

"Nitrile Rubber - Past, Present & Future"

by D. L. Hertz, Jr.\* and Hermann Bussem

Seals Eastern, Inc., P.O. Box 519, Red Bank, NJ 07701

and

T. W. Ray

Halliburton Energy Services, Inc., P.O. Box 819052, Dallas, Texas 75381-9052

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\*speaker

## ABSTRACT

### NITRILE RUBBER - PAST, PRESENT & FUTURE

Nitrile rubber (NBR) has been the work-horse elastomer in oil & gas production for the past fifty years. As wells began producing increasing amounts of hydrogen sulfide ( $H_2S$ ) through stimulation or reservoir conditions coupled with higher production temperatures, sporadic seal and packer failures have been encountered. Future applications of nitrile rubber in higher temperature production should only be considered after reviewing the range of chemical attacks capable by the well fluids, completion fluids and stimulation fluids this paper briefly outlines.

## INTRODUCTION

For the past fifty years nitrile rubber (NBR) has been the logical elastomer of choice for service in the oil and gas industry. As wells became deeper, production temperatures logically increased. Occasional field failures would surface due to excessive elastomer hardening which in turn could result in leaks, inoperative controls and nonretrievable "retrievable packers". Working jointly with Halliburton Engineering Services (formerly Otis Engineering), numerous failed field sample components were analyzed by Seals Eastern. Additionally, several in-house test programs were initiated at Seals Eastern using typical fluids the production elastomeric components might routinely be subjected to. These media included inhibitors, acidizing mixtures, sea water and completion fluids.

## EXPERIMENTAL

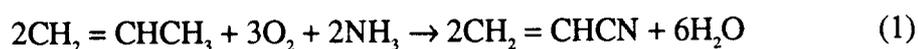
Nitrile rubber (NBR) is the work horse oil-resistant elastomer of choice for typical sealing applications. A copolymer of butadiene (BR) and acrylonitrile (ACN), is produced by emulsion polymerization with the specifications defined by ACN level and Mooney viscosity. The briefest review of these elastomers will point out that the structure (molecular architecture) is relatively complex. The butadiene monomer copolymerizes into three distinct structures i.e.: trans, cis and 1,2-. The trans configuration dominates (~78%) in a typical nitrile, inevitably there will be blocks of these units.

A 100% *trans* butadiene polymer would be a plastic (like gutta-percha in polyisoprene), hence these blocks are sensitive to heat in terms of shear thinning. The *cis* configuration, (~12%), serves to break-up substantial crystallinity since it enters in a statistical pattern. The 1,2- sites (~ 10%), are free vinyl groups typically causing branching and often gel (insoluble polymer). The acrylonitrile (ACN) groups are inserted in a statistical pattern ranging from head-tail, head-head and tail-tail.

### Nomenclature

Butadiene. - (1,3-butadiene), a hydrocarbon gas is produced by numerous processes, ex: catalytic dehydrogenation of butene or butane-butene mixtures. It polymerizes readily to form either a polymer or copolymer and in terms of chemical reactivity it is a very stable, nonpolar hydrocarbon due to the symmetry of its' molecular structure consisting of carbon and hydrogen.

Acrylonitrile. - (2-propenenitrile), a liquid, is produced predominantly by the ammoxidation of propylene:



We are specifically detailing this chemistry as it points out the potential of driving a reverse reaction or what is commonly referred to as *hydrolysis* (cleavage by water). Acrylonitrile is a very polar molecule due to the lack of symmetry of the triplebonded nitrogen coupled with the nitrogens' *lone-pair electron* effect. The lone pair effect plus a large dipole moment created by the nitrogen developes a very strong H - *bonding* potential (witness NBR swelling in methanol-gasoline combinations).

Monomeric Stabilities. -The *butadiene* monomer as noted consists of a carbon backbone and hydrogen atoms. The hydrogen - carbon *bond energy is*  $411\text{kJ mol}^{-1}$ , there are no *lone pair electron* considerations for the M1 to M4 elements so we do not experience possible *reduced* bond energy consideration. The *acrylonitrile* (ACN) monomer is a different story. Considering the *cyano* (CN) group specifically, there is a *lone pair* effect on the M5 (nitrogen) to M8 elements which tend to *weaken* bond energies. Consider the varying bond strengths of possible carbon-nitrogen combinations:

$\text{C} \equiv \text{N}$	$891\text{ kJ mol}^{-1}$
$\text{C} = \text{N}$	$615\text{ kJ mol}^{-1}$
$\text{C} - \text{N}$	$305\text{ kJ mol}^{-1}$

it is apparent that the breaking of one or more of the carbon-nitrogen triple bonds can lead to a host of potential interactions.

Chemistry. -The fundamental issue is that any physical change in the elastomer (other than plasticizer loss) is due to a chemical reaction. 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 chemical reactions can be simplified to accomplish *three (3) basic mechanisms* and six *types of reactions*.

Mechanisms:

1. 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* (Lewis base) and the reaction - *nucleophilic*. An *Acceptor* is called an *electrophile* (Lewis acid) and the reaction - *electrophilic*.

2. Homolytic cleavage (free-radical mechanism) is the breakage of a single bond (two electrons) leaving one of the electrons on each of the fragments.
3. Pericyclic reactions. The third reaction mechanism is not common in this discussion.

Tyres of reactions.-

1. Substitution
2. Additions to multiple bonds
3.  $\beta$  elimination
4. Rearrangement
5. Oxidation and reduction
6. Combinations of above

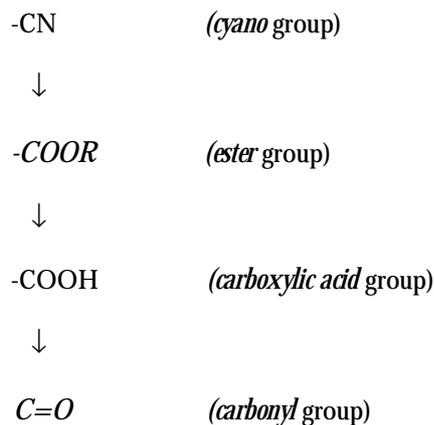
Knowing the elastomer chemical structure and reviewing a first year organic chemistry textbook will answer most questions of where these reactions might occur. Chemical reactions-butadiene, cis, trans sites.-Logically we consider the diene double-bond site as the weakest link. This is a problem for NBR components exposed to UV (sunlight, fluorescent lights-unshielded) ozone and oxidative environments. These conditions are not an issue in the down-hole environment. Sulfur (elemental) and hydrogen sulfide ( $H_2S$ ) might erroneously be considered potential crosslinkers in the production environment but this is not true. Sulfur might cause some surface hardening but it might be somewhat ingenuous to assume the atomic sulfur to be sufficiently mobile to permeate the elastomer.

H<sub>2</sub>S is also a very stable gas, a saturated solution of H<sub>2</sub>S and water creates an acidic environment with a pH of  $\cong 4$ . H<sub>2</sub>S (a Bronsted acid) does have the potential of adding to the double bond but only at higher temperatures in the presence of strong Lewis acid. Strong Lewis acids are not typical in the production environment.

1, 2-Sites. -Can thermally crosslink thru any of the CH<sub>2</sub> groups in a *reductive* environment causing excessive hardening, however temperatures have to be in excess of 200°C.

Chemical reactions-acrylonitrile. -Referring back to the acrylonitrile production reaction (1) it is apparent that this is a monomer not only vulnerable to *hydrolysis* but also *reduction*.

Hydrolysis. -of the nitrite group catalyzed by an acid (Bronsted) or base typically follows the following path:



However, the reaction path listed is not rigid. Nitrite conversion direct to carboxylic groups or amides is possible. Additional possible routes are carboxylic groups yielding esters initiated by ROH presence.

Reduction-of the nitrite group catalyzed by a Lewis acid with a source of hydrogen ( $H_2O$ ) yields a primary ( $1^\circ$ ) amine ( $-CH_2NH_2$ ).

Physical basis of chemistry.-Chemical reactions are generally temperature dependent with the reaction proceeding more rapidly as the temperature increases. Considering now that all of the precursors of nitrite rubber were gases (butadiene, propylene and ammonia) our elastomer can be defined as a supercondensed gas. The most stable thermodynamic state (highest entropy) is a gas. An elastomer is a solid, hence, the eventual progression to thermodynamic stability is the procession from a solid, to a liquid, ultimately - a gas. Since the elastomer does not spontaneously move from the solid state to a gaseous state there must be a barrier. This barrier (or intermediate state) is called the *transition* state. The energy difference between the *reactant* and the *transition* state is called the activation energy,  $E_a$ , (Fig. 1). Heat increases the mobile energy of atoms and only molecules with energy comparable to the *transition state* can get over the energy barrier to rearrange. Not every molecule in the transition state will rearrange due to statistical considerations and collisions with other molecules which often deactivate the active molecule. Since we have a random dissociation situation there *is* *time* dependency. We should consider the elastomer under any condition as being in a *metastable* state (an excited stationary energy state whose lifetime is unusually long).

Catalysis.-Many reaction rates are increased by substances called *catalysts*. A catalyst speeds up a reaction by providing an alternative pathway from the reactants to products. The new pathway has a rate - determining step with a lower activation energy  $E$ , than the original pathway (Fig. 2). One of the earliest catalyst combinations was hydrochloric acid (HCl) and iron.

Catalysis can be initiated by *acids, bases, metal ions, phase transfer agents, zeolites, enzymes*, etc.

The acids, and/or bases can be either Bronsted or Lewis. A Bronsted acid is any molecule or ion that can act as a proton donor. The conjugate base is any molecule that can act as a proton acceptor. Water can serve as either a Bronsted acid or base ( $\text{H}_3\text{O}^+$ ,  $\text{OH}^-$ ).

A Lewis acid is an electron pair acceptor - ex: metal halides. A Lewis base is an electron pair donor - ex: amines. Phase transfer agents (not specifically identified as such) are common ingredients in inhibitors and corrosion preventatives. Zeolites are crystalline aluminosilicate materials i.e.; clays that might be used as fillers in the rubber formulation.

#### EXPERIMENTAL

Standard -214 O-rings (25mm ID X 3.53 CS) were molded from the model compound;

Table I.

Six (6) each samples were aged in PTFE lined Parr acid digestion bombs, 125 ML capacity in 100 ML of test fluids:

- (1) Water-calcium chloride 100/140 wt. ratio
- (2) Water-calcium chloride-Tretolite 37L, 100/140/1 wt. ratio
- (3) Seawater, Tretolite 37L (100/1 wt. ratio)
- (4) Seawater
- (5) Fisher reagent-pH 4
- (6) Fisher reagent-pH 7
- (7) Fisher reagent-pH 11
- (8) Water/zinc bromide (100/150 wt. ratio)

These combinations represent weak and strong Lewis acids (1 & 8), Bronsted acid (5), bases (7) and combinations of Lewis acid & a possible phase transfer agent (2). Field failures at operating temperatures of 110°C dictated initial testing at this temperature. No specimens showed any unusual hardness increases after 288 hrs. @ 110°C. Raising test temperatures to 150°C and retesting after 72 additional hours showed little physical change. Additional aging at 160°C and 288 hours showed mixed results of physical hardness. It was now noted that aged samples increased measurably in hardness over a period of shelf time. Sample hardness's of 90 to 98 Shore A were common. Immersion in boiling water (100°C) indicated a pronounced thermoplastic softening (10 - 20 durometer points).

Sample (8) aged in zinc bromide/water was an exception. Seals increased in volume about 25%, were very hard with no evidence of thermal plasticity. With the exception of Sample (8) there was little consistency of test results.

## RESULTS

The lack of physical consistency is due to the fact that we are developing a strongly time-dependent range of intermolecular forces. These forces are both ionic and *intermolecular* - primarily *H-bonding*. All of the reactions are occurring at the CN (*cyano*) existing and breakdown sites. The *ionic* attractions would be via the *carboxyl* groups providing "crosslinks" thru a divalent ion (zinc, calcium). The *H-bonding* attractions are occurring thru interactions of the *carboxylic*, *ester* and *carbonyl* groups with the unreacted *cyano* groups as well as each other. Table II<sup>1</sup> gives some comparative average bond energies and their interaction range. The characteristics of these forces are that they are both highly directional and heat sensitive hence the thermoplastic effect. Subsequently noted (and logical) is the time dependency that causes an increase in hardness due to the attractive effect of the interactions. This hardness increase would be due to the development of more "ordered domains" approaching that of crystallites or hard fillers.

## DISCUSSIONS

*Infrared analysis* (IR) of aged samples offer interesting background data. Hydrolysis and reduction are common reactions performed to cleave the *cyano* carbon - nitrogen triple bond. The *cyano (CN)* bond is very strong peak at  $\sim 2260 \text{ cm}^{-1}$ . Samples tested after aging indicated varying but fewer CN groups.

IR scans for different aging periods showed first the onset of -COOR (*esters*) followed by -COOH (*carboxylic acid*). Sample (8) showed not only complete disappearance of the CN group but additional *amide*, -OH and strong *H - bonding* peaks. The swelling of Sample (8) was probably due to the water solubility of the various CN breakdown products (primary amines). Concentrated acids (Bronsted) result in only partial hydrolysis leaving primarily *carboxylic* (-COOH) acid groups. Strong Lewis acids (zinc bromide) result in complete reduction of CN groups.

The thermoplastic aspect of Samples 1 thru 7 could be due to -COOH groups ionically crosslinked by the zinc in the compound formulation. Additionally, strong H - bonding of the carboxylic, ester or amide groups through remaining cyano nitrogen lone electron pairs would develop very strong, thermally sensitive intermolecular forces even without the presence of zinc. We have in effect created a "super" carboxylated nitrile rubber - Fig. 3<sup>2</sup>. The nature of the crosslink in the non-thermoplastic Sample (8) is not clear from this study but the possibility of ester crosslink by an ester interchange or a basic salt of zinc and the COO- ester are also crosslink possibilities..

Laboratory testing has not been able to duplicate the lower temperature field failures. This is no doubt due to a lack of metal ions as the other key component for much catalysis. Common to all field failures was the environmental presence of iron; iron and iron molybdate are relatively common catalysts. Iron and hydrochloric acid have often been referred to as the original "iron-age catalysts". Additional testing is planned at lower temperatures using iron complexes coupled with Bronsted and Lewis acids. Reactivity will be monitored using infrared analysis but due to the bulk nature of the elastomer we anticipate poor definition of CN breakdown products due to progressive reactions on the intermediates being formed.

## SUMMARY

Excessive hardening of nitrile rubber in the down-hole oilfield environment occurs at the acrylonitrile sites and can be due to either hydrolysis or reduction of the cyano group. Hydrolysis is driven by Bronsted acids (proton donors) and reduction via Lewis acids (electron donors). Catalysis via metal ions is a logical possibility that can cause these reactions (hydrolysis and reduction) to occur at a greatly reduced *activation energy* –  $E_a$  level. Oxidative attack at the butadiene sites is the primary cause of hardening in above-ground applications of NBR rubber. Hydrogenated nitrile rubber (HNBR) in the down-hole environment would be subject to the same reactions as described for NBR elastomers.

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TABLE I

NBR (34% ACN)	100.0
N550 carbon black	50.0
Zinc oxide	5.0
Stearic acid	1.0
Sulfur	1.5
MBTS	1.5

Cure: 15 minutes at 170°C.

TABLE II

## BOND ENERGIES AND DISTANCES

<u>Bond Type</u>	<u>Interaction Energy (~)</u> <u>kJ mol<sup>-1</sup></u>	<u>Distance Function (~)</u> <u>(angstroms)</u>
COVALENT (C-C)	344	1-2
IONIC	42-84	2-3
H-bond	15-40	2.3-3.2

# ACTIVATION ENERGY - $E_a$

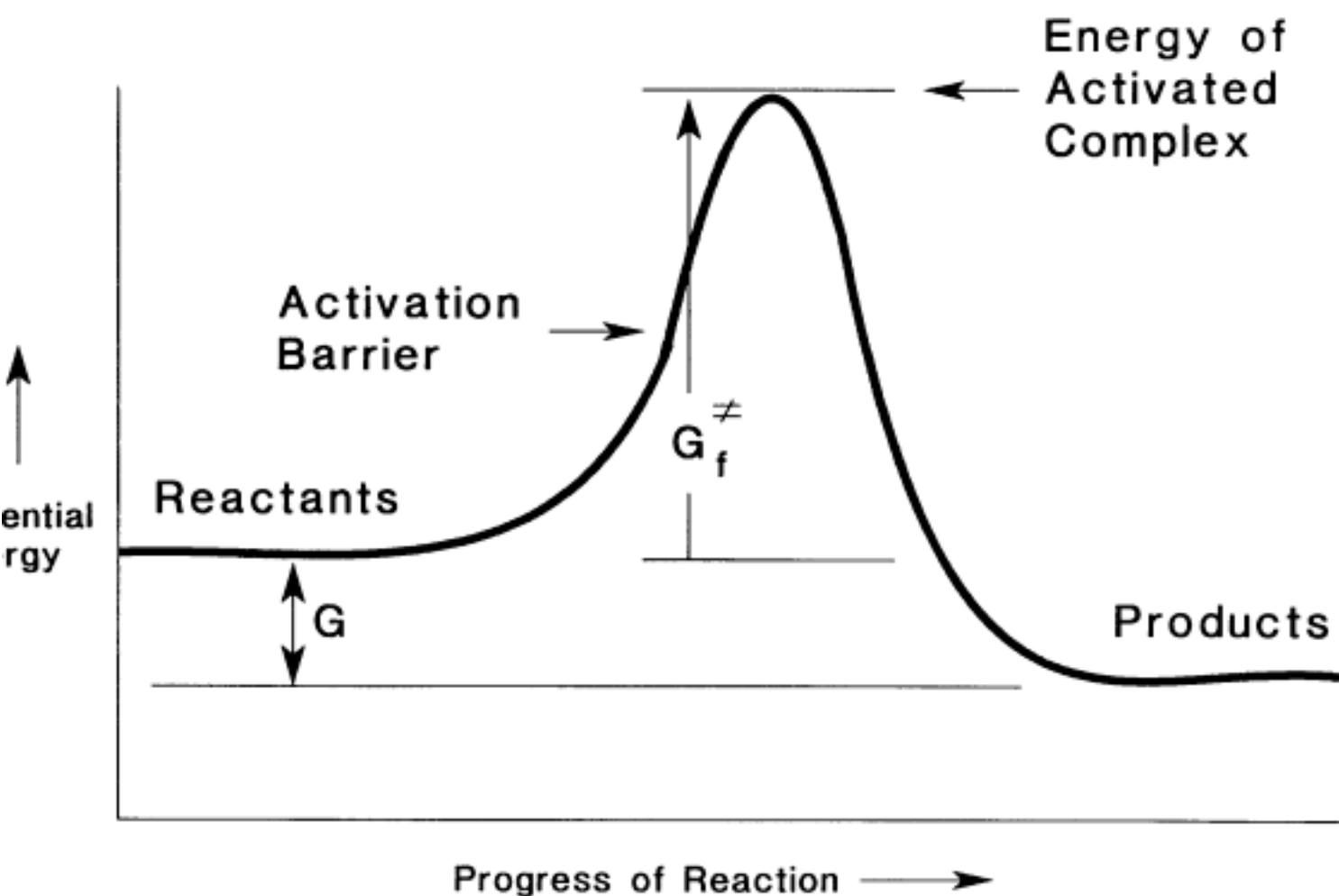


Figure 1

# ANALYSIS and ACTIVATION ENERGY - $E_a$

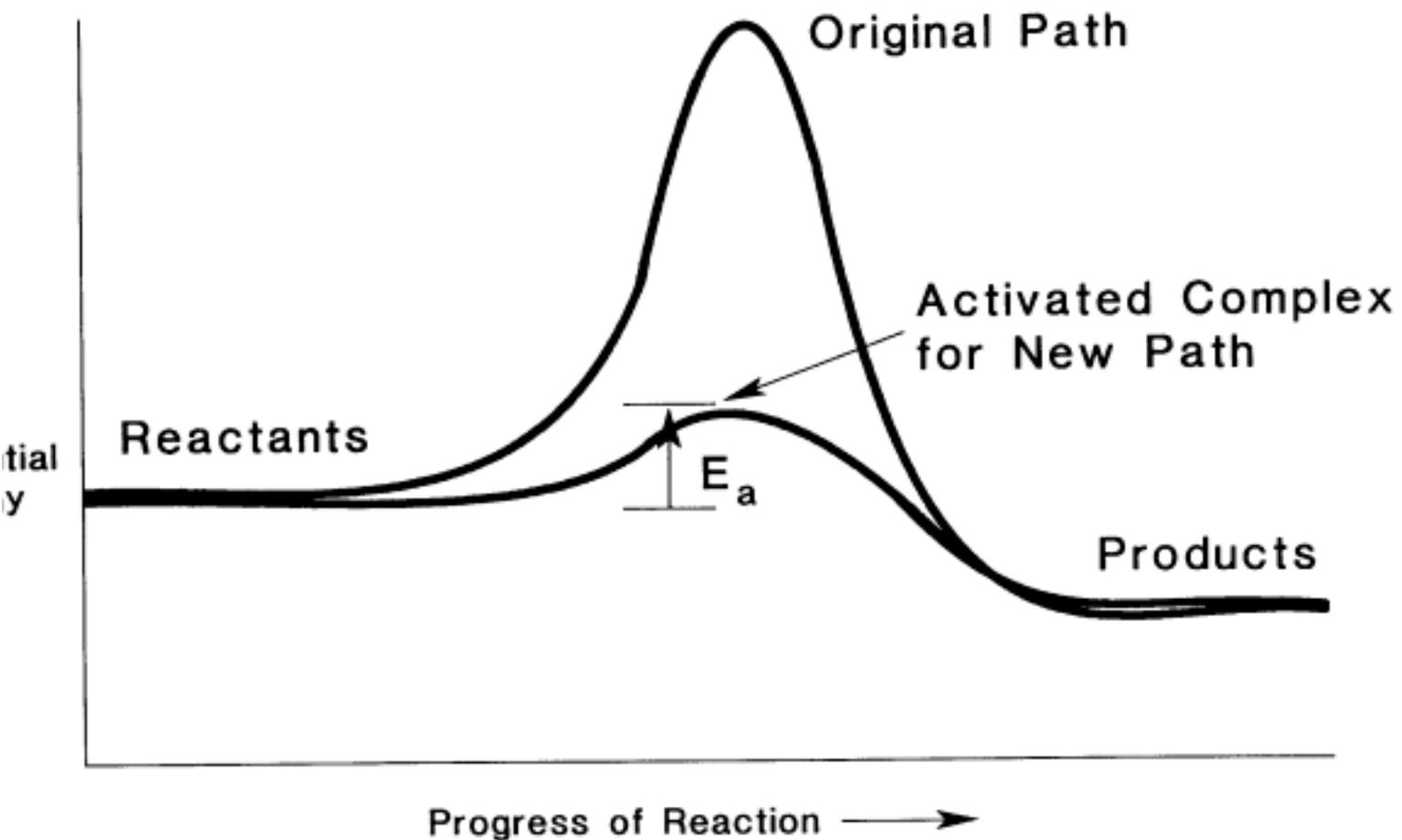


Figure 2

INFLUENCE OF ZINC OXIDE LEVEL ON A GUM VULCANIZATE  
 OF A BUTADIENE/ACRYLONITRILE/METHACRYLIC ACID (ref. 1)

55/35/10 Copolymer of 73% Conversion and 0.099 ephr COOH

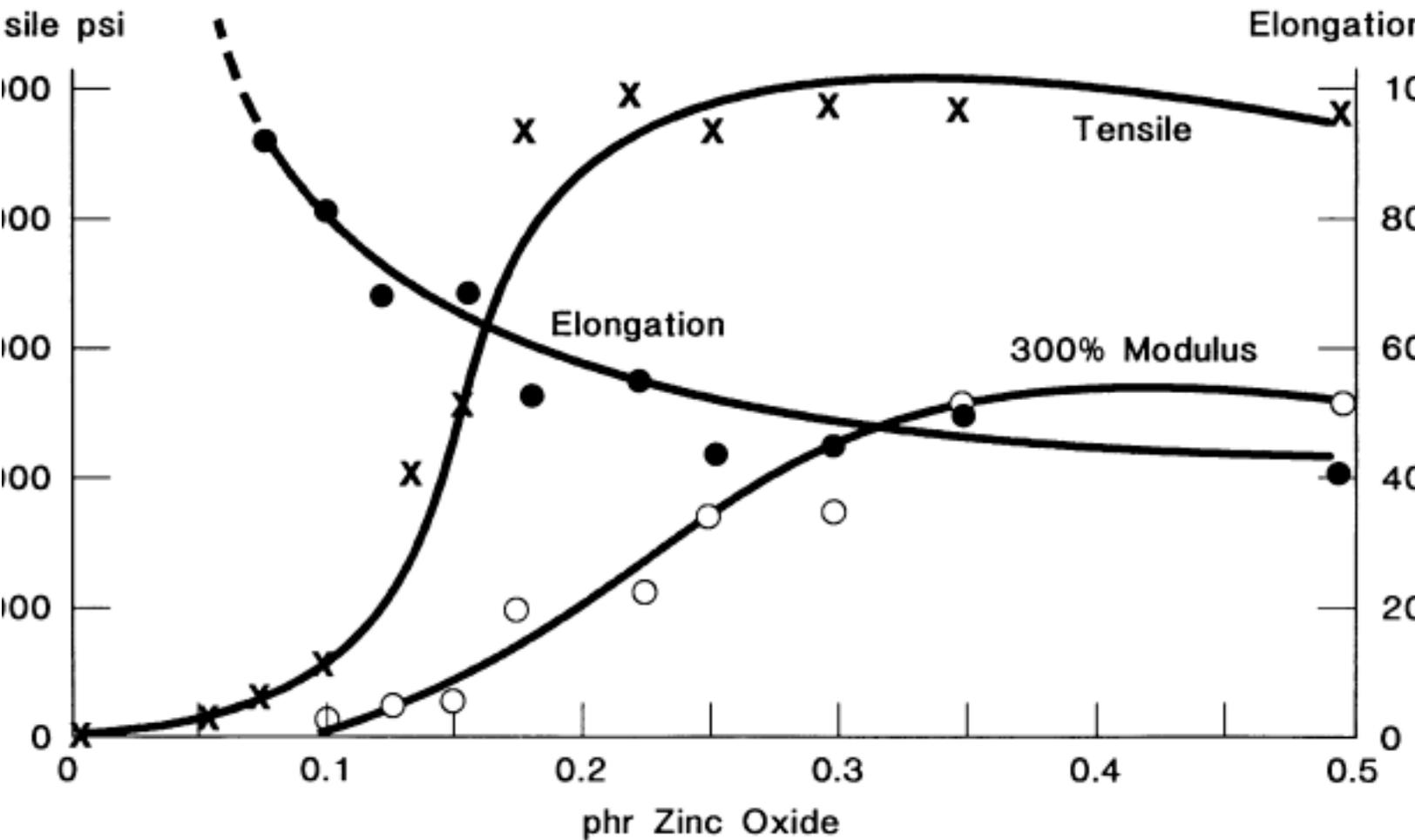


Figure 3

