



THEORY OF RUBBER COMPOUNDING
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Developed for:
Energy Rubber Group
Educational Symposium
September 24-25, 1991

Theory of Compounding

Introduction

To more completely appreciate the challenges of successful oilfield elastomer formulation we will briefly review the operating environment. Energy production has moved from the relatively benign "sweet" hydrocarbons to the very complex "sour" environment. The "sweet" environment, even if at higher temperatures, was straight forward in the sense that conventional nitrile and fluoroelastomer (Viton[®], Fluorel[®]) sealing technology was adequate and predictable in service life. The "sour" environment not only occurs naturally but is also developed in low-sulfur sweet wells during secondary recovery by water flooding.

The aggressive "sour" environment is more complex for many reasons:

1. The combinations of CO₂ and H₂S, with and without water creates aqueous and non-aqueous electrolytes. An understanding of Lewis acid-base interactions is necessary to appreciate the problem potential.
2. Gas concentrations (partial pressures) at temperatures above critical can act as supercritical solvents. Elastomers in this environment are subject to high swells and subsequent extraction of plasticizers, low molecular weight polymers etc.
3. Explosive decompression due to pressure or temperature shifts can cause catastrophic seal rupture.
4. The deliberate introduction of acids, (HCl, HF) bases (inhibitors) completion fluids (metal halides, carbonates etc.) and gases (CO₂, N₂) create another set of problems. These interactions are reasonably well understood by only a very few users.

The oilfield environment is unique, there is no other environment with similar problems so there is little technology transfer potential.

Consider the following problem potentials using conventional elastomer sealing technology where one might specify Viton[®] or Fluorel[®], 90 durometer.

- a. Explosive decompression problems due to differences in types of carbon black used for oilfield versus regular service. The molecular weight of the basic elastomer is equally critical.
- b. High swell in inorganic acids (acidizing) since conventional technology used different metal oxides in the cure system that are soluble in these acids.
- c. Excessive swelling and softening in the aqueous environment if non-black fillers are used (oxides become hydroxides or sols, silicates can convert to water-soluble bicarbonates by carbon dioxide/water mixtures etc.).

d. Rapid seal degradation in the presence of high pH (basic) environments such as inhibitors, carbonates (completion fluids).

Oilfield users must be made aware that the standard commercial seal compounds incorporate little if any of the specific compounding approaches necessary for successful oilfield compounds. This is due to:

a. Typical oilfield compounds are more difficult to process (high molecular weight and more reinforcing fillers).

b. Compounds for oilfield service typically have higher compression set values due to use of fillers and compounding ingredients dictated by the oilfield service requirements.

Discussion

Rubber is an engineering material, even the diehard chemists and chemical engineers that dominate our industry are beginning to appreciate this fact. In an engineering sense, molded elastomeric products may be utilized under strain (o-rings etc.) and stress (packers etc.). Compounding for each category can be dramatically different. Consider three basics:

1. Elastomers
2. Fillers
3. Crosslinks

Elastomers: Typically created from two or four carbon gaseous monomers. The resulting material has increased in density a thousand fold and the viscosity is 10^{14} higher than the gaseous state. The elastomer viscosity is sufficiently high that we can measure it in terms of megapascals (MPa), or in engineering terms of Youngs '(E) and shear (G) modulus. It is essentially a super-condensed gas. Nature does not differentiate between her own product (NR) and the various synthetic elastomers so G (shear modulus) = NkT , where N is the number of network chains, K - Boltzmann's constant and T - absolute temperature. This equation is saying a dimethylsilicone gum and a perfluoroelastomer gum will have the same modulus (G) or hardness at an equivalent temperature above their glass transition temperature. Rubber is a thermodynamic "system", the first law explaining quantitatively the property of elasticity and the third law illustrating the thermal pressure created in the molding process. The very basic Ideal Gas Law, $PV = nRT$ is in evidence since the applications of rubber components by nature are subjected to changes in temperature. Although gas dynamics (hard sphere models) can explain polymeric responses up to approximately 100°C over P_c (critical pressure), at higher temperatures it is necessary to convert to the "beaded chain" models. Consider now the effect of increasing molecular weight on mechanical properties:

Table I

When considering molecular weight, remember that a more legitimate value is the "constitutional repeating units" (CRU) or number of monomeric units creating a typical polymer chain. A low Mooney value might be 500-750, medium 1000-1500 and high 2200 and up. Remember also that molecular weight values can also be misleading, emulsion-type high Mooney elastomers such as SBR and NBR have extensive branching, often creating "gel" or an insoluble residue (due to crosslinks). Factory Processing: What is typically helpful to the molding plant manager (low viscosity, low die swell etc.) is a disadvantage to the end user ie: low viscosity is typically low molecular weight (M.W.) giving reduced mechanical properties (Table I). Low die swell usually indicates both low M.W. and high gel. Both are a distinct disadvantage for applications such as packers. Surprising only to those not paying attention to rheology, narrow distribution higher molecular elastomers have better flow characteristics than their lower Mooney, branched analogs. Die swell is higher for these elastomers however.

Chemical Resistance: A typical elastomer selection for service in the sour environment is often based on what might logically be described as "best of a bad lot" in selection process. Elastomers based on "addition polymerization reactions" ie: NBR, FKM, CR, EPDM are more predictable in the aqueous and non-aqueous oilfield applications. Ringopening polymerizations (polyphosphazenes, polyalkylene oxides) as well as condensation reaction polymerization (FVSi, AU and EU) are very vulnerable to acid - base environments and caution is urged when they are utilized.

Fillers: Fillers serve numerous functions but common to all events is their effect brought about by increasing the viscosity of the formulation. This effect is defined by a modification of the Einstein viscosity equation by Guth:

$$G = G_0(1 + 2.5 c^* + 14.1 c^{*2}) \quad \text{Equation 1}$$

C* = volume fraction of filler

Equation 2 illustrates increase in viscosity based on volume concentration of fillers considered as suspended spheres. Many fillers have more complex structures which are treated with the Guth-Smallwood equation.

$$G = G_0(1 + 0.67 f^*c + 1.67 f^{*2}c^2) \quad \text{Equation 2}$$

f* = shape factor (typically - 6)

The basic premise is the volume relationship, thus the numerous filler studies based on weight equivalents are often creating false impressions on hardness change, reinforcing effects etc. Correctly approached, filler studies should be based on equivalent volumes (by correcting for density). Noted previously, fillers increase viscosity. Equation 1 illustrates this in a logical fashion. We all know that carbon blacks behave differently even though we might have equal volumes of an N990 or N330. Obviously there is surface activity involvement so we should at least understand "Adhesion and Wetting: Similarities and Differences" (1). Briefly summarizing Shanahan's timely review:

Table 2

Mechanical adhesion (1.0) is intuitive i.e.: penetration of a fabric weave to mechanically "lock" the composite.

Specific adhesion (2.0) becomes more complex i.e.: a. Electrostatic (a) adhesion might be promoted by fracturing carbon black agglomerates (of which there are many). The possibility of an electron transfer from the elastomer to carbon black is now more in favor. Chemical (b) adhesion is more accepted I.e.: brass-sulfur, silanes, epoxy-cellulose, phenolic-cellulose, amine-alkyd, etc. Diffusion (c) due to migration of thermodynamically soluble materials developing first an "interface" and subsequently a broader "interphase" between the interface and the bulk phase. Finally Adsorption (d) based on the thermodynamic reversible work of adhesion - W_a based on Dupre's work:

$$W_A = \gamma_1 + \gamma_2 - \gamma_{12} \quad \text{Equation 3}$$

This equation basically states $\gamma_1 + \gamma_2$ (surface free energy of two phases) and γ_{12} (combined interfacial free energy) = $-(W_a)$, and must be positive or there is no adhesion.

Bulk adsorption (3.0), is based on the more recent work of Alan Gent. We cannot treat it adequately in this discussion. For the more rigorous oilfield applications particularly downhole my preference is carbon black, noting:

Table 3

Carbon is a Group IV element, considering the Group IX (argonomic) elements are essentially inert, this places carbon in the exact middle group from an acid-base standpoint. Assuming Group 1 elements to be electrophilic in character and the Group VIII nucleophilic, Group IV might be characterized as amphoteric (having both acidic and basic characteristics). Since the oilfield production environment, i.e.; CH_4 , H_2S and CO_2 spans this Lewis acid-base definition, coupled with the potential of acidizing (low pH) and the inevitability of inhibitors (high pH), nonblack fillers can create additional potentially serious complications. Consider that these nonblack fillers are typically metal oxides, silicates etc. having a broad range of zeta potentials (pH value which the particle is electrically neutral). With these values ranging from acidic (silicon dioxide - pH 1.8) to basic (MgO - pH 12.0) (Table 4).

Table 4

We have the strong possibility of a vigorous attack by the operating environment on what is basically the reinforcing mechanism of the elastomer. Edward's basic paper(2) is not only recommended but should be required reading by any serious rubber compounder.

Explosive Decompression: The reinforcing effect of fillers cannot be overlooked. Briscoe and Zakaria et al in one of their many papers (3) offer some additional enlightenment. The authors note the degree of adhesion of a filler (glass beads) in an elastomer (RTV silicone) influences the carbon dioxide (CO_2) gas mass sorption as indicated by Table 5.

Table 5

<u>Condition</u>	<u>% Gas Uptake</u>
1. No filler	133%
2. Untreated filler (20% volume)	145%
3. Release coated filler (20% volume)	150%
4. Filler-silane coated (20% volume)	120%

(Conditions: CO₂ - 20MPa @ 42°C, values corrected to 100% elastomer)

Understandably, the release-coated filler essentially "defined" the size of the cavity which is expanded by the CO₂ dissolved in the elastomer matrix.

Crosslinks and Vulcanization: The function of crosslinks requires no elaboration. How they are created and how they subsequently perform is another story. Consider first the problem: dispersing typically an ionic solid (curative) uniformly throughout what is often a nonpolar medium (elastomer). The basic physical quantities which control the distribution of materials in a host medium are diffusion coefficients and solubility. The speed at which a large molecule can diffuse thru an elastomeric media was elegantly demonstrated by Wang et al (4). A good example: Crosslinking of a typical hydrofluorcarbon (FKM) elastomer.

Figure 1

The curing system, consists of a dihydroxy salt of Bisphenol AF (crosslink) and an "onium" complex, typically benzyl triphenyl phosphonium chloride. The "onium" complex probably serves multiple functions:

- a. "solvent" to break ion-pairing characteristics of curative
- b. phase transfer catalyst to transport curative
- c. decompose at curing temperature

Essentially what is being accomplished is the bringing together of two mutually insoluble reagents to affect a rapid reaction rate by phase transfer catalysis. Crosslink mobility directly affects physical properties such as heat-buildup, tear strength, elongation. Try comparing the properties of EPDM cured with sulfur-containing curatives (difunctional) versus a triazine such as triallyl cyanurate (trifunctional).

References:

1. "Adhesion and Wetting: Similarities & Differences"
M.E.R. Shanaham
Paper No. 37 138th Meeting
Rubber Division - ACS
October 9-12, 1990
Washington, DC.
2. "Water Absorption Phenomena in Elastomers"
D.C. Edwards
Paper "b", Educational Symposium No. 13, 126th
Meeting
Rubber Division - ACS
October 22-26, 1984
Denver, CO.

3. "Role of Interfacial Quality on Gas Induced Damage of Elastomeric Composites"
B.J. Brisco S. Zakaria
Imperial College, London - UK
Presented at "Explosive Decompression Seminar"
June 4, 1990
Red Bank, NJ

4. "Fluorescent Measurements of Diffusion in Polymer Systems"
F. Wang, NBS
Paper "g", Educational Symposium No. 13, 126th Meeting
Rubber Division - ACS
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Suggested Books:

1. Organic Chemistry - 4th Edition
R.T. Morrison
R.N. Boyd
Allyn and Bacon, Boston 1982.

2. Advanced Organic Chemistry - 3rd Edition
J. March
Wiley-Interscience, NY 1985

3. Advanced Inorganic Chemistry - 5th Edition
F.A. Cotton
G. Wilkinson
Wiley-Interscience, NY 1988

4. The Lewis Acid-Base Concepts
W.B. Jensen
Wiley-Interscience, NY 1980

5. Zeta Potential in Colloid Science
R.J. Hunter
Academic Press, NY 1981

6. Phase Transfer Catal.
E.V. Dehmlow
S.S. Dehmlow
Verlag Chemie - 1983
Weinheim, Deerfield Beach, FL.

7. Calixarenes
C.D. Gutsche
Royal Society of Chemistry - 1989
Cambridge CB4 4WF

RUBBER FORMULATION DESIGN

Remember we can design formulations for:

STRAIN (o-rings)

STRESS (packers etc.)

ENERGY (intermittent loads)

Since elastomers are "single phase" materials there is little or no carryover in a formulation

TABLE 1
FKM MOLECULAR WEIGHT EFFECTS*

(Equivalent Compounding)

	<u>Low</u>	<u>Medium</u>	<u>High</u>
Tensile (psi)	1650	1825	2100
Elongation (%)	170	180	200
Permeometer	79	78	76
Modulus (psi)	850	850	850
Tear Strength (24° C)	190	200	210
(150° C)	54	56	63
Compression Set (%)			
70 hrs @ 232° C	75	53	32
Tensile-Strain @ 177° C			
Tensile (psi)	425	425	575
Elongation (%)	90	90	100

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TABLE 2

Adhesion Theories*

1.0 Mechanical

2.0 Specific

3.0 Bulk Adsorption

a. Electrostatic

a. Weak Bound
Layers

b. Chemical

b. Rheological
Theory

c. Diffusion

d. Adsorption

* There is no "Universal Theory of Adhesion"

TABLE 3

PERIODIC CHART - ACID/BASE CONCEPTS*

	G	S1	S2							
P										
	1	H	He							

	G	P1	P2	P2	P3	P4	P5	P6	P7	P8
P										
2		Li	Be		B	C	N	O	F	Ne
3		Na	Mg		Al	Si	P	S	Cl	Ar
4		K	Ca	Zn	Ga	Ge	As	Se	Br	Kr
5		Rb	Sr	Cd	In	Sn	Sb	Te	I	Xe
6		Cs	Ba	Hg	Tl	Pb	Bi	Po	At	Rn
7		Fr	Ra	112	113	114	115	116	117	118

	G	D3	D4	D5	D6	D7	D8	D9	D10	D11
P										
4		Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu

truncated "three block" periodic table emphasizing hydrogen's unique position
 s-block (H and He) use only filled and/or empty s orbitals for bonding
 p-block use filled and/or empty s and p orbitals
 d-block use filled and/or empty s, p and d orbitals

TABLE 4

Electric pH Values for Oxide Pigments (Zeta Potential = 0)

<u>Oxide Pigment</u>	<u>pH</u>
Sb_2O_5 (antimony pentoxide)	0.3
SiO_2 (silica gel)	1.8
SiO_2 (quartz)	2.2
TiO_2 (rutile)	4.7
$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ (kaolin)	4.8
$\text{Al}(\text{OH})_3$ (hydrated aluminum oxide or gibbsite)	5.0
Fe_2O_3 (hematite)	5.2
TiO_2 (anatase)	6.2
Fe_2O_3 (maghemite)	6.7
Cr_2O_3 (chrome green)	7.0
Al_2O_3 (alumina)	9.0
ZnO (zinc oxide)	9.0
PbO (litharge)	10.3
MgO (magnesia)	12.0

TABLE 5

Silicone^① / Filler^② Swell Phenomena in Carbon Dioxide

<u>Condition</u>	<u>% Gas Uptake</u>
No filler	133%
Untreated filler (20% volume)	145%
Release-coated filler (20% volume)	150%
Silane coated filler (20% volume)	120%

1. RTV silicone

2. 60 micron glass beads

Conditions: Carbon dioxide, 20Mpa @ 42°C

% Gas Uptake calculated on equivalent elastomer volume

FIGURE 1

PHASE TRANSFER CATALYSIS EXAMPLE

Curing Characteristics of VITON[®] E-60C



