

Elastomers and aging

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Mechanical properties of elastomers

Shear modulus G and Young's modulus E are standard engineering terms. For an isotropic solid (rubber) $E = 3G$ since elastomers are incompressible. A tensilegram in engineering language is a stress-strain diagram and the area under the curve is the thermodynamic equivalent of work (figure 1). Work as we will describe later is the product of applying a force through a distance (length). Approximately 85% of the work value is due to an entropy S change, the balance is due to the internal energy U of the system. By integrating the area under the stress-strain curve a finite value for work is determined (refs. 1 and 2). Most tensile testers can be upgraded at a reasonable cost to perform this calculation. Work is a product of shear modulus G times an extension ratio λ , a nonlinear function; (extension ratio $\lambda = 1 + \text{elongation}$)

$$W = G/2 * (\lambda^2 + 2/\lambda - 3) \quad 1$$

Shear modulus G for an unfilled elastomer is generally accepted as being defined by:

$$G = \rho RT/M_c \quad 2$$

where ρ is density, R the universal gas constant and T , temperature Kelvin. M_c , a somewhat controversial term, is molecular weight between crosslinks. We will consider M_c as the variable product reflecting chemical changes that occur during the aging process. By measuring work before, during and after aging the progression of aging can be monitored in "real time." This testing can be done using the "multi-wave" testing procedure developed by Rheometrics (ref. 3). Logically, the new Monsanto - RPA2000 instrument can also be programmed to develop the same data, as both instruments are operating in a shear mode.

Thoughts on the aging of rubber

Rubber is an engineering material, albeit having somewhat different characteristics than what we normally consider in this category. Historically not considered long-lived but why? Consider the following properties and their associated disciplines: monomeric precursors - typically a gas (chemistry), a rubbery solid (thermodynamics and physics) and engineering applications (mechanics). The interaction of these disciplines are best studied in a "materials science" sense since they are interactive with each other. The major consideration is that no chemical reaction can occur unless there is a favorable thermodynamic environment. We can simplify these chemical reactions to three basic mechanisms and six types of reactions and briefly illustrate their relevance

to rubber chemistry and their aging mechanisms (ref. 4).

Introduction

Loan and Winslow (ref. 5) offer some relevant comments, several of which I will quote to set the tone for this discussion: "Much of our understanding of polymer chemistry is based upon the very basic assumption that the reactivity of a given group is unaffected by the size of the molecule of which it forms a part. Thus, in principle, the reactivity of chemical groups in polymer molecules is the same as in small molecules." The authors then note; "However, many apparent anomalies have been observed due to complications related to the polymeric environment. These include neighboring group effects, limited diffusion of reactants, and morphology." Some of these anomalies enhance polymeric properties but others are not as desirable as we will subsequently note. The organic chemist will recognize this effect which is called anchimeric assistance (Gr. for neighboring parts).

Aging process

The aging process of rubber is logically a chemical change ultimately manifesting itself in a physical shift of mechanical properties. What we will review in this article is the progression of the aging process as dictated by the chemistry and thermodynamics of the reaction processes. By using mechanics we can demonstrate how to measure in "real time" the onset of elastomer degradation, concurrently tracking the shift in engineering properties.

Experimental

Chemistry

In most organic reactions, one or more covalent bonds are broken, this normally causes a conversion of a functional group in the molecule from one category to a higher one. In the breaking of a covalent bond, electrons are never unpaired (not for long anyway as we will note shortly). All organic changes are accomplished by one of three basic mechanisms:

- Heterolytic cleavage, when a single bond (two electrons) breaks leaving both the electrons on one of the fragments. In the case of carbon-carbon bonds, we will consider the carbon atom the substrate and the attacking reactant the reagent. A reagent generally brings a pair of electrons (donor) or takes a pair of electrons (acceptor). A donor is called a nucleophile and the reaction - nucleophilic. An acceptor is called an electrophile and the reaction - electrophilic.
- Homolytic cleavage (free-radical mechanism) is the breakage of a single bond (two electrons) leaving one of the electrons on each of the fragments.
- Pericyclic reactions, the third reaction mechanism are not common in this discussion.

The types of reactions are:

- Substitution;
- Additions to multiple bonds;
- β - elimination;



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- Rearrangement;
- Oxidation and reduction;
- Combinations of above.

Knowing the elastomer chemical structure and reviewing a first year organic chemistry textbook will answer most questions of where these reactions might occur.

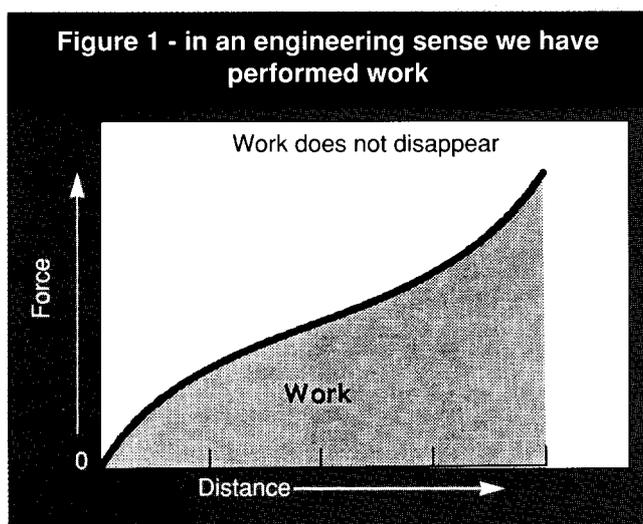
Thermodynamics

This is the study of heat and its conversion to mechanical, chemical and electrical energy. A typical thermodynamic text usually incorporates calculus operators such as d , ∂ and Δ to indicate total differential change, partial differential change or finite change respectively. Since it is understood we are considering macroscopic or global change we will delete these operators from the various equations for simplicity's sake. This discussion is somewhat simplified because we can treat unaged elastomers as a closed system i.e., one having no mass transfer as opposed to the more complex open system. Thermodynamics is an extension of mechanics which of course dwells on the interactions of mass, length and time. As an example,

force = mass x acceleration or $F = MA$, acceleration (A) is length/time². Work (W) is the product of applying a force through a distance. With the advent of the steam engine, J.P. Joule noted 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" (ref. 6). Borrowing again from Fenn and using his analogy i.e., consider your bank account;

balance = deposits - withdrawals
(energy E) (heat Q) (work W)

This is essentially a statement of the First Law which gives the connection between heat and other forms of energy and states that in any process heat is conserved. The Second Law states that it is impossible for any continuous self-sustaining process for heat to be transferred spontaneously from a colder to a hotter body. Thus the second law, distinguishes heat from the other forms of energy bringing in the term entropy S (Gr. for transformation) for the energy lost or economically unavailable. When a system is in a state of equilibrium, entropy S is equal to heat Q/temperature T. Entropy you might say is a cousin of energy. In an isolated (equilibrium) system heat Q is normally not present ($Q = 0$ and entropy always tends to increase (like taxes, cost of living, etc.)



energy of a system originally called "heat content" is called enthalpy H and is related to internal energy U by the relationship $H = U + pV$ where p = pressure and V = volume. For changes under constant pressure $H = Q$, where Q is constant pressure heat capacity, C_p . Exothermic reactions (liberating heat) are accompanied by a reduction of enthalpy H. Endothermic reactions (requiring heat) are accompanied by an increase in enthalpy H. "Latent heats" are enthalpy changes. This leads us to the Gibbs free energy G, (not to be confused with shear modulus G) which defines the maximum work a process can perform under a constant pressure thus;

"A negative G value is necessary but often not sufficient for a reaction to spontaneously occur ex: hydrogen and oxygen can be stored as a mixture for centuries with no reaction occurring."

$$G = H - TS$$

3

Gibbs free energy G is equal to heat content (enthalpy H) minus temperature T times entropy S.

Some basic points of thermodynamics:

- 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 (consider ice/water/gas).

Back to chemistry and thermodynamic considerations

In order for a reaction to take place spontaneously, the free energy G of the reaction must be lower than the free energy of the reactants (exothermic), figure 2, in other words G must be negative i.e., back to:

$$G = H - TS$$

Conversely if G is positive, by increasing T (temperature), ΔG will become negative at some value and the reaction will occur. A catalyst can increase and an inhibitor decrease the free energy of activation $G_f \neq$ (basically the barrier to a spontaneous reaction) required to initiate the reaction, figure 3. Back to nature again, the preferred conditions are low enthalpy H and high entropy S thus in any reaction enthalpy decreases and entropy increases.

Reaction kinetics

A negative G value is necessary but often not sufficient for a reaction to spontaneously occur ex: hydrogen and oxygen can be stored as a mixture for centuries with no reaction occurring. What is required is a few joules J from somewhere, these might come from a mass transfer, heat transfer or work exchange noted earlier (how about a match?).

In a nonequilibrium state the rate of entropy generation increases by the square of temperature as you depart from the equilibrium temperature. Entropy has been called "time's arrow" since it only increases. As noted earlier, thermodynamics does not define work or energy but borrows them from mechanics and electromagnetism. The laws of conservation of energy are axiomatic thus in any system a definite amount of energy is trapped in the system and is called "internal energy U." Because of the conservation of energy, the internal energy can only be altered by an external change such as mass transfer, heat transfer or work exchange. Free

What is being added is free energy of activation G_f^\ddagger . G_f^\ddagger is not a fixed value in elastomers as it can be decreased by catalysis and increased by inhibitors, G , most importantly, of course is not affected. It is probably time to go back and remember that simple statement; "Heat is work and work is heat but energy's the difference." It is also the time to remember that heat, work and energy are expressed in base or derived units of joules J using the SI system.

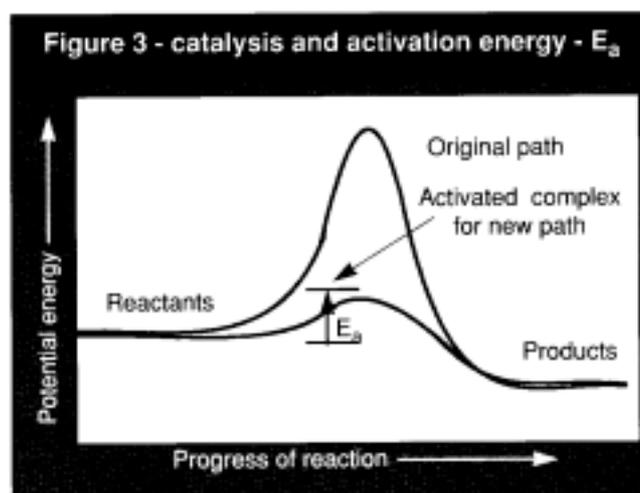
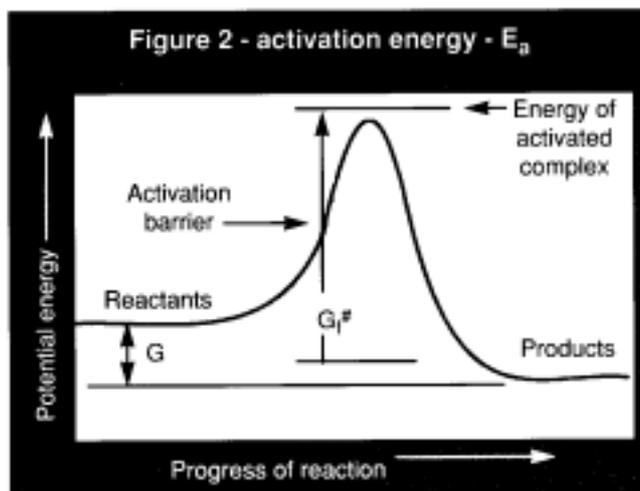
Gibbs free energy G and elastomers

It is reasonable to assume that carbon-backbone elastomers would have negative ΔG values so aging is inevitable. Conversely inorganic-backbone elastomers (silicone, phosphonitrile) probably are positive ΔG depending on the type of organic branches present.

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Free energy of activation G_f^\ddagger

Noted previously was the effect of catalysts on lowering the activation barrier G_f^\ddagger , trace metal ions notably copper have a very aggressive effect on natural rubber. Diamine complexes serve effectively as chelating complexes. Some copper complexes have a stabilizing effect on nitrile elastomers. A description of the reaction mechanisms is beyond the scope of this article other than to refer back to the three basic mechanisms and the six types of reactions noted earlier. Inhibitors (antioxidants) are often a necessary ingredient to stabilize many synthetic elastomers during the manufacturing stage. Additional levels are added during the compounding process. Antiozonants would be added to diene-containing elastomers to prevent ozone attack at the double bond site (reaction 2). What we are doing is essentially adding sacrificial agents to maintain a higher activation barrier. Stabilization is provided by numerous other compounding ingredients such as metal oxides and metal complexes (electron acceptors). EPDM compounded with 1,2-butadiene resins is very stable after an aggressive postcure converts the diene into a phenol complex (stabilizer). Noted earlier by Loan and Winslow was the "apparent anomalies" such as "neighborhood-group effects" ex.: vinylidene fluoride (VF_2) containing di (hexafluoropropylene-HFP) and terpolymers (HFP and tetrafluoroethylene-TFE) often use the HFP- VF_2 -HFP random site for crosslinking. The HFP dual presence has a strong destabilizing effect on the VF_2 site leading to an easy β elimination (reaction 3) of an HFP fluorine and a VF_2 hydrogen creating a double-bond site and of course a mole of HF which must be scavenged. There is nothing to prevent this reaction from continuing after curing other than site availability. Elastomers, as organic materials, are susceptible to the whole spectrum of mechanisms/reactions. The important statement to remember is that covalent bonds are broken causing a conversion of a functional group from one category to a higher one.



In a polymer this means we might be undergoing main chain or crosslink scission or both. New crosslinks might be formed, any or all of which will change the polymeric network structure thereby affecting its mechanical properties.

Summary

By monitoring change in shear modulus G which is proportional to changes in M_c (chemical changes) the earliest onset of elastomer aging can be determined. Since aging is often autocatalytic, a better estimation of the useful life of an elastomeric compound can be determined. Hopefully, this brief review of interactions between chemistry thermodynamics and mechanics offers a more cohesive understanding of the aging of elastomers.

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