

POLYMERS:
A BRIEF TUTORIAL



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by

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INTRODUCTION

Seals, insulation, cordage, tires etc. all share a common heritage: polymers whose physical state can range from rubbery, glassy or crystalline and combinations thereof. Unfortunately (or not) polymers cannot be successfully understood by applying a single scientific discipline. Generally, a “materials science” approach should be utilized so that polymers can be thoroughly understood and properly engineered for an application. This approach to learning about and engineering with polymers requires knowledge not only of Chemistry and Physics, but also of Thermodynamics, Mechanical Engineering, and Rheology. In industry today, the engineer that understands both chemical compatibility issues as well as the mechanical behavior of polymers is a unique and valuable individual.

This paper deals with polymers in the general sense, but is aimed primarily at the examination of elastomers. An elastomer is a polymeric material characterized by a glass transition temperature well below room temperature, as well as the ability to elastically deform over very large strains. Both elastomers and plastics are part of the larger group of materials classified as polymers.

The word *polymer* comes from the Greek, *polymeres*, or having many parts¹. The word describes a long chain molecule with a repeating pattern, or a *macromolecule*.

Macromolecular science is probably best introduced with a discussion of the rubber industry after World War I. Prior to 1920, it was generally assumed that natural rubber was a colloid (like milk) consisting of possibly 5 to 8 units of isoprene forming a ring structure. The possibility of a high molecular weight (i.e. long chain) molecule had been previously advanced but never seriously defended until Herman Staudinger, a German professor having outstanding academic credentials (and apparently a minimum of tact) began to aggressively expound the large molecule concept. Staudinger postulated that rubber is composed of long molecules (polymers) in which the recurring units (monomers) are combined by primary valences or covalently bonded (a bond having a shared pair of electrons). His academic peers had an attitude best summed up by a letter from a contemporary stating: *“Dear Colleague, Leave the concept of large molecules well alone...there can be no such thing as a macromolecule.”* Staudinger's extensive investigations left no doubt as to the legitimacy of the “long chain” concept. His work was described by one scientist as a *“Rock of Gibraltar against which other views beat in vain.”* This work withstood the test of time and earned him a Nobel Prize in Chemistry in 1953 and on his death, election to the Rubber Science Hall of Fame in 1966. The science of Macromolecular Chemistry was then firmly established. Perhaps the following statement illustrates the problem of advancing any new concept: as the late Nobel Prize-winning (1908) physicist Max Planck once observed: *“A new scientific truth does not triumph by convincing its opponents and making them see the light, but rather because its opponents eventually die and a new generation grows up that is familiar with it.”*

¹ Merriam-Webster Dictionary, ©1997

MATERIALS SCIENCE

Polymers are best understood by examining the species from a materials science perspective. Materials science is defined as “the study of the nature, behavior and use of materials applied to science and technology.” This perspective is appropriate when one considers the various disciplines often involved in the successful processing and application of a polymer. Relevant sciences include:

Physics – the study of forces that exist between objects and the interrelationship between matter and energy;

Thermodynamics – “a science that includes the study of energy transformations and of the relationships among physical properties of substances which are affected by these transformations”²; heat and work interactions.

Chemistry – composition of monomers, mechanisms of polymerization, cross-linking and aging;

Mechanics – interactions of three basic properties: mass, length and time; the study of force and deformation, stress and strain in solid bodies.

Rheology – deformation and flow of non-Newtonian materials.

Perhaps the least known and most relevant scientific discipline is that of polymer physics. “It’s a matter of fact that polymer physics is largely unknown to the majority of physicists.” It defines chain conformations, compatibility of mixtures, phase behavior, mechanical response, dynamic models, relaxation processes, elasticity, non-linear behavior, and fracture.

1. Physics

The understanding of rubber in a materials science sense is analogous to the studies of physical sciences. *Physics* is the study of the fundamental aspects of nature in terms of elementary principles and laws. Consider the scaling laws: “double the size, square the area, cube the volume.” Do we understand this in terms of a rubber component? Where typical mechanical components of steel or other metals are designed with little or no regard to surface area to volume ratios, heat dissipation, or compressibility issues, such items cannot be ignored in the design of polymeric parts.

Physical principles allowed Galileo (1564 -1642) to develop the basis of reason for *mechanics*: the interactions of mass, length, and time. Newton (1642-1727), by using his discovery of *calculus* (a branch of mathematics that deals with changing quantities), was able to rationalize mechanics in terms of *statics*, *dynamics*, and *kinematics* using the *zeroth*, *first*, and *second* derivatives with respect to time. This in turn led to statistical mechanics allowing us to predict properties of systems composed of a large number of particles, or atoms, such as rubber.

By measuring the temperature and forces in his “cannon-boring” experiment, J.P. Joule (1818-1889) determined that work could be converted directly into thermal energy (heat). Joule was intrigued with rubber and studied it as well. The Gough-Joule principle, whereby a strained piece of rubber contracts when heat is applied, is a phenomena still often overlooked today. The fact that “work” (done by applying a force through a distance) can develop heat (Joule's cannon-boring experiment) added three other dimensions to ordinary mechanics: *entropy*, *temperature* and *free energy*. These three quantities plus mass, length, and time formed the basis for thermal physics or *thermodynamics*.

² *Thermodynamics*, 5th Ed. Wark, Kenneth, Jr., McGraw-Hill, Inc. New York, NY, 1998.

2. Thermodynamics

Thermodynamics is the extension of mechanics which otherwise dwells on the interactions of mass, length and time. Joule not only recognized that heat was associated with work and work with heat but there was something not adding up. This might be summarized by stating: "Heat is work and work is heat but energy's the difference." Borrowing an analogy articulated by J. B. Fenn, consider your bank account:

Balance = Deposits – Withdrawals

(Energy, E) = (Heat, Q) - (Work, W)

This is essentially a statement of the first law of thermodynamics for closed systems which holds that energy can be converted from one form to another but cannot be created or destroyed.

It may be desirable to determine the spontaneity of a chemical reaction or process (for instance, the polymerization of monomers or aging of elastomers). One thermodynamic property that helps predict the direction of a process is *entropy*. The second law of thermodynamics introduces the concept of entropy (Greek for "transformation") for the energy lost or economically unavailable. Consideration of energy changes alone (i.e. compliance with the first law) is not enough to predict the spontaneity of a process.

The second law holds that the entropy of the universe increases in a spontaneous process and remains unchanged in an equilibrium process. It is here we find the connection between entropy and the spontaneity of a reaction. The entropy change of the universe (ΔS_{univ}) is made up of the change in entropy of the system (ΔS_{sys}) and that of the surroundings (ΔS_{surr}). When a system is in a state of equilibrium, $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0$. For a spontaneous process, $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$. Entropy has been called "time's arrow" since it only increases. Some basic principles of entropy follow:

- Entropy can only increase over a period of time.
- Nature always strives for the highest state of entropy.
- Entropy increases as the physical state proceeds from a solid to liquid to a gas - (e.g. ice/water/gas).

There have been no exceptions to the laws of thermodynamics found to date. At this point we might recall the three laws of thermodynamics as stated by Hertz: 1. You can't win; 2. You can't break even; 3. You can't get out of the game!

The "Ideal Gas Law", $PV = nRT$, is alive and well in the realm of polymers, particularly elastomers. Elastomers are essentially super-condensed gases since most of the precursor monomers are gases. Elastomer density is greater by approximately 3 orders of magnitude (10^3) and the viscosity greater by 14 orders of magnitude (10^{14}) when compared to the gaseous state. Considering rubber as a super-condensed gas, we find temperature is a disproportionate determinant of rubber's properties and behavior. Since "n" (number of atoms or molecules) does not normally change in a polymer, we have what is called a "closed" system or one of "constant mass." The value "R," the universal gas constant, is constant as well. Thus, as temperature changes, there will be subsequent changes in "P" (pressure) and "V" (volume). Anyone having worked with elastomers is well aware of their ability to exert thermal pressure.

3. Chemistry

General Molecular Structure

Polymers are relatively simple monomer units joined to create a long-chain molecule. A long-chain molecule is the primary structure of any polymeric material. The secondary (micro) structure is dictated by the actual molecular constitution that in turn influences the development of the tertiary (macro) structure.

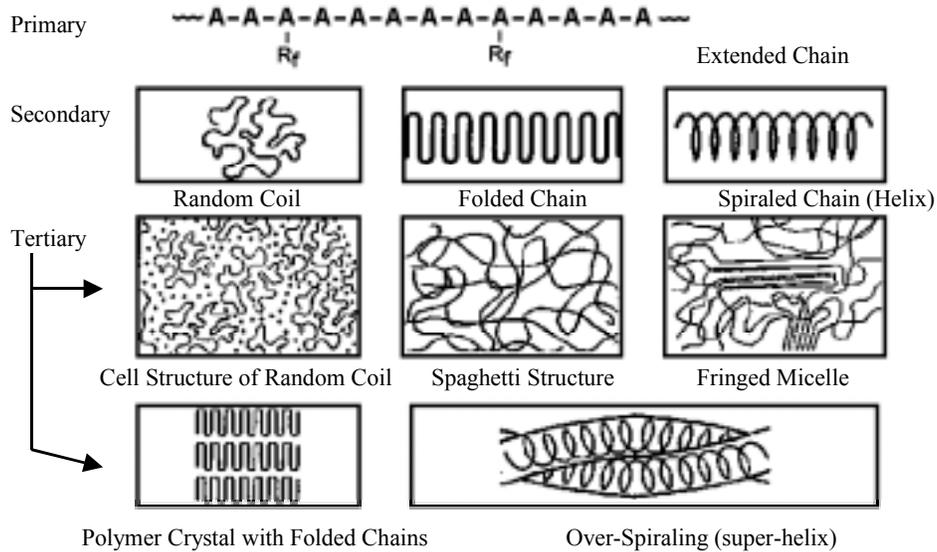


Figure 1: Polymer Structures

The typical elastomer has a random coil microphase and the spaghetti structure macrophase. The random or amorphous structure of the long-chain molecule is created by inherent molecular asymmetry (as opposed to the symmetry of polyethylene). Bulky branch groups such as benzene rings (SBR), methyl groups (EPDM) or cyano groups (NBR), prevent the growth of a symmetrical polymer chain.

Most polymers can be divided into three classes:

- "Rubbery" or elastomeric polymers, having glass transition temperatures (T_g) below room temperature, e.g., natural rubber, silicone, butyl, etc.
- Rigid polymers, having T_g above room temperature, e.g., polystyrene, polymethylmethacrylate, polycarbonate.
- Partially crystalline polymers, having T_g either above or below room temperature, e.g., polyethylene, polypropylene, nylons, polytetrafluoroethylene, etc.

Class "a" and "b" polymers are often categorized as "glass-forming liquids" and as such they are clear like a glass as well as having similar fracture-type failures at temperatures below their glass transition (T_g) values. Class "c" polymers are typically less transparent due to the crystalline domains. In either of the different categories the physical response to temperature versus volume change is illustrated below.

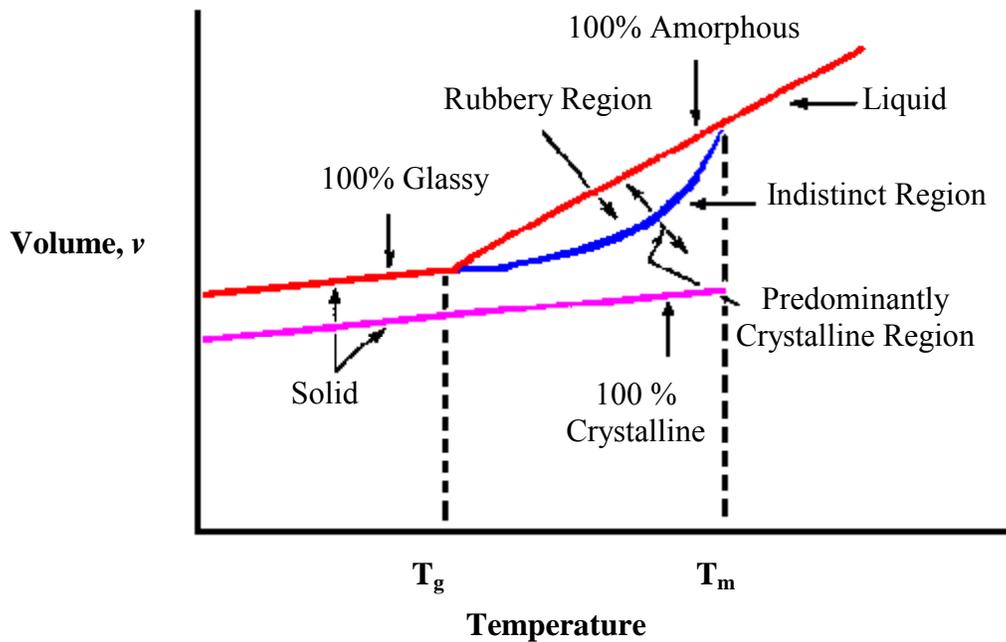


Figure 2: Elastomer Volume vs. Temperature

Long-chain molecules occur commonly in nature (e.g. Hevea latex) and are synthetically produced by polymerization. Polymers are created by covalently bonding one or more monomers to create the long-chain molecule. There are two fundamental polymerization processes- addition and condensation (as shown in Fig. 3 below).

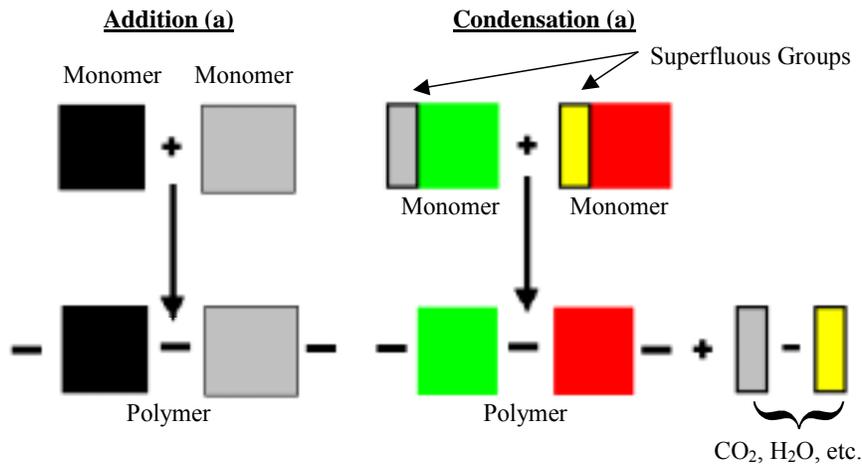


Figure 3: Polymerization Techniques

The “backbone” of most of these long-chain molecules is comprised of carbon. Thermodynamics predicts the eclipsed state (see Figure 4) for all of the CH₂ segments with the attendant rotational energy barriers, the basis of rubber elasticity.

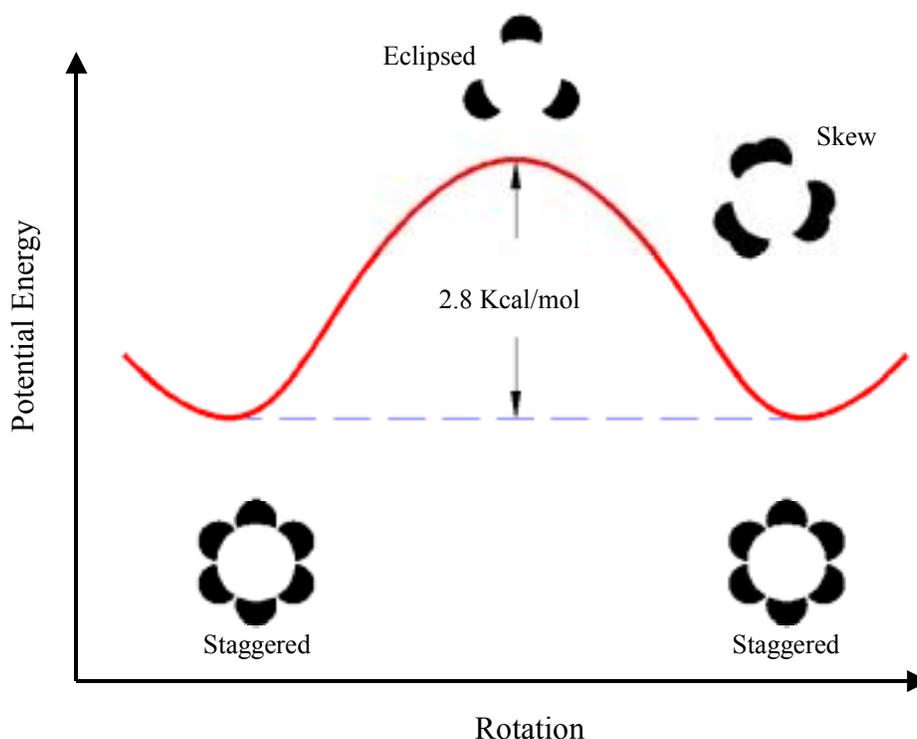


Figure 4: Potential Energy vs. Rotational Position (CH₂ Segments)

Molecular Weight and Dispersion Force

The ultimate physical properties of polymers are strongly influenced by one or more molecular interactions loosely categorized as “van der Waal’s force”. A good starting point in understanding polymers is to study a simple table of alkanes (also referred to as paraffins). This table of data may further help you appreciate what we might call the "polymer paradox". In other words, polymers as an engineering material are commonly being defined within the framework of chemistry rather than using a more appropriate "materials science" concept.

Table I – n-Alkane (C_nH_{2n+2}) Homologous Series

Chemical Formula	Common Name	Molecular Weight	Physical State	Boiling Point (°C)	Melting Point (°C)
CH ₄	Methane	16	Gas	-161.5	-183
C ₂ H ₆	Ethane	30	Gas	-88.6	-172
C ₃ H ₈	Propane	44	Gas	-42.1	-188
C ₄ H ₁₀	Butane	58	Gas	-0.5	-135
C ₅ H ₁₂	Pentane	74	Liquid	36.1	-130
C ₁₂ H ₂₆	Kerosene	170	Liquid	216.0	-10
C ₁₈ H ₃₈	Paraffin	254	Solid-soft	303.0	28
C ₅₀ H ₁₀₂	Hard Waxes	702	Solid-brittle	--	92
C ₁₀₀ H ₂₀₂	LMW Polyethylene	1402	Solid-hard	--	115
C ₁₀₀₀ H ₂₀₀₂	MMW Polyethylene	14002	Solid-brittle	--	138

It is apparent that as we increase the number of backbone atoms we proceed through a change in physical states: gas → liquid → solid. Upon examining the progressive changes in physical state of the alkanes in Table I, we might ask what causes this change. We know that alkanes have no permanent dipole moment. In fact, the hydrogen atom (which has only one electron) has borrowed an available electron from

its carbon neighbor. This creates a stable two electron orbital, covalently bonding the hydrogen to the carbon atom. The electrons are now traveling in circular orbit about the atomic nuclei creating a spherical cloud. We know that approximately 95% of the time there is no dipole moment in the alkane molecule. However, the other 5% of the time a transient dipole occurs due to electron travel outside the spherical “envelope,” resulting in physical attractive forces called the “*London Dispersion forces*.” These are the weakest of the so-called “Van der Waals forces” but they are cumulative. Dispersion forces usually increase with molar mass. In the case of alkanes, the more carbon atoms there are the stronger the attractive force will be. Thus, as the molecular weight of the alkane increases, we see the transition from a gas to a solid.

The phenomena of dispersion force can explain another paradox: why we can use polyethylene to make a container for gasoline. A general rule of solubility when examining the polarity or dipole moment of a molecule is that “likes dissolves likes”. This general rule explains why oil and EPDM should not be used together: they are both non-polar. We would further suspect that gasoline and polyethylene, both being hydrocarbons of a non-polar nature, would be readily soluble within one another. However, this is not the case. Specifically, polyethylene has varying degrees of crystallinity depending upon molecular weight and polymerization process. The forces creating the crystallinity are the organic equivalent of the lattice energy of an ionic solid, for example table salt (Na^+Cl^-). This energy of the crystalline domains at normal temperatures is greater than the solvating energy of the gasoline; hence we can contain the gasoline in the polyethylene container.

Covalent Bond Energies and Intermolecular Forces

Covalent bond energy values are readily available from any organic chemistry text. They are typically described as “dissociation energy” and are measured in kilo Joules/mole (kJ/mole). Two examples are:

carbon – carbon	347 kJ/mole
carbon – hydrogen	414 kJ/mole

Six types of “intermolecular forces” are generally recognized with their attractive forces ranging from 10-60 kJ/mole. These forces are strongly distance sensitive (varies as the inverse sixth power of the distance r or $1/r^6$). The math is straightforward: increasing “ r ” by a factor 2, the attractive force is now 1/64 of the original value. The discussion on paraffin illustrates the effect of heat on these intermolecular forces. As you increase temperature at atmospheric pressure, the volume expands while the number of molecules remain constant (recall $PV = nRT$). As a consequence, the dispersion forces are now insignificant and the solid becomes a liquid. Another important intermolecular force is the hydrogen bond or H-bond. Polymers containing oxygen, nitrogen, sulfur and the halogens as well as carbon owe their physical properties to these atoms. Common examples are PEEK[®], VESPEL[®], RYTON[®], TORLON[®] among others. The very strong physical attraction is a by-product of acid-base interactions or more specifically through the lone pair of (unshared) electrons of oxygen, nitrogen and sulfur and the π orbital of carbon in the presence of a hydrogen group.

Monomers

The chemistry of vulcanization is a combination of organic (rubber) and inorganic (crosslinking). We will not dwell on this other than to note it was “simultaneously” discovered by Charles Goodyear (1839) in America and Thomas Hancock (1852) In England.

The chemistry of the rubbery polymer, on the other hand, is relatively straightforward and a brief review of the alkane, alkene and diene hydrocarbon structures is informative.

Alkanes –

Table I, *supra*, illustrates the saturated hydrocarbons ($\text{C}_n\text{H}_{2n+2}$), where we previously noted the change in physical state from a gas to a liquid, finally a solid.

Alkenes –

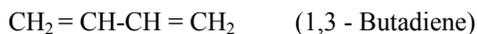
Table II below illustrates the unsaturated hydrocarbons (C_nH_{2n}). Ethylene and propylene are the most common building blocks for many polymers. Removing one hydrogen from an ethylene creates a *vinyl* group and the replacement group at that site creates a vinyl complex.

Table II – n-Alkene ($C_n H_{2n+2}$) Homologous Series

Chemical Formula	Common Name	Molecular Weight	Physical State	Boiling Point (°C)	Melting Point (°C)
$CH_2=CH_2$	Ethylene	28	Gas	-102.0	-169
$CH_2=CHCH_3$	Propylene	42	Gas	-48.0	-185
$CH_2=CHCH_2CH_3$	1-Butene	56	Gas	-6.5	--
$CH_2=CH(CH_2)_2CH_3$	1-Pentene	70	Liquid	30.0	--
$CH_2=CH(CH_2)_3CH_3$	1-Hexene	84	Liquid	63.5	-138
$CH_2=CH(CH_2)_4CH_3$	1-Heptene	98	Liquid	93.0	-119
$CH_2=CH(CH_2)_5CH_3$	1-Octene	112	Liquid	122.5	-104
$CH_2=CH(CH_2)_6CH_3$	1-Nonene	126	Liquid	146.0	--
$CH_2=CH(CH_2)_7CH_3$	1-Decene	140	Liquid	171.0	-87

Dienes –

Dienes are simply alkenes that contain two (2) carbon - carbon double bonds, for example:



Popular Elastomeric Structures -

Natural rubber is polyisoprene; the monomer is chemically: (2- methyl-1,3 butadiene)

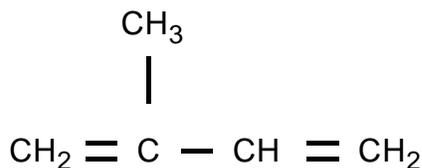


Figure 5: Isoprene

As a polymer, the structure becomes:

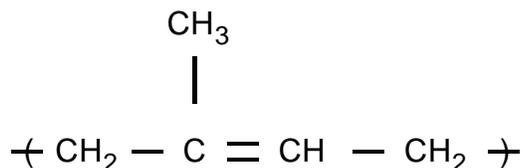


Figure 6: Polyisoprene

Neoprene® (polychloroprene) rubber (CR) is created by replacing the 2-methyl group (i.e. CH_3) in isoprene with a chlorine (Cl).

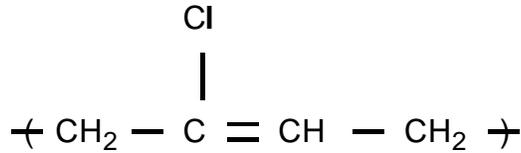


Figure 7: Polychloroprene (Neoprene®)

Alternatively, if we *hydrogenate* (add hydrogens to the unsaturated carbons) isoprene we have a new elastomer:

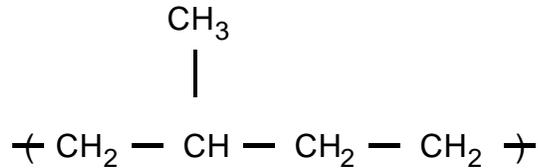


Figure 8: Ethylene-Propylene Rubber

This new structure, essentially hydrogenated polyisoprene, is created synthetically by copolymerizing ethylene and propylene (Table II) and is called *ethylene-propylene* rubber (EPM).

The most widely used synthetic, styrene-butadiene rubber (SBR), is created by copolymerizing styrene with butadiene. To impart additional oil-resistance, the vinyl styrene in SBR is substituted with acrylonitrile, a very polar molecule. However, this is more than enough chemistry for what is basically a broader lecture than this tutorial should contemplate.

4. Mechanical Properties of Elastomers

After being properly compounded, and molded into an engineered product, the material at some point will be subject to an external force, or load. When a solid body is deformed, an internal reactive force called stress, acting across a unit area, tends to resist this deformation. The measure of deformation is called strain (an alternate measure is extension ratio). Consider now Figure 9, a tensile stress-strain diagram for three physical states of a polymer:

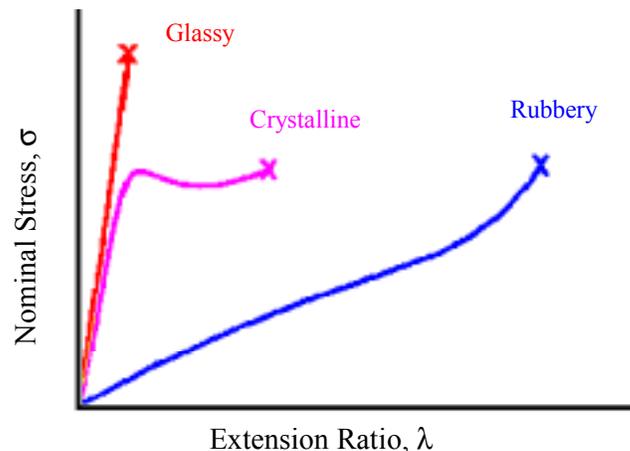


Figure 9: Stress vs. Extension Ratio for Three Types of Polymers

glassy, crystalline, and rubbery. Glassy polymers are hard and brittle. The failure (i.e. rupture) point for each curve is shown with an "X." Crystalline polymers go through a succession of changes: elastic, yield, plastic flow, necking, strain hardening and fracture. Rubber is unique in being soft, highly extensible, and highly elastic. Considering rubber as an engineering material, we can employ the term, shear modulus, $G = NkT$, where N is the number of network chains, k is Boltzmann's constant and T is temperature, in Kelvin. With reasonable accuracy, we can state that many rubbery materials have a similar shear modulus, G or hardness at equivalent temperatures above their glass transition temperature. One can also look upon rubber as a thermodynamic "system." In a static sense, we have an engineering material that has a broad response to external influences such as temperature and pressure (of course, there is no truly static application of rubber).

5. Rheology

The science of Rheology offers additional insight into the behavior of polymeric materials. The successful design of rubber components in particular often requires in-depth knowledge of the viscoelastic nature of the rubber compound. Rheological data could certainly have illustrated the temperature dependence of viscosity and stiffness for the o-rings used in the Challenger space shuttle.

Typical in the rubber industry today is the use of a Mooney rheometer or oscillating disk rheometer. These instruments are useful for quality control, but do not offer useful engineering data for design of components. Various other instruments (such as capillary, parallel plate, cone-and-plate, etc.) produce a range of data useful for design of seals, extrusion dies, and many other polymeric parts. Such data includes frequency and temperature dependence of elastic and viscous moduli, temperature at which modulus begins to degrade, and stress relaxation curves. Information on molecular weight* can be determined from rheometer data as well.

REFERENCES & SUGGESTED LIBRARY

My definition (probably a somewhat parochial one) of a good author is one who writes the way I like to read. One of the more interesting events in the publication of technical literature is the challenge of finding an author who can write lucidly on challenging subjects. Listed below are a few of my favorites:

Materials Science:

"Materials Science" Second Edition, J. C. Anderson et. Al., 1974. Halstead, John Wiley, ISBN 0-470-02830-0

Physics:

"Fear of Physics" L. M. Krause, 1993. Basic Books, NY, ISBN 0-465-05745-4

Thermodynamics:

"Engines, Energy, and Entropy", J. B. Fenn, 1982. W. H. Freeman, NY, ISBN 0-7167-1281-4
"The Second Law", P. W. Atkins, 1984. Scientific American Books, ISBN 0-7167-5004-X

* For homopolymers

Chemistry:

General Chemistry. P. W. Atkins, 1989. Scientific American Books, ISBN 0-71672-1940-1

Molecules. P. W. Atkins, 1987. Scientific American Books, ISBN 0-7167-5019-8

The Periodic Kingdom. P. W. Atkins, 1995. Basic Books, NY, ISBN 0-465-07265-8

Rheology

Rheology Principles, Measurements, and Applications. Macosko, Christopher, W. VCH Publishers, Inc., New York, NY, 1994. ISBN 1-56081-579-5.

Viscoelastic Properties of Polymers, 3rd Ed. Ferry, John D. John Wiley & Sons, New York, NY, 1980. ISBN 0-471-04894-1.

Polymer Science:

Last but not least, and certainly the contention of this paper: where is the book on polymers? There is not one that I would recommend for entry level. For a better understanding of rubber, however, the Vanderbilt Handbook, 13th Edition is an interesting addition to any library.

THERMODYNAMIC DEFINITIONS

Entropy:

(Statistical Mechanics) Measure of the disorder of a system, equal to the Boltzmann constant times the natural logarithm of the number of microscopic states corresponding to the thermodynamic state of the system. This statistical–mechanical definition can be shown to be equivalent to the thermodynamic definition. (Thermodynamics) Function of the state of a thermodynamic system whose change in any differential reversible process is equal to the heat absorbed by the system from its surroundings divided by the absolute temperature of the system. It is also known as thermal charge.

Heat:

(Thermodynamics) Energy in transit due to a temperature difference between the source from which the energy is coming and a sink toward which the energy is going; other types of energy in transit are called work.

Temperature:

(Thermodynamics) A property of an object which determines the direction of heat flow when the object is placed in thermal contact with another object; heat flows from a region of higher temperature to one of lower temperature; it is measured either by an empirical temperature scale, based on some convenient property of a material or instrument, or by a scale of absolute temperature, for example, the Kelvin scale.

Work:

(Mechanics) The transference of energy that occurs when a force is applied to a body that is moving in such a way that the force has a component in the direction of the body's motion; it is equal to the line integral of the force over the path taken by the body; a force exerted through a distance in the direction of the force.