Crosslinking of fluoroelastomers and the influence on final properties

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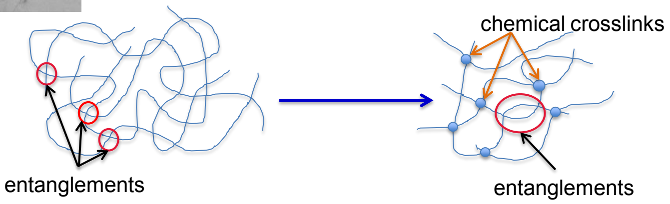
Overview

- ☐ basics on curing of rubber and fluoroelastomers
- ☐ ionic cure with bisphenol
  - requirements
  - crosslinking mechanism
  - effect of cross linker to accelerator ratio
  - role of metal oxides and influences of level change
  - ionic cure without “standard” cure activators
- ☐ radical cure with peroxides
  - requirements
  - crosslinking mechanism
  - effect of cross linker and accelerator level on cure speed and mechanical properties
  - different coagents
  - Influence of peroxide level
- ☐ conclusions

Some Basics on Curing of Rubber

- hydrocarbon rubbers are mainly cross-linked with systems based on sulfur or peroxides
- chemical crosslinking minimizes viscous flow and leads to material with high elasticity



- the occurring chemical bonds have following energy:
  C-S-C: 285 kJ/mol C-S-S-C: 268 kJ/mol
- with increasing bond energy the thermal stability is increasing
- special rubbers like FKM are used in demanding environments and the cross-linked materials have to withstand high temperatures and should have high chemical resistance
- crosslinking with bisphenol forms C-O-C bonds; bond energy C-O: 358 kJ/mol
- crosslinking of FKM with peroxides forms C-C bonds; C-C: 352 kJ/mol

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Ionic Cure vs. Peroxide Cure

ionic cure:

- ➢ Bisphenol AF most common cross linker; phosphonium and ammonium salts most common accelerator
- ➢ curative Masterbatches support dispersion
- ➢ best scorch safety, low mould fouling and good mould release
- ➢ lowest compression set
- ➢ excellent heat resistance

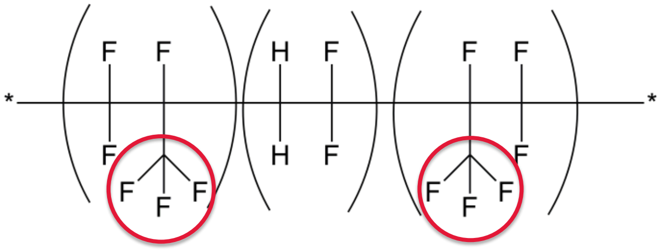
crosslinking of fluoroelastomers

radical cure:

- ➢ cure sites are incorporated into the polymer (DuPont™ Viton® **G** types)
- ➢ peroxide controls the rate of cure, DBPH most common peroxide
- ➢ coagent controls the number of crosslinks, TAIC most common coagent
- ➢ best resistance to hot water (or other aqueous fluids like coolants)
- ➢ improved chemical resistance (e.g. high and low pH)
- ➢ metal oxides not necessary but lead to higher heat resistance and more efficient cure

Requirements for Curing with Bisphenol

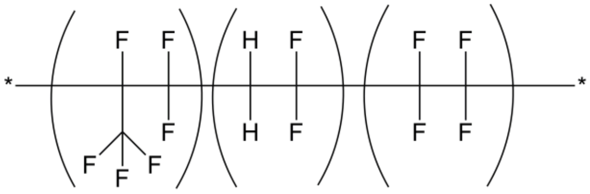
- **CH_2 between two carbon (or longer) perfluorinated monomer units**
  - easy dehydrofluorination (as for HFP:VF_2:HFP or TFE:VF_2:TFE)
- **CF_3 group aids cross link formation later in the process**



Viton® A;
F-content 66%

Requirements for Curing with Bisphenol

B and F types also cured via C=C, formed at isolated VF_2 sequences but less efficiently because curatives are less soluble in the polymer - they cannot find the cure sites easily



Viton® B, F;
F-content 66-70%

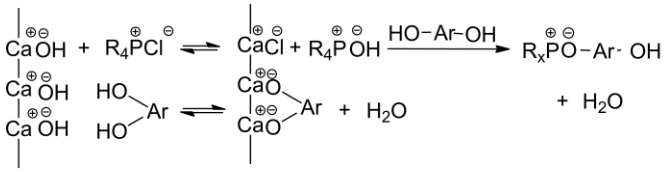
HFP:VF_2:HFP easy formation of C=C, crosslink very efficiently

TFE:VF_2:TFE easy formation of C=C, don't crosslink as easily because no CF_3

- H and F combine with acid acceptors to form water and metal fluorides

Bisphenol Cure System – Curing Mechanism

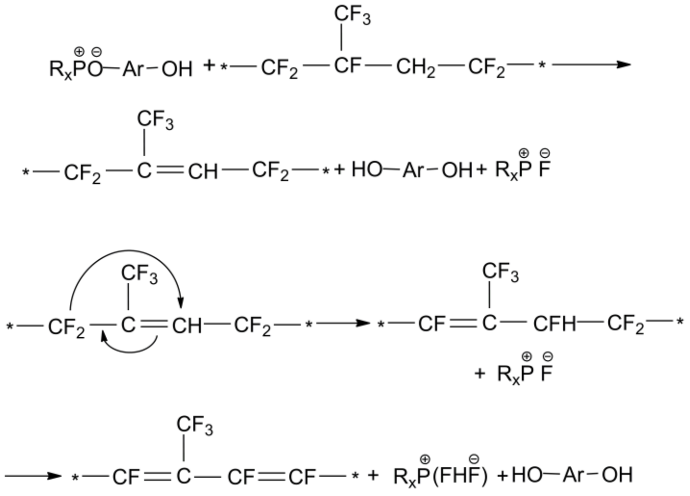
1. Formation of the soluble bisphenol monophosphoniumsalt, for nucleophilic reaction with the polymer



[adapted from Schmiegel, Kautschuk Gummi Kunststoffe, **1978**, 31, 137]

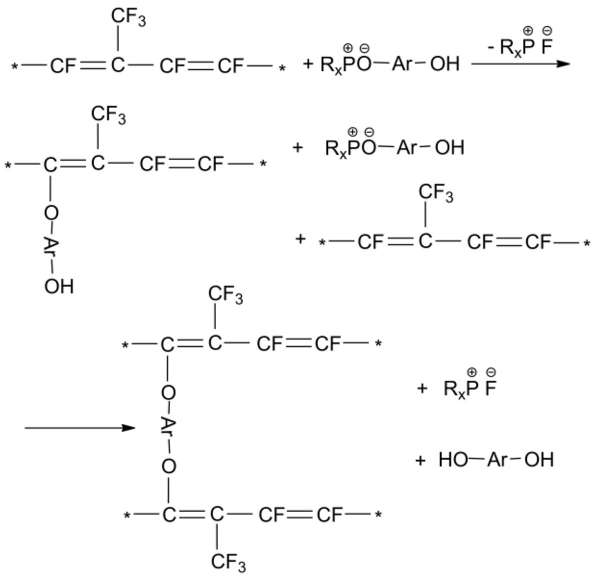
Bisphenol Cure System – Curing Mechanism

2. Creation of diene functionality in the polymer chain, through reaction of the soluble base (bisphenol monophosphoniumsalt) with the FKM (dehydrofluorination)



Bisphenol Cure System – Curing Mechanism

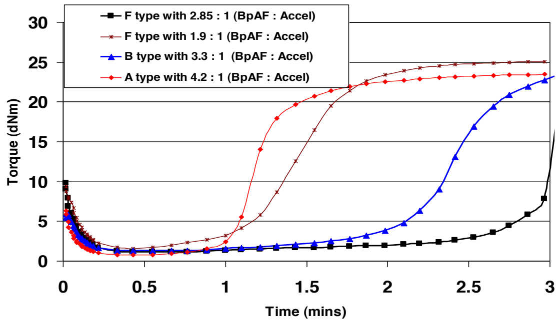
3. Crosslinking of two polymer chains



Influence of Polymer Type on Cure Rate

- **A types cure very quickly**
- **B types are slower**
- **F types need very high levels of accelerator**
- **Ratios for reasonable cure rates**
  - A type about 4 : 1 (BP-AF to Accelerator ratio)
  - B type about 3 : 1
  - F type about 2 : 1

Test at 180° C, 0.5°, 3 mins



Ratio of Bisphenol to Accelerator – Impact on Properties

Higher curative level results in :

- **higher modulus**
- **higher hardness**
- **lower elongation**
- **better compression set**
- **poorer TR-10**
- **better flow**
- **better mould release**

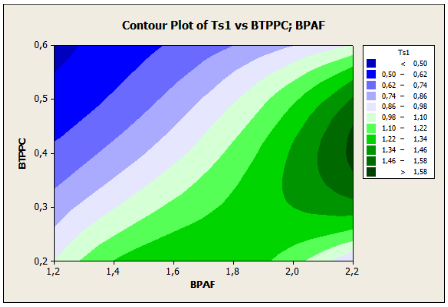
Lower BP-AF : Accelerator ratio results in :

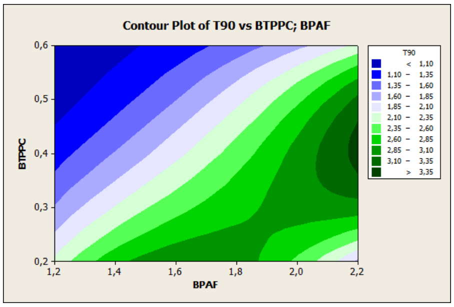
- **faster cure**
- **increases scorch**
- **poorer compression set**
- **more mould fouling**

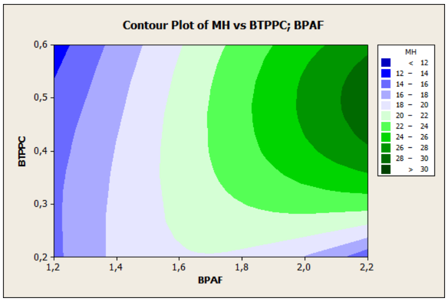
Higher BP-AF : Accelerator ratio results in :

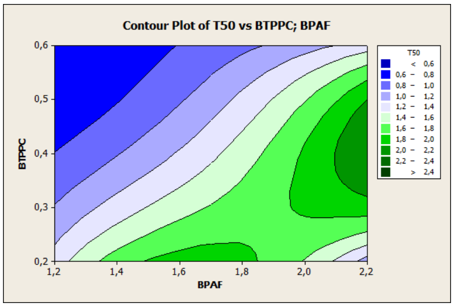
- **slower cure**
- **less scorch**
- **better compression set**

BPAF / BTPPC Ratio – Impact on Curing

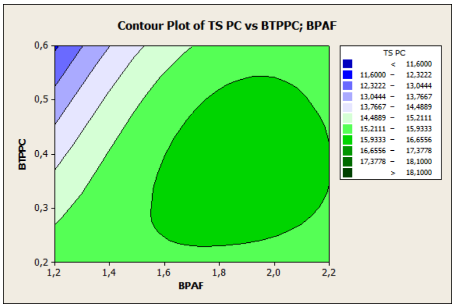


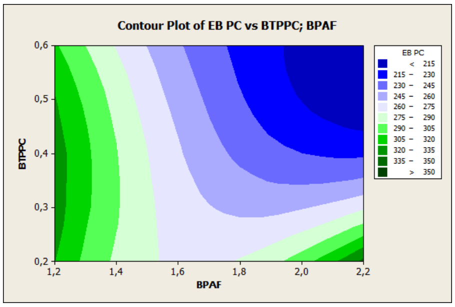


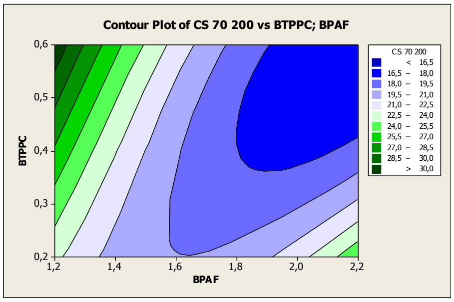




BPAF / BTPPC Ratio – Impact on Properties


Contour Plot of TS PC vs BTPPC; BPAF


Contour Plot of EB PC vs BTPPC; BPAF


Contour Plot of CS 70 200 vs BTPPC; BPAF

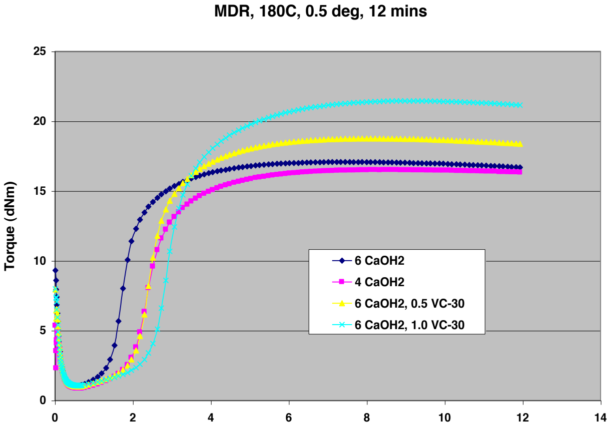
Effect of Metal Oxides During Bisphenol Cure

- ☐ cure site creation and acid acceptors
  - usual metal oxides are Ca(OH)2 and MgO : **6 phr Ca(OH)2 and 3 phr MgO**
- ☐ effects of metal oxide levels
  - **higher Ca(OH)2** results in faster curing but poorer compression set and properties
  - **higher MgO** results in better heat resistance and better bonding
  - **high metal oxide** levels adversely affect for flow (injection)
  - **metal oxides promote** mould sticking and fouling
- ☐ types of MgO
  - usual levels are 3 phr high activity or 15 of low activity MgO (processing!!!)

Metal oxides are hygroscopic and are often the cause of scorch problems

Effect of Metal Oxides During Bisphenol Cure

using Calcium Hydroxide to control cure rate



General Trends:

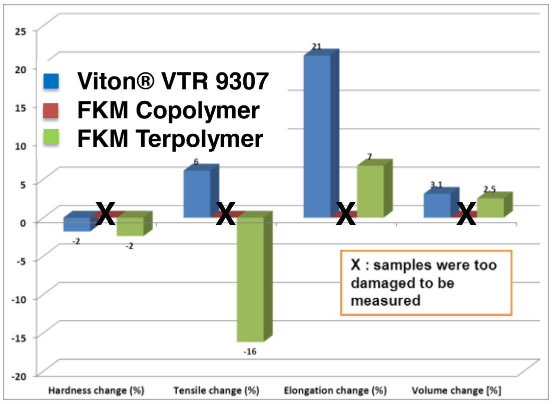
- reducing calcium hydroxide level from 6 to 4 phr reduces cure rate
- similar reduction in cure rate by adding 0.5 phr VC-30 but increasing the modulus
- adding 1.0 phr VC 30 significantly reduces cure rate but increases modulus
- adding VC-30 gives a reduced cure rate because of a higher curative to accelerator ratio

New Bisphenol Curable Grade

- ➢ standard bisphenol compounds provide poor resistance to organic acids due to MO
- ➢ development with new cure activator and good acid resistance

⇒ **Viton® VTR 9307 new bisphenol curable precompound**

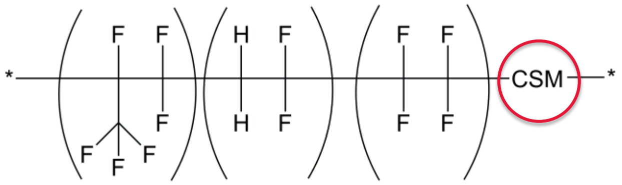
test conditions: acetic acid, 504h @ 100° C



X : samples were too damaged to be measured

VTR 9307 vs Viton® A331C

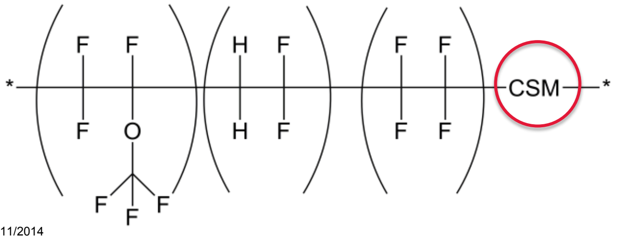
Requirements for Curing with Peroxides



Viton® GAL-S, GBL-S, GF-S

65.5-70%F

- peroxide cured fluoroelastomers for best hot water resistance, improved acid and base resistance and low post cure capability
- bromine or iodine containing cure site monomers have to be incorporated
- no need of metal oxides but could be incorporated for improved cure efficiency and heat resistance

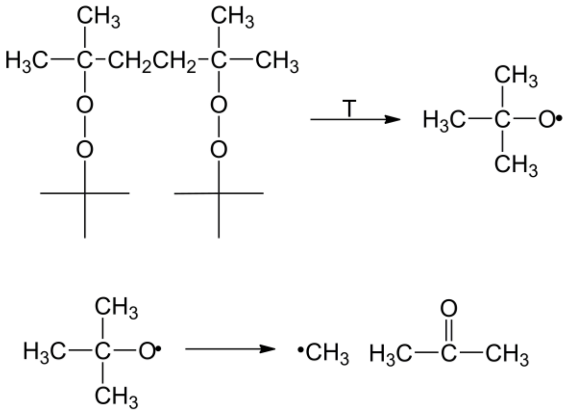


Viton® GLT-S, GBLT-S, GFLT-S

64.5-67%F

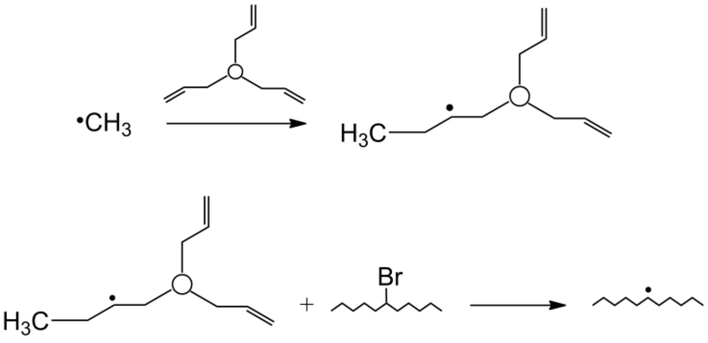
Peroxide Cure System – Curing Mechanism

1. t-butoxy radical generation and beta scission to the methyl radical and acetone



Peroxide Cure System – Curing Mechanism

2. Adding methyl radical to TAIC and abstracting bromine from polymer chain

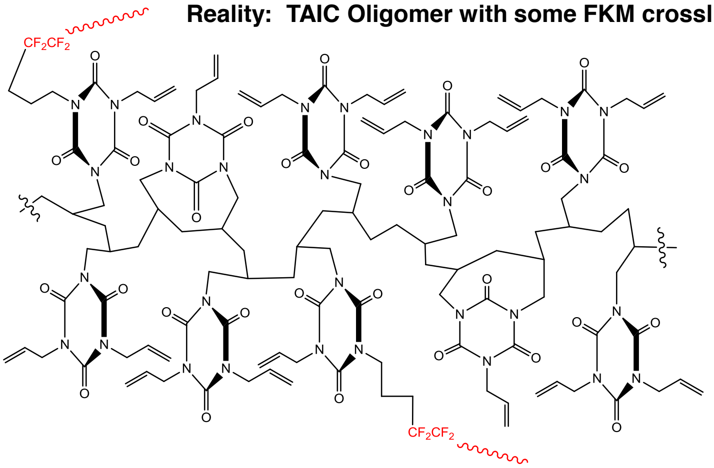


more likely the TAIC radical polymerizes

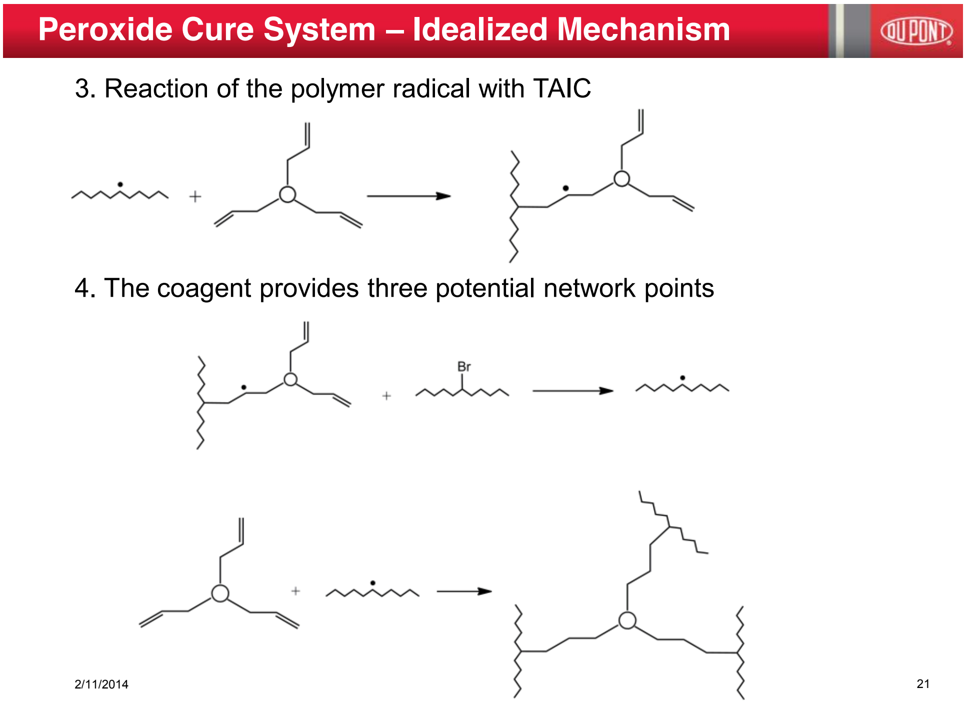
Peroxide Cure System – Curing Mechanism

1. polymer radical is formed by reaction of methyl radical with CSM
2. polymer radical reacts with the (poly)coagent

Reality: TAIC Oligomer with some FKM crosslinks



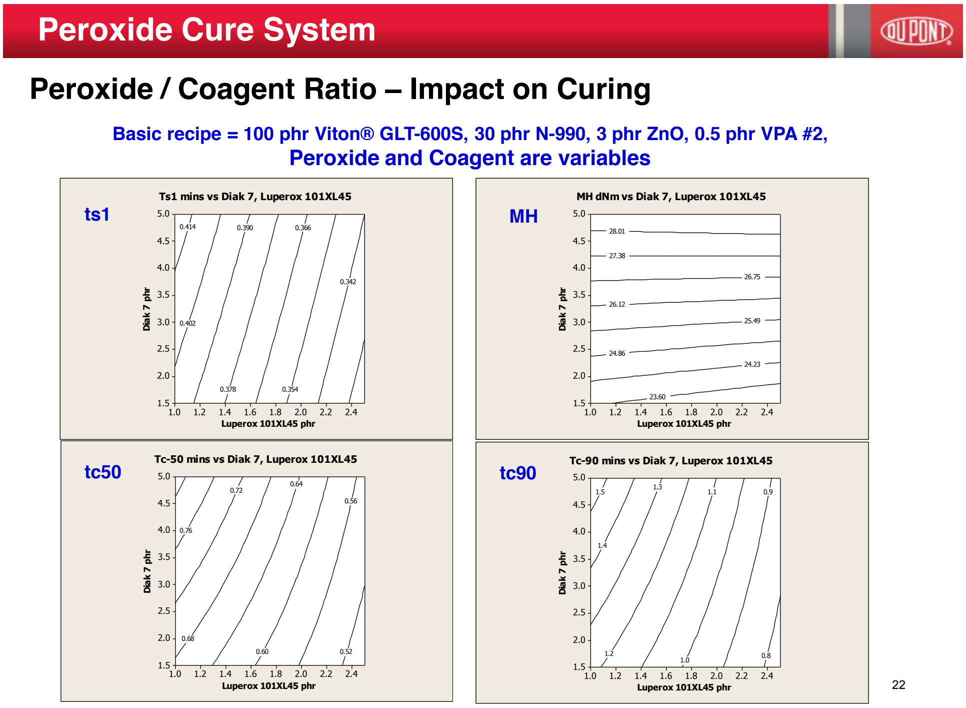
adapted from Matsumoto, *Macromolecules* **2008**, *41*, 7938



Peroxide Cure System – Idealized Mechanism

3. Reaction of the polymer radical with TAIC

4. The coagent provides three potential network points



Peroxide Cure System

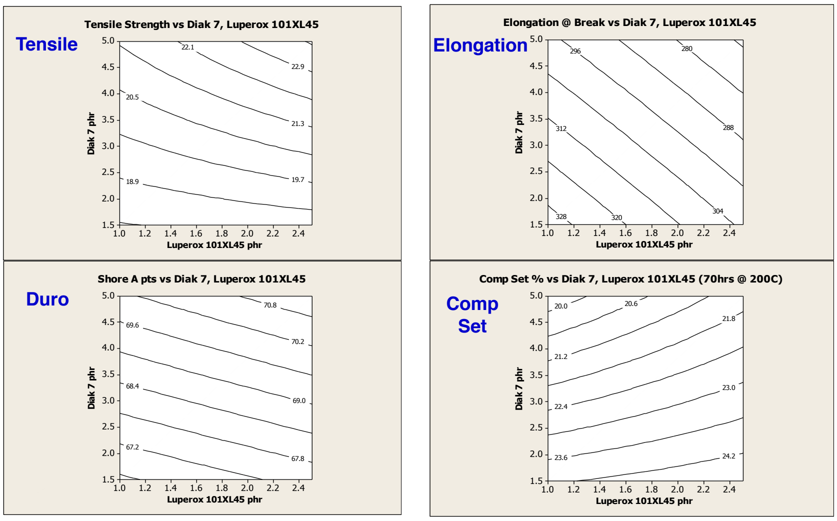
Peroxide / Coagent Ratio – Impact on Curing

Basic recipe = 100 phr Viton® GLT-600S, 30 phr N-990, 3 phr ZnO, 0.5 phr VPA #2, Peroxide and Coagent are variables

Peroxide Cure System

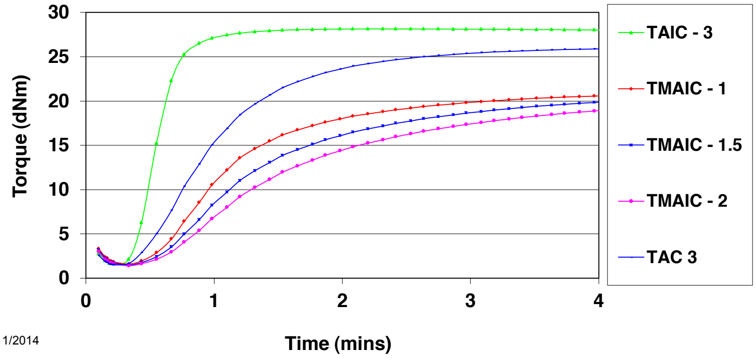
Peroxide / Coagent Ratio – Impact on Properties

Basic recipe = 100 phr Viton® GLT-600S, 30 phr N-990, 3 phr ZnO, 0.5 phr VPA #2, Peroxide and Coagent are variables



Influence of Different Coagents on Cure Speed

- **Coagent** controls the number of cross links - the most common coagents are
  - Triallylisocyanurate (TAIC) – should be used with Viton® APA polymers
  - Trimethallylisocyanurate (TMAIC) – not recommended for Viton® APA polymers
  - Triallylcyanurate (TAC) sometimes used
- **TMAIC and TAC**
  - will give slow and inefficient curing with Viton® APA polymers



Conclusions

- two relevant curing mechanisms – ionic and radical

- **Ionic Mechanism – Bisphenol AF cure**
- for high efficiency, VF_2 units surrounded by HFP units
- BTPPC and BPAF commonly used for ionic cure
- ratio of BPAF and BTPPC influences cure rate, cure state and mechanical properties
- Novel BPAF cure system overcomes deficiencies in dilute acids

- **radical cure**
- requires cure site monomer that contains bromine or iodine
- most common peroxide and coagent are DBPH and TAIC
- cure rate depends mainly on peroxide level
- cure state depends mainly on coagent level
- properties influenced by ratio of peroxide and coagent

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