# Characterisation of Crosslinks in Vulcanised Rubbers: From Simple to Advanced Techniques

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#### Rubber & Elastomer

- <u>Rubbery</u>: 1) Sufficient long chain; 2) Flexible molecules with noncollinear single bonds that allow segmental rotations along the backbone; 3) Non crystalline at service temperature
- <u>Rubber vs Elastomer</u>: Rubber commonly refers to elastic materials that requires vulcanisation before they can be used in the products. However, there are elastic polymers that do not require vulcanisation such as polyurethane (PU), styrene-isoprene (SIS) copolymer. These elastic materials are classified under elastomer, which normally also includes rubbers.
- <u>Unvulcanised Rubbers</u>: Unvulcanised rubbers are normally weak when put under stress during use. With very few exceptions, such as rubber glues almost all rubber products require vulcanisation to provide the required strength for a longer design life.
- <u>Elastomers</u>: Polyurethane (PU), styrene-isoprene (SIS) copolymer, do not require vulcanisation to have good strength properties as they contain the hard segment <u>copyrig</u> which is good for strength and the soft segment good elasticity properties.

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# Rubber Vulcanisation & Crosslink Density

- <u>Vulcanization or vulcanisation</u>: A reaction that leads to the formation of inter-molecular bonding among the unsaturated rubber molecules with 3 dimensional network such that the mechanical properties such as tensile strength is enhanced. The vulcanising agent originally referred to was elemental sulfur. Later, sulfur donor was included. It now also includes non sulfur systems such as metal oxide and peroxides.
- <u>Other terms</u>: Crosslinking, curing, cure, interlinking reactions
- <u>Crosslink density, v</u>: A measure of crosslinked points per unit volume (normally expressed in mol/cm<sup>3</sup>).
- <u>M</u><sub>c</sub>: Average molecular weight of rubber segment between crosslinks (in g/mol).
- <u>Correlation</u>:  $v = 2\rho/(\phi M_c)$  where  $\rho$ = Density of crosslinked <u>rubber (in g/cm<sup>3</sup>)</u>,  $\phi$ = 3, 4 for tri- & tetra-functional network junctions, respectively <sub>3</sub>



# Effects of Crosslink Density on Mechanical Properties

• <u>Effects</u>: Increase in crosslink density of rubber – High is not necessary good

Friction coefficient, permanent set, hysteresis	Decrease with increasing xlink density
Hardness, static & dynamic modulus	Increase with increasing xlink density
Tensile & tear strength, toughness, fatigue life	Increase to a maximum value & then
	decrease

- <u>Unvulcanised rubber</u>: When stretched slowly, rubber molecules extend from coiled form, disentangle and break due to viscous flow without breaking bonds.
- Branched molecule: Higher force is needed to break the rubber with few crosslinks
- <u>Gelled rubber</u>: As crosslinks increase, the rubber molecules eventually become insoluble in solvent and hence the force needed to break the rubber is significantly higher as chemical bonds have to be raptured. However, strength does not increase indefinitely with increasing crosslink density. When under deformation, the input energy is converted into rubber elasticity, and also heat via molecular motion, both of which help to prevent the breaking of rubber chains.

- <u>Highly crosslinked rubber</u>: When heavily crosslinked, the rubber chain mobility becomes highly restricted and the chains are unable to dissipate heat generated by deformation through molecular motion, resulting in easy and brittle rapture at low elongation.
- <u>Optimum level</u>: In practice, crosslink density must be sufficiently high to prevent failure by viscous flow but not too high to avoid brittle fracture <u>Types of Crosslink</u>
- <u>Impact</u>: Affect the chemical and mechanical properties of rubber 1) Covalent a) Polysulfidic; b) Mono- and di-sulfidic & carbon-carbon bonds; 2) Ionic
- <u>Factors</u>: For sulfur crosslinking reactions, the crosslinks depend on 1) sulfur level;
  accelerator type; 3) accelerator /sulfur ratio; and 4) cure time. High accelerator: sulfur ratio, longer cure time increase the mono- and di-sulfidic linkages
- <u>Sulfidic</u>: Mono & disulfidic crosslinks have better solvent and heat resistance, set resistance, reversion resistance but are generally stiffer, hence lower tensile strength, crack resistance. Polysulfidic crosslinks have a better tensile strength,
   <u>Copyrig</u> Softer, Crack resistance but lower set resistance, heat and solvent resistance.

- Continue heating will cause polysulfidic crosslinks to revert to disulfidic, disulfidic to monosulfidic and monosulfidic crosslinks revert back to the gum state.
- <u>Peroxide system</u>: Unlike sulfur vulcanisation, peroxide curing does not require carbon-carbon double bonds to form crosslinks. This system is suitable for both rubbers with or without double bonds. Like monosulfidic linkage, carbon-carbon crosslinks formed by peroxide give the rubber a stiffer feel (high modulus).
- <u>Metal oxide system</u>: Polychloroprene and carboxylated acrylonitrile rubbers can be crosslinked with metal oxides such as zinc oxide and magnesium oxide. The crosslinks in chloroprene rubber by zinc oxide are covalent bonding while the nitrile rubber are ionic bonding.
- <u>Ionic crosslinks</u>: Ionic clusters in carboxylated nitrile rubber improve tensile strength, abrasion, & tear resistance but poor stress retention compared to noncarboxylated nitrile rubber.
- <u>Other properties</u>: lonic crosslinks have a poorer solvent resistance and poorer copyright 2004 by K and A.H. Eng

Effects of Different Crosslinking Systems on Tensile Properties of NR

- High sulfur / accelerator > polysulfidic crosslinks > high tensile strength & tear resistance
- Sulfur donor system > mono-, disulfidic  $\bullet$ crosslinks > moderate tensile strength & tear strength
- Peroxide cure > C-C crosslinks > low tensile ulletstrength & tear resistance
- Radiation cure > C-C crosslinks > lowest tensile strength and tear resistance
- The mechanism of high strength in polysulfidic crosslinks is thought to be the ability to interchange with one another and redistribute local stress.
- Sulfur donor, peroxide and radiation curing systems could produce more intracopyrig molecular, C-C links which do not contribute to the mechanical properties



Crosslink Density, mol/kg Rubber (x100)

Soluble Branched Rubber Molecule – Determination of Branching Huggins' equation:  $\eta_{sp}/c = [\eta] + \kappa'[\eta]^2c$ where c = concentration of rubber solution;  $\eta_{sp}$  = Specific viscosity =  $\eta_r$  – 1  $\eta_r$  = Relative viscosity =  $\eta / \eta_0$ Ubbelohde capillary  $\eta$  = Viscosity of rubber solution in solvent viscometer  $\eta_0$  = Viscosity of pure solvent  $[\eta]$  = Intrinsic viscosity  $\kappa'$  = Huggins' constant In practice,  $\eta_r = t / t_o$  $\eta_{sp} = (t - t_o) / t_o$  $= \eta_r - 1$ where t = Rubber solution flow time in a viscometer and t<sub>o</sub>= Pure solvent flow time in a viscometer

 $\kappa'$  Huggins' constant is a function of the polymer/solvent/temperature of the system, but is independent of molecular weight and molecular weight distribution. It increases with a decrease in solvent power and <u>branching</u>. For a thermodynamically good solvent  $\kappa' \approx 0.3$  For linear polyisoprene,  $\kappa' \approx 0.2$ . Higher  $\kappa' >>$  Higher branched entities

## Intrinsic Viscosity & $\kappa'$ of Fractionated Natural Rubber - Qualitative

Fraction	Intrinsic viscosity [η]	κ′	
1	8.2	0.82	
2	7.5	0.80	
3	5.2	0.75	
4	1.1	0.40	

#### Verification by Osmometry & <sup>13</sup>C-NMR (J. Appl. Polym. Sci. Polym. Symp. 1994, <u>53</u>, 5-14)

Fraction	M <sub>n(O)</sub> by	<sup>13</sup> NMR		M <sub>n(NMR)</sub> by	Branching
	Osmometry x10 <sup>-5</sup>	Trans /chain	Cis / chain	<sup>13</sup> NMR x 10 <sup>-5</sup>	IVI <sub>n(O)</sub> /IVI <sub>n(NMR)</sub> - T
1	10.9	2	2630	1.79	5.1
2	8.7	2	2480	1.69	4.1
3	6.1	2	2010	1.37	3.4
4 Copyright © 2017 by K.I	Mok and A.H. Eng	2	606	0.41	0.8 <sub>9</sub>

**Determination of Crosslink Density – Solvent Swelling Method** 

- Crosslink density of a vulcanised rubber can be measured using the solvent swelling method.
- A good solvent (for the unvulcanised rubber) should be used such that the crosslinked rubber can absorb and swell as much as possible until the retractive forces in the network balance the forces of swelling.
- The rubber test piece is normally allow to swell in the dark at room temperature until it reaches equilibrium.
- The weight of swollen gel is then measured,  $m_3$ , followed by the dry rubber weight  $m_1$  after removing the solvent. Weight of solvent in the swollen rubber  $m_2 = m_3 m_1$
- The volume fraction of the rubber in swollen state, V<sub>r</sub> is as follows:
  - V<sub>r</sub> = Volume of rubber/ [(Volume rubber) + (Volume of solvent)]
    - =  $(m_1/\rho_1) / [(m_1/\rho_1) + (m_2/\rho_2)]$
  - $m_1$  = weight of dry polymer sample;  $\rho_1$  = densities of the dry polymer sample  $m_2$  = weights of solvent in the swollen sample;  $\rho_2$  = density solvent

# Solvent Swelling Method – Vulcanisates with & without Filler

 The Flory-Rehner equation is normally used to calculate the crosslink density of vulcanised rubber without filler, v:

$$\mathbf{v} = \frac{1}{2V_s} \frac{\ln(1 - v_r) + v_r + \chi v_r^2}{v_r^{1/3} - v_r/2}$$

Note: For tetra-functional network

- v = Crosslink density mol per unit volume (mol/cm<sup>3</sup>)
- V<sub>r</sub> = Volume fraction of rubber in equilibrium swollen vulcanised rubber sample
- V<sub>s</sub> = Mole volume of used solvent at room temperature
  - in cm<sup>3</sup>/mol (from molecular weight and density)
- $\chi$  = Flory-Huggins polymer-solvent interaction parameter.
- For vulcanised rubber containing filler, V<sub>r</sub> is obtained from the following equation:

$$\frac{v_r}{v_{rf}} = 1 - \left\{ 3c \left[ 1 - v_r^{1/3} \right] + v_r - 1 \right\} \frac{\phi}{1 - \phi}$$

- $V_{rf}$  = the volume fraction of filled rubber in swollen gel,
- $\phi$  = the volume fraction of filler in the unswollen filled rubber,
- *c* = the filler rubber interaction parameter.
- Repyrigh Failing to consider the filler effect will lead to over estimation of crosslink density.11

<u>Methods of Determining Polysulfidic and Mono/disulfidic Crosslinks</u>

- The sulphur-sulphur bond in polysulfidic crosslinks are more susceptible to nucleophilic attack by thiolate ions
- This selective reaction is achieved by use of a secondary thiolate ion such as propane-2-thiol (0.4 M) for 2 hours at 20°C, leaving mono- and di-sulfidic intact

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• To cleave the di and polysulfidic crosslinks, the sample is exposed to 1 M hexane 1thiol for 48 hours at 25°C.

-<mark>\$</mark> n]<sup>-</sup>

- The total crosslink density from swelling tests performed before and after treatment with the thiolate ions allows the calculation of the mono, di, and polysufidic crosslink densities.
- Tri, tetra and higher sulfides could not be separated by this method because their chemical reactivity is similar.

# Effects of Aging on Polysulfidic Crosslinks of NR



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# Effects of Different Curing Systems on Crosslinks of SBR

polysulfidic crosslinks disulfidic crosslinks C-C and monosulfidic crosslinks



Methods of Determining Ionic Crosslinks in Carboxylated NBR

- The total crosslink density (covalent & ionic) can be determined by equilibrium swelling the sample in acetone (>72 hours, solvent changed twice), based on the Flory-Rehner equation.  $1 \ln(1 - v_r) + v_r + \chi v_r^2$ 
  - $V_r = (m_1/\rho_1) / [(m_1/\rho_1) + (m_2/\rho_2)]$

$$V_{T} = -\frac{1}{2V_{s}} \frac{ln(1-v_{r}) + v_{r} + \chi}{v_{r}^{1/3} - v_{r}/2}$$

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- m<sub>1</sub> = weight of dry polymer sample;  $\rho_1$  = densities of the dry polymer sample m<sub>2</sub> = weights of solvent in the swollen sample;  $\rho_2$  = density solvent The total crosslink density V<sub>T</sub>
- $V_s = 73.4 \text{ cm}^3/\text{mol}$ ; the molar volume of acetone
- $\chi$  = XNBR-acetone interaction parameter, 0.345 from the literature.
- A new sample is allowed to swell in a mixture of acetone and dichloroacetic acid (90:10 in mass) for at least 120 h (solvent changed twice) to remove the ionic crosslinks.
- The solvent is drained and replaced with acetone and swollen for > 72 hours.
- The crosslink density ( $V_c$ ) is the calculated using the same equation from the copy swelling results of the ionic crosslink density  $V_i = V_T - V_c$

# Determination of Crosslink Density: Stress-Strain Method

• The Mooney-Rivlin equation can be used to calculate the crosslink density of vulcanised rubber without filler using the stress-strain data:

F = load in newton;

$$F = 2A_0 (\lambda - \lambda^{-2})(C_1 + C_2/\lambda)$$

$$\frac{F}{2A_{0} (\lambda - \lambda^{-2})} = C_{1} + C_{2} / \lambda$$

$$2C_1 = \rho RT/M_c$$
 (1)

$$A_o$$
 = Initial cross-sectional area  
 $\lambda$  = extension ratio

- $\rho$  = sample density
- R = gas constant
- T = absolute temperature
- $M_c$  = Average molecular weight of rubber segment between crosslinks (g/mol)  $C_1$  = Mooney-Rivlin elastic constant
- A plot of  $F/[2A_0/(\lambda \lambda^{-2})]$  versus  $\lambda^{-1}$  yields  $C_1$  at the intercept, which can be used to calculate  $M_c$  using equation (1) and hence crosslink density can be determined.



**Determination of Crosslink Differential Scanning Calorimetry Method** 

- Crosslinking reduces the segmental mobility of rubber molecules leading to a significant increase in the glass transition temperature
- This effect is dependent on the types of crosslink
   The impact of crosslinks
- The impact of crosslinks formed by peroxide on mobility of T<sub>g</sub> is less compared to those formed by sulfur
- Grafting of peroxide curing agent reduces swelling but has less impact on chain mobility

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**Determination of Crosslink Density: Atomic Force Microscopy Method** 

Deformation in a cone shape with an half angle of 25°.  $F/d_R^2 = (8/\pi)$  G cot (25)

F= Applied force

d<sub>R</sub>= Penetration depth of AFM tip

where

G = 2AnRT

A= Constant (1-1.5)

*n*= Crosslink density

R= Gas constant

**T= Absolute temperature** 

Rubb. Chem Technol. 1996, <u>69</u>, 801-806

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# Determination of Crosslink Density: Intrinsic Viscosity Method

- Degree of prevulcanisation is normally estimated by swelling ratio, chloroform 3.8 number, tensile strength, relax modulus. 3.6
- A recent study reported that there was a correlation between the intrinsic viscosity of prevulcanised latex and swelling ratio of the rubber film.

$$\eta = 2.9345 + (9.1143 \times 10^{11}) \exp(-16.4375S)$$

- S = Swelling ratio
- However, the correlation was rather scattered and more detailed studies are needed to confirm



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# Latex Systems

- Rubber molecules are contained in particles when in latex state.
- Crosslinking reactions within the same latex particles restrict the molecular mobility. This may inhibit the inter-particles integration when the rubber molecules are heavily crosslinked, or the latex particles are heavily surrounded by surfactant, leading to poor mechanical properties, particular for rubbers with high glass transition temperature (T<sub>q</sub>).
- For rubber with low T<sub>g</sub>, such as natural rubber, optimum mechanical properties may be obtained when the rubber molecules are optimally vulcanised in latex, which is commonly known as prevulcanised latex film. For latex films partially vulcanised in latex and optimally vulcanised in dry film, they are known as post-vulcanised latex films.
- Therefore, for latex systems, it is important to differentiate between inter-particle crosslinking and intra-particle crosslinking.
- Solvent swelling method is unable to differentiate the two crosslinking systems.
  Can-be visualised using TEM after being swollen with styrene and polymerised.

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## Latex particles in Polystyrene: Pre-vulcanised and Post-vulcanised NR films



Pre-vulcanised NR Film (1 bar = 1 $\mu$ m) Post-vulcanised NR films (1 bar = 1 $\mu$ m) Copyright © 2017 by K.L. Mok and A.H. **Rubb. Chem. Technol. 1997**, <u>70</u>, 549-559

## Latex Particles in Polystyrene: Nitrile Glove and NR Glove



Electron Micrograph of Polystyrene swollen Nitrile glove (100,000X)



Electron Micrograph of Polystyrene swollen NR glove (100,000X)

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**Unpublished results** 

# Summary

- Crosslink density of vulcanised rubbers can be determined using the simple solvent swelling method.
- When a filler is used in the rubber formulation, appropriate correction must be made so as not to over estimate the crosslink density.
- Further analysis can be performed to quantify covalent crosslink and ionic crosslink, mono-, di- and polysulfidic crosslinks in vulcanised rubbers.
- Latex systems, it is important to distinguish intra-particle crosslinking from interparticle crosslinking
- Excessive intra-particle crosslinking in a latex system may not contribute to the desired mechanical properties of vulcanised rubber.
- There are many other methods of measuring crosslink density of vulcanised rubber such as solvent freezing point depression, NMR signal linewidth, transverse relaxation decay, longitudinal relaxation in rotating frame techniques