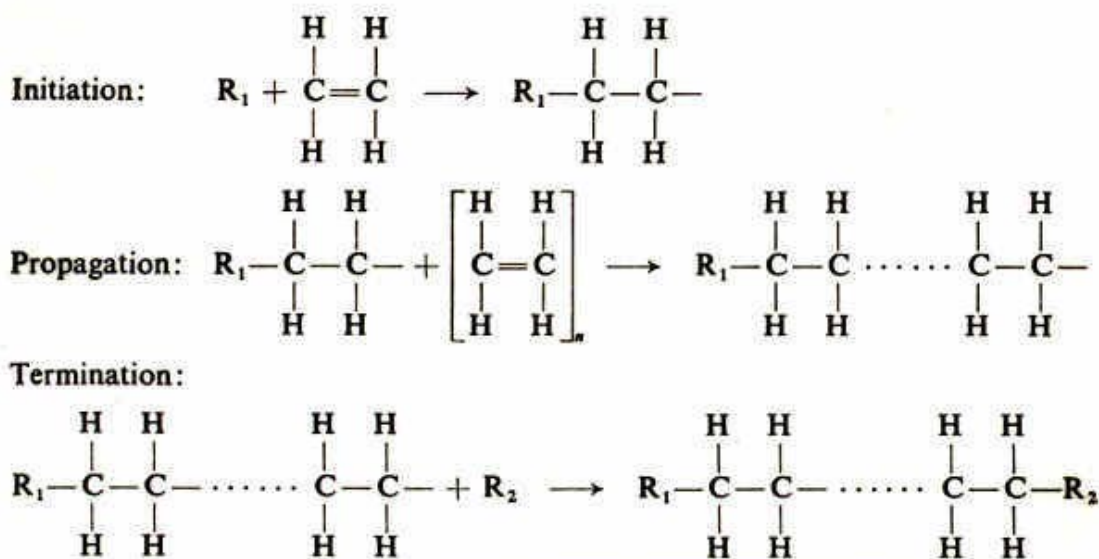


Figure 7- Addition Polymerization reactions occur very rapidly (up to 10000 reactions per second). The Driving Force for the reaction is the decrease in potential energy which occurs upon formation of two single C bonds. [Shackelford, 1992]

Condensation Polymerization occurs by the reaction of two molecules with the formation and loss of a small molecular by-product such as water or ammonia. The reaction is stepwise with each step requiring initiation and reaction.

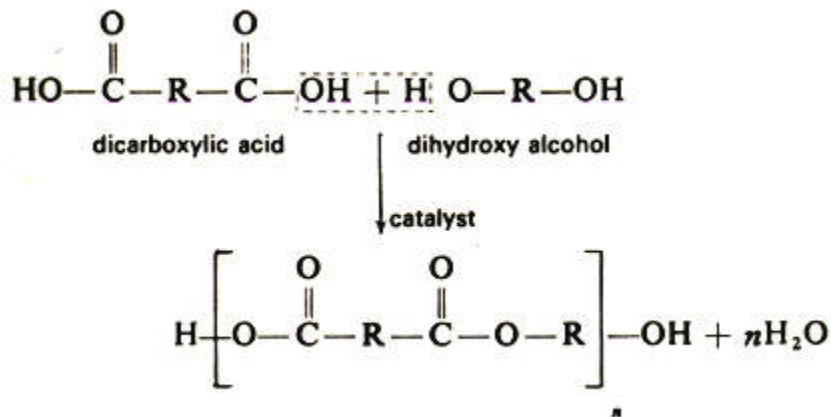


Figure 8 - Condensation Polymerization is a much slower process than Addition Polymerization since Condensation Polymerization involves individual reactions in a step-by-step process. [Shackelford, 1992]

Polymer Chemistry and Nomenclature

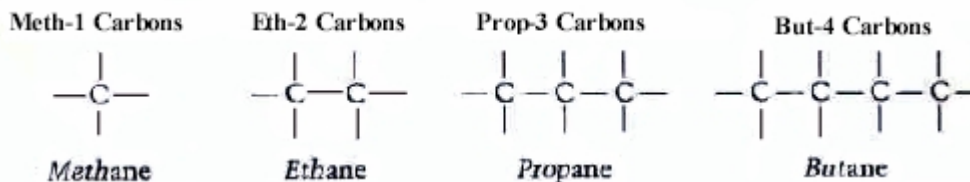
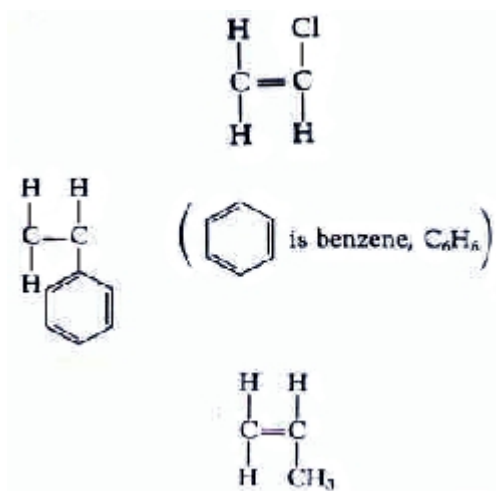


Figure 9 – Carbon configurations for the four most common mer prefixes. [Callister, 1991]

When only single bonds between carbon atoms are present, the suffix is "ane" as in propane. When a double bond is present, the suffix is "ene" as in ethylene.



The term "vinyl" implies that a hydrogen atom has been replaced by another atom. Example - Vinylchloride.

The term "styrene" implies that a benzene ring has replaced a hydrogen atom.

The term "amide" implies that an organic group (ex. NH_3) has replaced a H atom.

Figure 10 - Examples of Vinyl, Styrene and Amide. [Callister, 1991]

Isomerism refers to compounds with the same composition that may have different atomic arrangements.



Figure 11 – Example of Isomerism. [Callister, 1991]

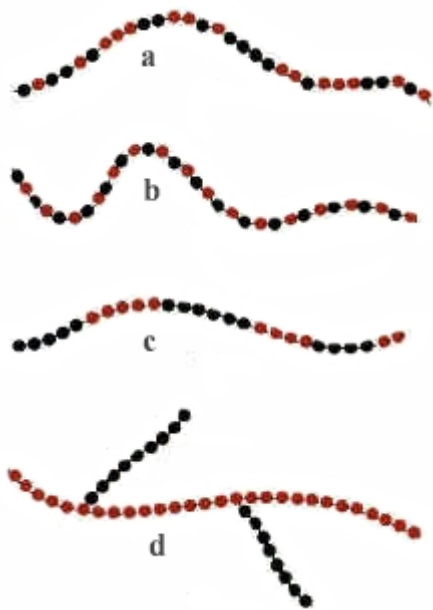
Copolymers

Homopolymers are comprised of only one type of repeating mer unit.



Copolymers are polymers which are compounds of more than one mer type.





Depending on the polymerization process and the relative fraction of mer types, different sequencing arrangements along the polymer chains are possible:

- a) **Random Copolymer**
- b) **Alternating Copolymer**
- c) **Block Copolymer**
- d) **Graft Copolymer**

Figure 12 – Schematic representation of Random, Alternating, Block and Graft Copolymers. [Callister, 1991]

Synthetic Rubbers are generally composed of various copolymers. **Copolymers** are formed by **Blending** which is equivalent to alloying in metals.

The following types of **Additives** are often utilized modify polymer properties:

- 1.) **Plasticizers** are added to enhance ductility and flexibility.
- 2.) **Fillers** are added to enhance strength by restricting chain mobility.
- 3.) **Stabilizers** are added to reduce polymer degradation.
- 4.) **Colorants** are added to provide the desired color for appearance.

Types of Polymers

Polymers are large, high-molecular-weight macromolecules constructed from a repeating series of smaller structural units called "mers".

"Poly"-> Many; thus the term Polymer

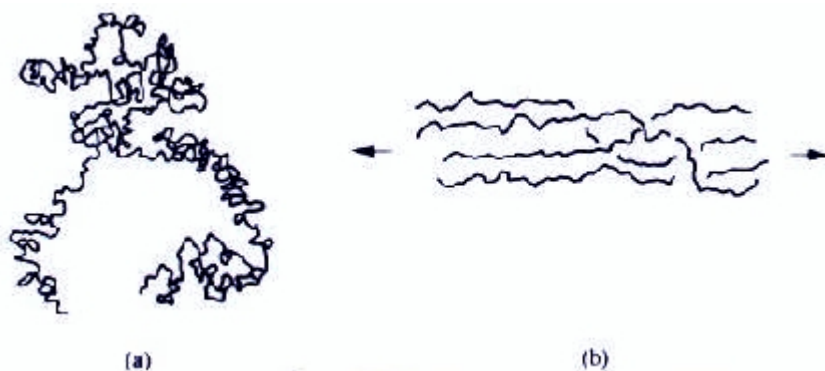


Figure 13 – Straightening of linked and/or folded linear polymers (a) unloaded, (b) in tension. [Callister, 1991]

1. High Polymers versus Low Polymers are classified based on molecular weight; low polymers have molecular weights < 20000 amu's.
2. Organic Polymers versus Inorganic Polymers: **Organic Polymers** are based on the Carbon Chain. Carbon atoms form macromolecules by covalently bonding with other carbon atoms as well as oxygen, sulfur and nitrogen. Organic Polymers are susceptible to high temperature degradation and tend to react with oxygen at temperatures above 150°C. **Inorganic Polymers** are based on inorganic elements, such as silicon, and are more resistant to high temperatures.
3. Thermoplastics, Thermosets and Elastomers

Thermoplastic Polymers (PVC, PVC, Polyester, Nylon, ABS, etc.) are generally composed of long coiling chains which are NOT crosslinked. Thermoplastics soften when heated and harden when cooled; this process is reversible and repeatable. Thermoplastics plastically deform when loaded beyond σ_{ys} .

Thermosetting Polymers (Epoxies, Phenolics, Polyurethane, etc.) are generally composed of crosslinked space networks. Crosslinks form between chains when the material is cured. Thermosetting polymers become hard after curing (heating facilitates crosslink formation) and do not soften upon reheating.

*Note: Polymer chains are generally composed of covalently bonded atoms; the bonds between chains are generally secondary except for the crosslinked thermosets.

Elastomers (Polybutadiene, Neoprene, Isoprene, etc.) generally return to their original shape upon unloading. The long chained elastomers do not crosslink and generally return to their minimum energy coiled positions when unloaded.

4. Linear, Branched, Cross-Linked, Ladder and Network Polymers:

Linear Polymers - Mers are joined end-to-end in long, single chains. Examples - PVC, PMMA.

*Note: linear polymers are not straight, but are coiled and bend.

Branched Polymers form when linear polymers develop side branches which extend from the main chains.

Crosslinked Polymers form when adjacent chains form covalent bonds at repeated intervals. Thermosets are usually crosslinked. Example - Rubber.

*Note: Atoms are generally covalently bonded within polymer chains while weaker, molecular or secondary bonds exist between the chains.

Ladder Polymers form when two linear polymers are linked in a regular sequence. Generally rigid thermosets.

Network Polymers - Instead of the typical chains associated with polymers, three dimensional networks develop around the covalently bonded Carbon. Example - Epoxy.

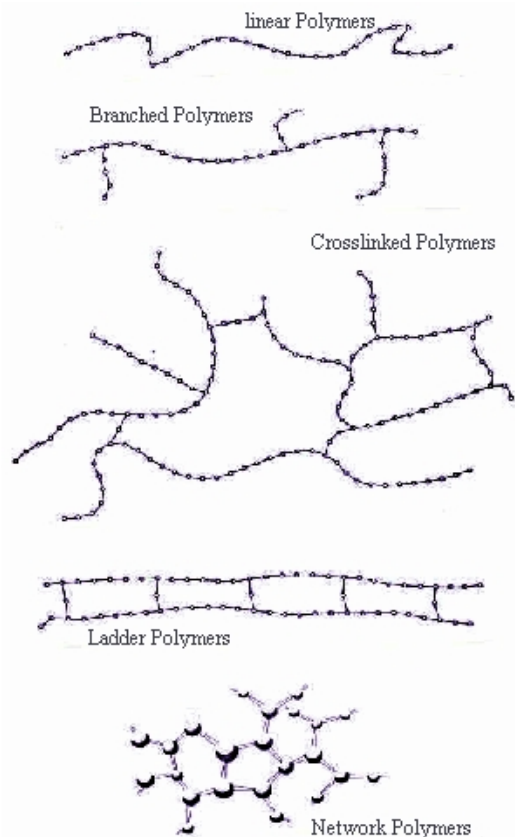


Figure 14 - Linear, Branched, Cross-Linked, Ladder and Network Polymers. [Callister, 1991]

5. Crystalline Polymers - Polymers can also be partially crystalline. Crystallization involves the efficient packing of molecular chains. Substances which contain relatively small molecules (water or methane) generally have some crystalline character. Crystalline polymers are comparatively strong and heat resistant

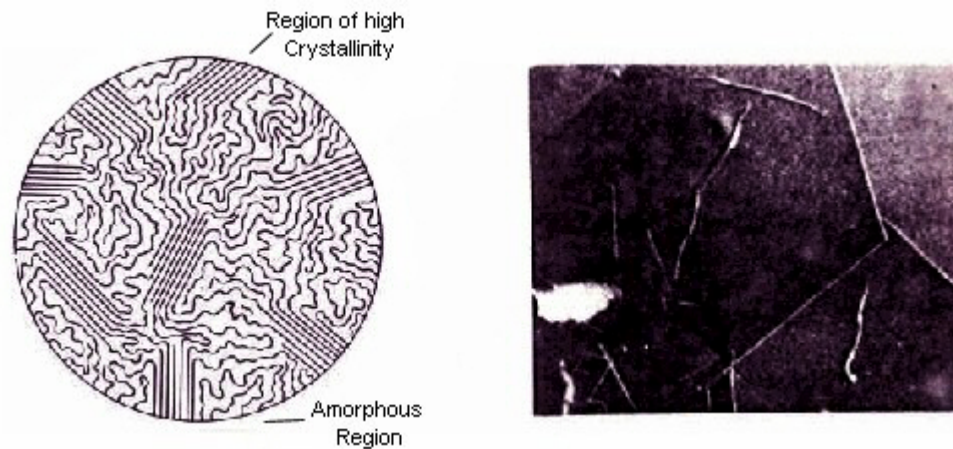


Figure 15 – Crystalline Polymers: (a) Schematic representation, (b) Photomicrograph. [Callister, 1991]

Lab Procedure

Apparatus

MATERIALS- Nominally 1/8" Sheets of Acrylic, High Density Polyethylene (HDPE), Nylon 6/6, Phenolic (Garolite), Polycarbonate, PolyVinylChloride (PVC) and Natural Rubber.

SAFETY- Safety Glasses Must be Worn by ALL Students in the Lab During Testing!

CALIBRATIONS- (Instron - 10,000 lb, Screw-Driven)

In this experiment, stroke is correlated to time based on the A Shaft – D Gears driving the system. All of the tests will be conducted at a constant stroke rate (Low Setting) which was found to be 0.04175 inches/second. A - 0.09 second offset is needed to zero out the stroke (it takes 0.09 seconds for the clock to stop when commanded to do so during startup).

Load readings will be obtained from the load cell that is mounted directly to the upper specimen grip and emits mV signals that are linearly correlated to the applied load. A factor of 36700 was found to convert from mV to Pounds with an offset of - 2.1E-4 necessary to account for the weight of the grip.

Procedure

Turn on the 10 Kip Instron universal testing machine in the ME 3701 classroom and boot the Mac/SE computer.

Using the B controller buttons, raise the Instron Crosshead such that the upper and lower grip ends are separated by 6" nominally (machine should be set to stop at this position). Measure and record the separation distance (this should be the gauge length for all of the tests).

Each lab section will be given three polymer samples to test (1 thermoplastic, 1 thermoset, and 1 elastomer); each individual will need to collect the test results for the three specimens tested in the lab session.

For each specimen to be tested (all samples are nominally 3/4" X 10"), note the polymer designation then measure and record the width and thickness of the specimen.

Mount the specimen to be tested in the wedge grips being careful not to damage the specimen while assuring that the specimen will not slip during testing.

Note*- Apply significant pressure when mounting the Natural Rubber sample.

Data Acquisition

Select "Roger's Disk" -> "ME 3701" -> "POLYMER 3701"; Press Control immediately when the "Analog Connection WORKBENCH" logo disappears from the screen (this stops the clock).

When the Data Acquisition setup appears on the screen, check to see that the meter indicating "Stroke" reads zero; if it does not, quit the program and return to the previous step.

Open the L01 Log Icon by double clicking then select Save As.

Enter the filename to which the data will be saved: _____ .txt; use an abbreviation for the polymer with the section for the filename (ex. HDPE02.txt).

Note: If the Save As step is skipped then the previous data file will be overwritten and the data lost!

To begin the test, Simultaneously Press "Control R" on the computer (starts the clock) and the "B Controller Arrow Down" Button on the Instron.

When the test is complete (specimen rupture or end of stroke), press "Stop" on the Instron and "Control R" on the computer (stops the clock).

Select "Quit" from the file menu

Check that the Data File is located in the appropriate ME 3701 folder; if it's not, move it to the proper folder.

Stress Relaxation

Follow the same basic procedure as described for conducting a tensile test, including Data Acquisition with the following modifications:

- Save the files as SR files by adding SR after the polymer type (ex. HDPE SR02.txt).

- Load the specimen to approximately 350 pounds then press the STOP button on the Instron, but do NOT stop the Data Acquisition! Allow the specimen to remain at the stopped position (constant strain) for 10 minutes then stop the Data Acquisition (control R).

- Unload and remove the specimen.

Lab Requirements - Tensile Testing

1. Follow the procedure outlined in the "Procedure" section of this module for collecting Load-Displacement data for the three nominally 1/8" thick polymer specimens provided.
2. Plot Stress versus Strain (engineering) for each polymer tested
3. Determine the following for each polymer: Modulus of Elasticity, 0.2% Offset Yield Strength, Ultimate Strength, Percent Elongation and Modulus of Toughness. Develop a Table containing these results in addition to the type of polymer (Thermoplastic, Thermoset, Elastomer) and the cost.
4. Answer the Following:
 - a. How do the measured properties of the Thermoset tested compare to the properties of the Thermoplastic? Why are they different?
 - b. Which polymer(s) would you choose to minimize deflection at low load levels? Why?
 - c. Which polymer(s) would you choose for absorbing energy? Why?
 - d. Briefly discuss the Macro and Micro-scopic failure progression in the thermoset and the thermoplastic tested.
 - e. Why are Acrylic and Phenolic considered to be high risks for "Catastrophic Failure"?

- f. Why do you think PVC is a commonly used polymer for piping systems and yard furniture?
- g. What are the major drawbacks of using thermosetting polymers for sundry-type items?

Lab Requirements - Stress Relaxation

1. Follow the procedure outlined in the "Procedure" section of this module for collecting Stress Relaxation data for nominally 1/8" thick specimens for the two specimens provided (1 thermoset and 1 thermoplastic).
2. Plot Stress versus Time for the two polymers tested.
3. Determine the Relaxation Time Constant for each material tested.
4. Compute the anticipated stress for each sample if the constant strain applied in the experiments were held for one full week.
5. Answer the Following:
 - a. How and why do the Relaxation Time Constants differ between Thermosets and Thermoplastics?
 - b. Why is Stress Relaxation important in polymers but not in ceramics?
 - c. How are Stress Relaxation and Creep related?
 - d. Would you expect Phenolic to have a High or Low Relaxation Time Constant? Why?

Homework

1. Most polymer structures involve coiling chains of atoms. Briefly describe the bonding along the chains and between the chains.
2. What are the major differences between Thermoplastics, Thermosets and Elastomers?
3. Most polymers are non-crystalline; what is a "Crystalline Polymer"?
4. Briefly describe the Addition Polymerization Process. Why is Condensation Polymerization generally much slower than Addition Polymerization?
5. In terms of composition, what's the difference between Polyester, Polyvinyl and Polystyrene?
6. Define Copolymer and explain why Copolymers are important.
7. Define Glass Transition Temperature and explain why it's important.
8. What's the difference between Creep and Stress Relaxation?
9. What happens to the properties of polymers when they are steadily heated?
10. Summarize the properties of Thermoplastics.
11. Summarize the properties of Thermosets.
12. Summarize the properties of Elastomers.