

**Search And Compiled By Z. Tarabali**

# **Rubber Curing Systems**

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## 1 Introduction

Crosslinking or curing, i.e., forming covalent, hydrogen or other bonds between polymer molecules, is a technique used very widely to alter polymer properties. The first commercial method of crosslinking has been attributed to Charles Goodyear (a.1) in 1839. His process, heating rubber with sulfur, was first successfully used in Springfield, Massachusetts, in 1841. Thomas Hancock used essentially the same process about a year later in England. Heating natural rubber with sulfur resulted in improved physical properties. However, the vulcanisation time was still too long (>5 h) and the vulcanisates suffered from disadvantages, e.g., ageing properties.

Since these early days, the process and the resulting vulcanised articles have been greatly improved. In addition to natural rubber, many synthetic rubbers have been introduced over the years. Furthermore, many substances other than sulfur have been introduced as components of curing (vulcanisation) systems.

The accelerated sulfur vulcanisation of general purpose diene rubbers (e.g., natural rubber (NR), Styrene butadiene rubber (SBR), and butadiene rubber (BR)) in the presence of organic accelerators and other rubbers, which are vulcanised by closely related technology (e.g., ethylene-propylene-diene terpolymer (EPDM) rubber, butyl rubber (IIR), halobutyl rubber (XIIR), nitrile rubber (NBR)) comprises more than 90% of all vulcanisations.

### 1.1 Conventional Vulcanisation, Semi-Efficient Vulcanisation and Efficient Vulcanisation

Over the years three special types of cure systems have been developed. They are:

- efficient vulcanisation (EV) systems,
- semi-efficient vulcanisation (SEV) systems and
- conventional vulcanisation (CV) systems.

EV systems are those where a low level of sulfur and a correspondingly high level of accelerator or sulfurless curing are employed in vulcanisates for which an extremely high heat and reversion resistance is required. In the conventional curing systems, the sulfur dosage is high and correspondingly the

accelerator level is low. The CV systems provide better flex and dynamic properties but worse thermal and reversion resistance. For optimum levels of mechanical and dynamic properties of vulcanisates with intermediate heat, reversion, flex and dynamic properties, the so-called SEV systems with an intermediate level of accelerator and sulfur are employed. The levels of accelerator and sulfur in CV, SEV and EV systems are shown in **Table 1**.

**Table 1 CV, SEV and EV vulcanisation systems**

Type	Sulfur (S, phr)	Accelerator (A, phr)	A/S ratio
CV	2.0-3.5	1.2-0.4	0.1-0.6
SEV	1.0-1.7	2.4-1.2	0.7-2.5
EV	0.4-0.8	5.0-2.0	2.5-12

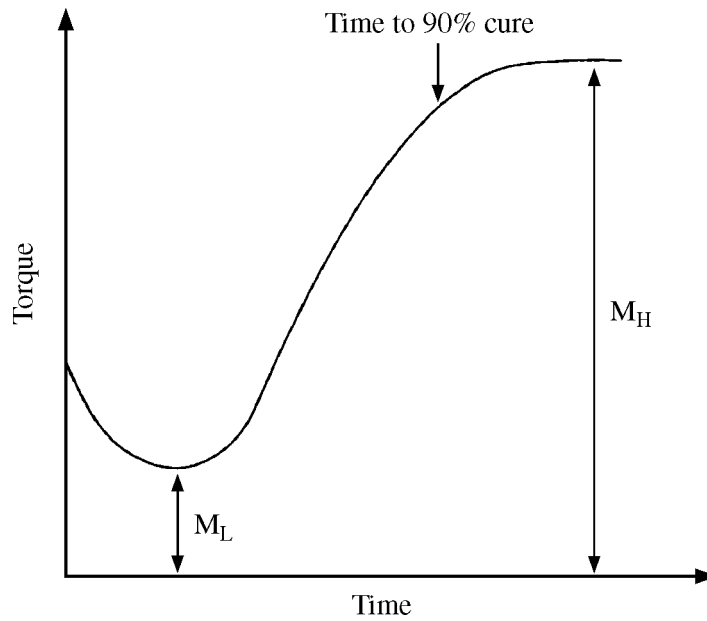
Many studies have documented both the advantages (increased age resistance), and the disadvantages (impaired fatigue resistance) of EV and SEV systems. The worse fatigue resistance correlates to lower amounts of polysulfidic crosslinks in the network. The CV systems provide higher amounts of poly- and disulfidic crosslinks and higher proportions of sulfidic and non-sulfidic modifications. This combination provides high flex fatigue resistance but at the expense of heat and reversion resistance. The vulcanisate structures and properties for CV, SEV and EV systems are shown in **Table 2**.

It is evident that there are trade-offs in the use of efficient vulcanisation systems. Besides the technical trade-off of improved ageing but inferior fatigue resistance, there are cost considerations – a 10% increase might be expected.

### 1.2 Measuring Cure

The vulcanisation characteristics of a rubber are usually followed using a rheometer. In one version of such a device the sample of rubber is enclosed within a heated chamber. Vulcanisation is measured by the increase in the torque required to maintain a given amplitude of oscillation at a given temperature. The torque is proportional to low strain modulus of elasticity. The torque is plotted against time to give a so-called rheometer chart, rheograph or cure curve. A typical cure curve is shown in **Figure 1**.

Table 2 Vulcanisate structures and properties			
Features	Systems		
	CV	SEV	EV
Poly- and disulfidic crosslinks (%)	95	50	20
Monosulfidic crosslinks (%)	5	50	80
Cyclic sulfide (conc.)	High	Medium	Low
Non-sulfidic (conc.)	High	Medium	Low
Reversion resistance	Low	Medium	High
Heat ageing resistance	Low	Medium	High
Fatigue resistance	High	Medium	Low
Heat build up	High	Medium	Low
Tear resistance	High	Medium	Low
Compression set (%)	High	Medium	Low



**Figure 1**

A typical cure curve

The curve exhibits a number of features which are used to compare cure:

- Maximum torque,  $M_H$
- $ts_2$ ,  $T_2$  or  $T_5$ : There is a delay or induction time before the torque or resistance value begins to rise. Because the onset of this rise is difficult to determine precisely, it is normal to note the point

at which the torque rises to a prescribed level above minimum. Suitably chosen, this provides a measure of the scorch time at the curing temperature.

$ts_2$  or  $T_2$ : The time to reach a 2 unit increase in torque above minimum. This is another way to express scorch safety.  $ts_2$  is defined as the time to achieve 2% cure above minimum.

T5: The scorch time at lower temperature is of importance too. This can be obtained by using a Mooney Viscometer at lower temperature. A Mooney Viscometer is also used to measure the viscosity of the compounds (important for dictating injection-moulding behaviour). The viscometer is also used to assess the tendency to scorch, and sometimes the rate of cure of a compound. A useful estimate of scorch behaviour is represented by T5, the time taken from the beginning of the warm-up period to that at which the Mooney value rises five units above the minimum value.

- T90: The most useful information obtained from the rheometer curve is T90, which is defined as the time to achieve 90% cure. Mathematically, T90 is the time for the torque to increase to:

$$90/100(M_H - M_L) + M_L$$

- Cure rate: A rise in the value of torque with time, the slope of the curve, gives the measure of cure rate. Sometimes cure rates of various cure systems are compared with T90–ts2 data.

### 1.3 Test Equipment and Conditions

Later in this review many results are presented from tests on different cure systems carried out by the author. Conditions and equipment used are now briefly described. Cure characteristics were determined using an MDR 2000EA rheometer. Test specimens were vulcanised by compression molding in a Fontyne TP-400 press at temperatures and times indicated.

Stress-strain properties were determined according to ISO 37, tear strength according to ISO 34/1, DIN abrasion ISO 4649, fatigue to failure ASTM 4482/85 and hardness according to ISO 48. Ageing of the test specimens was carried out in a ventilated air oven at 100 °C for 3 days (ISO 188). Heat build up and permanent set after dynamic loading were determined using a Goodrich Flexometer (Load 11 kg or 22 kg; stroke 0.445 cm, frequency 30 Hz, start temperature 100 °C) according to ISO 4666/3-1982. Dynamic mechanical analysis was carried out using a RDA-700 (prestrain 0.75%, frequency 15 Hz and temperature 60 °C) according to ASTM D 2231.

Vulcanisate network structure was determined by equilibrium swelling in toluene using the method reported by Ellis and Welding. The volume fraction ( $V_r$ ) obtained was converted into the Mooney-Rivlin

elastic constant ( $C_1$ ) and finally into the concentration of chemical crosslinks. The proportions of mono-, di-, and polysulfidic crosslinks in the vulcanisates were determined using thiol amine chemical probes. Following the cleavage of the poly- and disulfidic crosslinks, the samples were treated with methyl iodide to distinguish carbon-carbon based crosslinks from monosulfidic crosslinks.

The brass coated steelcord used in adhesion tests was of a 3+9x 0.22+1 construction with a Cu content of 63%. The rubber to metal adhesion characteristics were determined according to ASTM 2229-85. The wire adhesion data quoted are averages of 10 individual tests. Wire adhesion samples were aged under the following conditions:

- Heat aged - 3 days at 105 °C in the presence of air
- Steam aged - 2 days at 121 °C
- Salt aged - 7 days at 25 °C in a 10% solution of NaCl.

## 2 Curing Systems

Curing systems can be classified into four categories. Guidelines, and examples of selecting different curing systems for crosslinking are reviewed in this section.

### 2.1 Sulfur Curing Systems

Initially, vulcanisation was accomplished by heating elemental sulfur at a concentration of 8 parts per hundred parts of rubber (phr) for 5 h at 140 °C. The addition of zinc oxide reduced the time to 3 h. Accelerators in concentrations as low as 0.5 phr have since reduced times to 1-3 min. As a result, elastomer vulcanisation by sulfur without accelerator is no longer of commercial significance. An exception is the use of about 30 or more phr of sulfur, with little or no accelerator, to produce moulded products of a hard rubber called ebonite.

#### 2.1.1 Accelerators

Organic chemical accelerators were not used until 1906, 65 years after the Goodyear-Hancock development of unaccelerated vulcanisation, when the effect of aniline on sulfur vulcanisation was discovered by Oenslayer (405, a.2).