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

K.L. Mok¹ and A.H. Eng²*
¹Malaysian Rubber Board, 148 Jalan Ampang, 50450 Kuala Lumpur, Malaysia
²Malaysian Institute of Chemistry (Institut Kimia Malaysia), 127 B, Jalan Aminuddin Baki, Taman Tun Dr Ismail, 60000 Kuala Lumpur, Malaysia
*Corresponding author: (e-mail: engaikhwee@gmail.com)

Crosslink density is a valuable property that affects the functional performance of a vulcanized rubber. It is generally determined by the solvent swelling method. The presence of filler can affect the results of crosslink density determination. While the information on the total crosslink density is useful, when more than one type of crosslinks are present in a vulcanized rubber, further characterization work is necessary to understand the contribution of these crosslinks to the performance properties of the rubber. Therefore, the ionic and covalent crosslinks of carboxylated nitrile butadiene rubber and natural rubber can be quantified individually using solvents of different polarities. By using suitable chemical probes, such as thiolate ion, this technique also allows the separate determination of the mono- di- and polysulphidic crosslinks in vulcanized rubbers. The crosslink density can also be determined using the Mooney-Rivlin equation based on stress-strain data of vulcanized rubbers. By swelling vulcanized rubbers in styrene, polymerizing the styrene, and observing the microtomed rubbers under a transmission electron microscope, crosslinks that formed within a latex particle, or intra-particle crosslinks, and those of inter-particle crosslinks can be visualized and determined semi-quantitatively. This characterization technique is useful for one to understand the extent of inter-particle and intra-particle crosslinking reactions.

Key words: Rubber; types of crosslink; crosslink density; methods of determination; network visualisation

Received: November 2017; Accepted: May 2018

Rubbery materials are normally elastic and stretchable. From the chemistry perspective, these materials need to meet several requirements in order to achieve these properties. Firstly, the molecules must be of sufficient long chain. When the molecular weight of a rubber is too low, it will be in liquid state at room temperature. Liquid natural rubber, for example, normally has an average molecular weight of below 20 000 g/mol [1]. Secondly, rubbers must have molecular structures that allow segmental rotation along their backbone at room temperature. To achieve this, the molecular backbone must have non-collinear single bonds and that it must not be substantially crystalline at service temperature. The term rubber commonly refers to elastic materials that require vulcanisation before they can be used in products [2]. This is because unvulcanised rubbers are normally weak when put under stress during use. Nevertheless, there are very few exceptions where vulcanisation is not required for product application. One of the examples is rubber glue where the rubber needs to be soluble in a solvent. Vulcanised rubber would not be soluble in any solvent. Other than these few exceptions, almost all rubber products require vulcanisation to provide the required strength for a longer designed service life. However, there are elastic polymers that do not require vulcanisation. These include polyurethane, styrene-isoprene-styrene block copolymer, styrene ethylene/butylene-styrene copolymer. These elastic materials are classified under elastomer which normally also includes rubbers.

Rubber Vulcanisation

Rubber vulcanisation is a crosslinking reaction that leads to the formation of inter-molecular bonding among the unsaturated rubber molecules with three dimensional network such that the mechanical properties such as force at break, tensile strength and tear strength are enhanced [2]. Initially, the vulcanising agent referred to elemental sulphur. However, it now also includes sulphur donors, non-sulphur crosslinking systems such as metal oxide and peroxides. One of the important parameters to monitor in rubber vulcanisation is crosslink density [2]. When an unvulcanised rubber sample is slowly stretched, the rubber molecules extend from coiled state, disentangle and break at low stress due to viscous flow without breaking bonds. For rubber molecules with branched entities or low crosslink density where the rubber is still soluble in solvent, a higher stress is required to break the rubbers when stretched. As the crosslink density increases, the rubber molecules eventually become insoluble in solvent and hence the stress needed to break the rubbers is significantly higher. This is because chemical bonds have to be ruptured to break the rubbers when stretched. When vulcanised rubbers are stretched, the input energy is converted into rubber elasticity and heat via molecular motion, both of which help to prevent the breaking of the rubber molecules. However, when the crosslink density is too high, the rubber chain mobility becomes highly restricted and the chains are unable to dissipate the heat generated by deformation through molecular motion, resulting in rupture of the rubbers at low elongation. This means that the stress required to break the rubbers does not increase indefinitely with increasing crosslink density. In practice, crosslink density of vulcanised rubbers must be sufficiently high to prevent failure by viscous flow but not too high to avoid brittle fracture. Table 1 shows the effects of increasing crosslink density on some of the mechanical properties of rubbers.

Crosslink density, \( v \) is normally expressed as the number of crosslinks in mol per unit volume in cm\(^3\). Therefore, the unit is mol/cm\(^3\). The relationship between crosslink density and average molecular weight of rubber segment between crosslinks, \( M_c \), is as shown in Equation 1 below:

\[
v = 2\rho / (\phi M_c)
\]

where, \( \rho \) = Density of crosslinked rubber (in g/cm\(^3\)), \( \phi \) = Functionality of the crosslink point.

The functionality of crosslink point \( \phi \), is 3 for tri-functional (T-shape) and 4 for tetra-functional (+ shape) networks. Generally, there are two types of crosslinks, covalent and ionic crosslinks which are formed by covalent bonding and by electrostatic attraction of opposite charges, respectively.

Sulphur Crosslinking System

When sulphur is used as a crosslinking agent, the presence of carbon-carbon double bonds is necessary and the covalent crosslinks that formed can be polysulphidic chain or mono- and di-sulphidic chains. The types of sulphidic crosslink depend on (1) sulphur level; (2) accelerator type; (3) accelerator /sulphur ratio; and (4) cure time. High accelerator to sulphur ratio, longer cure time both increase the concentration of mono- and di–sulphidic linkages. Mono- and di- sulphidic crosslinks have better solvent and heat resistance, set resistance, reversion resistance but are generally stiffer, hence have a lower tensile strength and crack resistance. Polysulphidic crosslinks have better tensile strength, softer, crack resistance but lower set resistance, heat and solvent resistance. Due to heat sensitivity, continuous heating of polysulphidic

<table>
<thead>
<tr>
<th>Properties</th>
<th>Changes with crosslink density</th>
</tr>
</thead>
<tbody>
<tr>
<td>Friction coefficient, permanent set, hysteresis</td>
<td>Decrease with increasing crosslink density</td>
</tr>
<tr>
<td>Hardness, static and dynamic modulus</td>
<td>Increase with increasing crosslink density</td>
</tr>
<tr>
<td>Tensile and tear strength, toughness, fatigue life</td>
<td>Increase to a maximum value and then decrease</td>
</tr>
</tbody>
</table>

Table 1. Effects of increasing crosslink density on the properties of rubber good.
crosslinks will cause them to revert to disulphidic, disulphidic to mono-sulphidic and monosulphidic crosslinks revert back to the gum state and eventually degradation of the rubber.

**Peroxide Curing System**

Unlike sulphur 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 monosulphidic linkage, carbon-carbon crosslinks formed by peroxide give the rubber a stiffer feel, i.e. high modulus.

**Metal Oxide System**

Polychloroprene and carboxylated nitrile 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 those in the nitrile rubber are ionic bonding.

**Ionic Crosslinking System**

Ionic crosslinks in carboxylated nitrile rubber in the form of clusters, improve tensile strength, abrasion, and tear resistance but poor stress retention compared to non-carboxylated nitrile rubber. Ionic crosslinks also have a poorer solvent resistance and poorer durability compared to the covalent crosslinks.

**Effects of Crosslinking System on Tensile Properties**

The use of high sulphur to accelerator ratio with appropriate curing conditions will lead to the formation of high polysulphidic crosslinks and hence giving high tensile strength and tear resistance properties to the rubber. When sulphur donor system is employed, the crosslinks that formed are mainly mono-, disulphidic, giving the rubber moderate tensile strength and tear resistance properties. In the case of rubber cured with peroxide system, it contains carbon-carbon crosslinks, which give low tensile strength and tear resistance properties. Rubber crosslinked with radiation also contains carbon-carbon crosslinks and the rubber has the lowest tensile strength and tear resistance properties among the four curing systems. The mechanism of high strength in polysulphidic crosslinks is thought to be the ability of polysulphidic chains to interchange with one another and redistribute local stress. In the case of sulphur donor, peroxide and radiation curing systems, more intra-molecular carbon-carbon links are normally formed which do not contribute to the mechanical properties such as tensile strength.

**Determination of Branching in Soluble Branched Rubber Molecules**

Most linear rubber molecules are soluble in certain solvents, depending on the polarity of rubber and solvents. However, not all soluble rubber molecules are linear in their structures. For lightly crosslinked or branched rubber molecules, they can remain soluble until they reach a point where they become insoluble. The Huggins constant $\kappa'$, has been known to be a fairly sensitive indicator of branching in rubber chains. The Huggins constant of rubber can be determined by measuring the viscosity of the rubber solution using an Ubbelohde viscometer (Figure 1) as shown in the Huggins equation in Equation 2 [3].

\[
\eta_{sp}/c = [\eta] + \kappa'[\eta]^2c
\]

where, $c =$ concentration of rubber solution;
$\eta_p =$ Specific viscosity = $\eta - 1$
$\eta_r =$ Relative viscosity = $\eta / \eta_0$
$\eta =$ Viscosity of rubber solution in solvent
$\eta_0 =$ Viscosity of pure solvent
$[\eta] =$ Intrinsic viscosity
$\kappa' =$ Huggins constant

In practice, the relative viscosity $\eta_r$, is obtained from the ratio $t / t_o$, i.e. $\eta / \eta_0 = t / t_o$, where $t$ is the rubber solution flow time in a viscometer and to is the pure solvent flow time in a viscometer. By plotting $\eta_{sp}/c$ versus $c$, the intrinsic viscosity $[\eta]$, can be obtained from the intercept while the $\kappa'$ is calculated from the gradient which is $\kappa'[\eta][3]$.

The Huggins constant is a function of the rubber, solvent and temperature of the system. It is independent of molecular weight and molecular weight distribution. However, it increases with decreasing solvent power but increasing branching density [4, 5]. For a thermodynamically good solvent, such as linear styrene butadiene copolymer in benzene, $\kappa' \approx 0.3$. For linear polyisoprene molecules, $\kappa' \approx 0.2$. Higher $\kappa'$ values imply the existence of branching entities. Table 2 shows the intrinsic viscosity values of fractionated natural rubbers and the corresponding Huggins constants, indicating that the higher molecular weight rubbers contain higher branching entities [6].
Branching in natural rubber molecules is expected to form after the termination reaction of rubber biosynthesis. By analysing the initiating terminal, which is known to contain 2 trans-isoprene unit [7], and the cis: trans isoprenes ratio using the $^{13}$C-NMR technique, it is possible to calculate number average molecular weight before branching. On the other hand, the number average molecular weight after branching can be determined using the membrane osmometry technique. The ratio of these two values will allow one to calculate the average branching per molecule for each fractionated rubber. The results shown in Table 3 confirm that the branching of natural rubber increases with increasing molecular weight [6].

**Figure 1.** A typical Ubbelohde viscometer for measuring intrinsic viscosity.

**Table 2.** Intrinsic viscosity & $\kappa'$ of fractionated natural rubber.

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Intrinsic viscosity [$\eta$]</th>
<th>Huggins Constant $\kappa'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8.2</td>
<td>0.82</td>
</tr>
<tr>
<td>2</td>
<td>7.5</td>
<td>0.80</td>
</tr>
<tr>
<td>3</td>
<td>5.2</td>
<td>0.75</td>
</tr>
<tr>
<td>4</td>
<td>1.1</td>
<td>0.40</td>
</tr>
</tbody>
</table>

**Table 3.** Verification branching by osmometry and $^{13}$C-NMR techniques.

<table>
<thead>
<tr>
<th>Fraction</th>
<th>$M_{\alpha O}$ by Osmometry, $\times 10^5$</th>
<th>$^{13}$NMR</th>
<th>$M_{\alpha NMR}$ by $^{13}$NMR, $\times 10^{-5}$</th>
<th>Branching $M_{\alpha O}/M_{\alpha NMR}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10.9 / chain</td>
<td>2630</td>
<td>1.79 / chain</td>
<td>5.1</td>
</tr>
<tr>
<td>2</td>
<td>8.7 / chain</td>
<td>2480</td>
<td>1.69 / chain</td>
<td>4.1</td>
</tr>
<tr>
<td>3</td>
<td>6.1 / chain</td>
<td>2010</td>
<td>1.37 / chain</td>
<td>3.4</td>
</tr>
<tr>
<td>4</td>
<td>0.7 / chain</td>
<td>606</td>
<td>0.41 / chain</td>
<td>0.8</td>
</tr>
</tbody>
</table>
Determination of Crosslink Density of Vulcanised Rubber by Solvent Swelling Method

Solvent swelling method is one of the most commonly used techniques in measuring the crosslink density of a vulcanised rubber. The method is simple and does not require any expensive instrument. A good solvent for the unvulcanised rubber is used such that the crosslinked rubber can absorb the solvent and swell as much as possible until the retractive forces in the network balance the forces of swelling. The rubber test piece is normally allowed to swell in the dark at room temperature until it reaches equilibrium. It normally takes about 3–7 days to complete the swelling process. The weight of swollen gel $m_2$ is then measured 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, $V_r$, is defined as follows:

$$V_r = \frac{\text{Volume of rubber}}{[(\text{Volume rubber}) + (\text{Volume of solvent})]}$$

$$= \frac{m_1}{\rho_1} / [(m_1/\rho_1) + (m_2/\rho_2)]$$

$m_1$ = 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

For a vulcanised rubber without filler [8], the crosslink density $\nu$, is shown in Equation 3.

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

where,

$v_r$ = Crosslink density mol per unit volume (mol/cm$^3$)

$V_r$ = Volume fraction of rubber in equilibrium swollen vulcanised rubber sample

$V_s$ = Mole volume of used solvent at room temperature in cm$^3$/mol (from molecular weight and density)

$\chi$ = Flory-Huggins polymer-solvent interaction parameter

$\phi$ = Functionality of the crosslink point, normally assumed to be tetra-functional where $\phi = 4$.

If the vulcanised rubber contains a significant amount of filler, a correction must be made because unlike rubber, filler normally does not swell significantly in the organic solvent of rubber. In this case, the volume fraction of rubber in the swollen gel is given by Equation 4. The crosslink density is then calculated from Equation 3. Failing to make this correction for the filler in rubber will lead to over estimation of crosslink density because of lower swelling ratio [9–12].

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

where,

$v_{rf}$ = Volume fraction of filled rubber in swollen gel,

$\phi$ = Volume fraction of filler in the unswollen filled rubber

$c$ = Filler rubber interaction parameter.

Methods of Determining polysulphidic and Mono/disulphidic Crosslinks

As explained earlier, sulphur crosslinking system is expected to generate polysulphidic, mono- and disulphidic crosslinks in the vulcanised rubber, depending on the several factors. Therefore, when the proportion of polysulphidic crosslink is higher, the mono- and disulphidic crosslinks will be low. Carbon-carbon crosslinks generated by radical reactions such as those initiated by peroxide and radiation have the same characteristics as those of mono- and disulphidic crosslinks. The proportion of mono-sulphidic or carbon-carbon crosslinks in the decreasing order of the curing systems below [13]. Dicumyl peroxide (DCP) > Tetrabenzylthiuram disulphide (TBzTD) > Tetramethylthiuram disulphide (TMTD) > Sulphur > 2-ethylhexyl zinc dithio-phosphate (ZDT) + sulphur > 1,6-bis(N,N'-dibenzylthiocarbamoyl-dithio)-hexane.
+ sulphur > 2,2’-dibenzothiazyl disulphide (MBTS) + sulphur > N-cyclohexyl-1-benzothiazyl sulphenamide (CBS) + sulphur > 1,3-diphenylguanidine (DPG) + sulphur.

It is essential to quantify the proportion of different sulphidic crosslinks because it influences the mechanical and chemical resistance properties of the vulcanised rubber. The sulphur-sulphur bond in polysulphidic crosslinks is more susceptible to nucleophilic attack by thiolate ions. Therefore, polysulphidic crosslinks can be selectively cleaved by use of a secondary thiolate ion such as 0.4M propane-2-thiol, leaving mono- and di-sulphidic crosslinks intact. The reaction conditions are 20°C for 2 h. Furthermore, di-sulphidic and polysulphidic crosslinks can be broken by treating the vulcanised rubber with 1 M hexane 1-thiol for 48 h at 25°C. Together with the results on the total crosslink density determination from the usual swelling test, calculated as per Equation 3 before the treatments with the thiolate ions, it allows the mono, di- and polysulphidic crosslink densities to be calculated [14]. These techniques could not be separated by tri, tetra and higher sulphides because their chemical reactivity is similar to that of polysulphidic crosslink.

Methods of Determining Ionic Crosslinks in Carboxylated NBR

When sulphur and zinc oxide are used in the vulcanisation of carboxylated nitrile rubber, both the covalent and ionic crosslinks will be formed. Both types of crosslink provide different properties to the vulcanised nitrile rubber as described earlier. Therefore, it is also important to determine the density of covalent and ionic crosslinks. The total crosslink density, both covalent and ionic, can be determined by equilibrium swelling the sample in acetone at room temperature for at least 72 h. The total crosslink density \( V_T \), is then calculated using the Flory-Rehner equation shown in Equation 3. The molar volume of acetone \( V_{\text{Ac}} \) is 73.4 cm\(^3\)/mol and the XNBR-acetone interaction parameter is 0.345. In a separate experiment, a new vulcanised sample is allowed to swell in a mixture of acetone and dichloroacetic acid (90:10 in mass) for at least 120 h. The presence of acid will cause the dissociation of ionic crosslinks, leaving the covalent crosslinks intact. The solvent is then drained and replaced with acetone and swollen for at least 72 h. The density of covalent crosslinks, \( V_c \), is then calculated using Equation 3. The ionic crosslink density \( V_i \), is then given by the result of subtracting \( V_c \) from \( V_T \) [15].

\[
\frac{F}{2A_o (\lambda - \lambda^{-2})} = C_1 + C_2 / \lambda \quad (5)
\]

\[
2C_i = \rho RT / M_c \quad (6)
\]

where, \( F \) = load in newton,
\( A_o \) = 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)
\( C_i \) = Mooney-Rivlin elastic constant.

The linearity plot is affected by the uncertainty in the initial length value when the \( \lambda^{-1} \) value is higher.
than 0.95. The $C_1$ constant is normally derived from measurements in the range $0.95 > \lambda^{-1} > 0.5$. To ensure the equilibrium is achieved, the stress-strain measurements must be carried out at a low strain rate. For automated testing, the $C_1$ value obtained is not strongly dependent on extension rate up 30 mm/min for a 100 mm test length [16].

**Determination of Crosslink Differential Scanning Calorimetry Method**

Glass transition temperature of a rubber is a measure of segmental mobility of the molecules. Crosslinking reduces the segmental mobility of rubber molecules leading to a significant increase in the glass transition temperature. However, this effect is also dependent on the types of crosslink. The impact of crosslinks formed by peroxide on mobility of $T_g$ is less compared to those formed by sulfur as shown in Figure 2. This is probably because grafting of peroxide curing agent reduces swelling but fewer effective crosslinks are formed and therefore has less impact on chain mobility [17].

**Determination of Crosslink Density by Atomic Force Microscopy (AFM) Method**

In this method, the AFM tip is pushed against the rubber sample similar to that of a standard hardness test. The distance of the AFM tip penetration is then measured and the force per unit square of the distance is then calculated. A plot of experimental value of the force per unit square of penetration distance versus crosslink density is comparable to a theoretical calculation on the half angle of conical probe tip as shown in Figure 3 [18]. With this plot, the crosslink density of a sample can be determined based on the force per unit square of penetration distance of AFM tip.

**Determination of Crosslink Density of Natural Rubber Latex by Intrinsic Viscosity Method**

Very recently, it has been reported that pre-vulcanisation of natural rubber latex, i.e. vulcanisation in latex state, led to a significant increase in the intrinsic viscosity of the latex. By measuring the crosslink density of the rubber isolated from the latex at various stages of pre-vulcanisation using the solvent swelling method, a correlation between the intrinsic viscosity and the swelling ratio was found as shown in Figure 4. The relationship between the two parameters is given in Equation 7 below [19].

$$\eta = 2.9345 + (9.1143 \times 10^{11}) \exp(-16.4375S) \quad (7)$$

where, $S$ = Swelling ratio

If the method is proven to be viable, it will allow one to determine the crosslink density of a rubber in latex state directly without the need to isolate the rubber out from the latex. However, as shown in Figure 4, the data are rather scattered and more work is needed to confirm this method.

**Latex System**

Rubber molecules in latex are contained in discrete particles. There is no inter-particle interaction among the rubber molecules. As such, any crosslinking reactions in latex state are confined to intra-particle rubber molecules. When the crosslinking reactions within the same particles are significantly high, the mobility of the rubber molecules becomes highly restricted. The inter-particle integration during latex drying may also be inhibited when the latex particles are heavily surrounded by surfactant. Both scenarios are expected to lead to poor mechanical properties, particular for rubbers with relatively high glass transition temperatures ($T_g$). For rubber with low $T_g$, such as natural rubber, optimum mechanical properties may be obtained when the rubber molecules are optimally vulcanised in latex state, which is commonly known as pre-vulcanised 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. The solvent swelling method is unable to differentiate the two crosslinking systems. They can be distinguished or visualised using the transmission electron microscopy technique (TEM) after being swollen with styrene, polymerised, and stained with Osmium Tetroxide (OsO₄). Figure 5 shows the TEM micrographs of microtomed...
nitrile glove and natural rubber glove. The black area indicates the staining effects of OsO₄ on rubber molecules, while the white area indicates the polymerised polystyrene. In these micrographs, the nitrile glove shows more inter-particle crosslinking than the natural rubber glove.

**Figure 2.** Glass transition temperatures of vulcanised rubber with different crosslink densities.

**Figure 3.** Force per unit square of penetration distance of AFM tip.
Figure 4. Relationship between intrinsic viscosity and swelling ratio of natural rubber pre-vulcanised at 40°C and 60°C.

Figure 5. Electron micrograph of polystyrene swollen (a) Nitrile glove (100 000×), (b) NR glove.

CONCLUSION
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 as the filler does not swell much in the rubber solvent. Further analysis can be performed to quantify covalent crosslink and ionic crosslink, mono-, di- and polysulphidic crosslinks in vulcanised rubbers. For latex systems, it is essential to distinguish intra-particle crosslinking from inter-particle crosslinking. Excessive intra-particle crosslinking in a latex system may not contribute to the desired mechanical properties of vulcanised rubber.
REFERENCES


