

# Effect of the Network Topology on the Tensile Strength of Natural Rubber Vulcanizate at Elevated Temperature

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Received 12 November 2004; accepted 20 January 2005

DOI 10.1002/app.22225

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** The influence of network topology on tensile strength at elevated temperature of natural rubber compounds vulcanized with different systems was studied. The tensile strength behavior of natural rubber at high strain is attributed to the capacity to crystallize on stretching. Variation of this property with the temperature and/or crosslink density was related, not only with the nature of the crosslinks, but also with their spatial distribution. In this

sense, measurements of the freezing point depression of cyclohexane imbibed in the rubber matrix were used to evaluate the spatial distribution of the crosslinks. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 1219–1223, 2005

**Key words:** crosslinking; elastomers; mechanical properties; networks; vulcanization

## INTRODUCTION

The strength of an elastomer vulcanizate is determined mainly by its molecular structure, crosslink density, and filler type and loading. Natural rubber (NR) shows a unique place in rubber technology due to its high tensile strength and tear growth resistance. These features are attributed to its capacity to rapidly crystallize on stretching.

The influence of elevated temperature on the tensile strength of rubbers has been studied by many researchers.<sup>1–5</sup> Early work of Thomas and Whittle<sup>2</sup> shows the loss of tensile strength of NR vulcanizates when the temperature is raised, a response attributed to the inability of the sample to undergo strain induced crystallization, which occurs at high strain.

In the present article our attention is mainly directed to studying the influence of different vulcanization systems on the tensile strength at high temperature of NR compounds. The study was centered on the strength properties of accelerated sulfur, and sulfurless and peroxide cured NR gum stocks.

On the other hand, it has been shown that the freezing point of swelling solvents imbibed in gels such as rubber vulcanizates is greatly depressed. This freezing point depression is significantly bigger than can be accounted for on the basis of colligative properties measurements. This anomalous freezing point depression has been widely described by various au-

thors.<sup>6–10</sup> McGill and coworkers<sup>7,8</sup> proposed a method based on the freezing point of a swelling solvent in the rubber gel, to study heterogeneity in the distribution of the crosslinks in the rubber network. The authors concluded that a linear relationship is expected for a uniformly crosslinked rubber, and deviations from linearity should be indicative of a non uniform network. In this way, the spatial distribution of crosslinks in the network could be studied.

Using this approach, within this work, we relate the capacity to crystallize on stretching of the compounds, not only with the nature of the crosslinks, but also with the homogeneity or heterogeneity grade of the network.

## EXPERIMENTAL

### Materials

All compounds are based on standardized natural rubber (NR, SIR3CV60), provided by Indonesia Rubber. Tables I, II, and III give details of the prepared compounds. Dicumyl peroxide (DCP) was supplied by Merck and recrystallized twice from methanol. Dipentamethylene thiuram tetrasulfide (DPTT) and *N*-cyclohexyl benzothiazil sulfenamide (CBS) were supplied by Flexsys and used without further purification.

### Blending and curing

The rubber compounds were prepared in an open two-roll mill (friction ratio 1 : 1.4) using conventional mixing procedures. The specimens were cured in a laboratory press at their respective optimum times ( $t_{97}$

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**TABLE I**  
Composition and Cure Characteristics of Accelerated Sulphur Cured

Natural rubber (NR)	100	100	100	100	100	100	100
Zinc oxide	5	5	5	5	5	5	5
Stearic acid	1	1	1	1	1	1	1
CBS	1.11	1.33	1.55	1.77	2.00	2.22	2.44
Sulphur	1.11	1.33	1.55	1.77	2.00	2.22	2.44
<i>Properties of curing compounds at 150°C</i>							
$\Delta T$ , dNm	5.6	6.5	7.5	8.1	9.1	9.7	10.4
$t_{97}$ , min	18.9	18.2	17.5	16.1	15.9	15.2	14.6
Crosslink density, $\nu \cdot 10^5$ mol/cm <sup>3</sup>	6.62	7.70	9.67	10.8	12.45	13.80	16.72

$\Delta T$  = maximum torque minus minimum torque.

of the rheometer) at different temperatures. Cure measurements were conducted using a Monsanto Moving Die Rheometer, model MDR 2000E, produced by Alpha Technologies.

### Determination of crosslink density

Equilibrium swelling in toluene was used to determine the crosslink density of the different compounds. Test samples were placed in reagent grade toluene and allowed to reach equilibrium swelling at 30°C (~3 days). The samples were blotted with tissue paper and immediately weighed on an analytical balance to the nearest  $10^{-4}$  g, then dried in a vacuum oven for 24 h at 60°C to completely remove the solvent, and reweighed. The  $v_r$  value (volume fraction of polymer in the swollen sample) was calculated by use of eq. (1):

$$v_r = \frac{1}{1 + \frac{\rho_r}{\rho_s} \left( \frac{W_s - W_D}{W_D} \right)} \quad (1)$$

where  $\rho_s$  and  $\rho_r$  are the densities of the solvent and rubber and  $W_s$  and  $W_D$ , the weight of the swollen and dried samples, respectively. The crosslink density of the cured unfilled compounds was obtained by using the Flory–Rehner equation:<sup>11</sup>

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

where  $\nu$  is the number of molar of crosslinking for unit volume,  $V_s$  is the molar volume of the swelling solvent,  $v_r$  is the volume fraction of rubber in the swollen gel, and  $\chi$  is the polymer-solvent interaction parameter.

### Determination of freezing point

Samples for freezing experiments were taken from the samples used to determine the crosslink density to remove unreacted cure agents. The samples were swollen in cyclohexane for 3 days. The vulcanizate samples that had reached equilibrium swelling were introduced in DSC pans with an excess of solvent to prevent deswelling of the sample by vaporization of the solvent. Cyclohexane was used as the swelling solvent because of its favorable crystallization behavior in DSC.<sup>7–9</sup>

The samples were cooled at  $5^\circ\text{C min}^{-1}$  in a Mettler Toledo differential scanning calorimeter (DSC 822<sup>e</sup>). This cooling rate was found to be the most acceptable compromise between solvent diffusion to the surface of the sample (when a slow cooling rate is used) and the interference between the signal of the free solvent and the gel solvent freeze (when a fast cooling rate is used).<sup>7</sup>

### Physical testing

Tensile strength was measured according to ISO 37 on small dumbbell test pieces using a Instron testing machine Mod 4361 fitted with an oven of an accuracy to  $\pm 1^\circ\text{C}$ . The samples were cut from sheets around 1.5 mm thick and tested at a rate of 500 mm/min. The

**TABLE II**  
Composition and Cure Characteristics of Peroxide Cured Compounds

Natural rubber (NR)	100	100	100	100	100	100	100
Dicumyl peroxide (DCP)	1.15	1.40	1.64	1.87	2.10	2.34	3.00
<i>Properties of curing compounds at 160°C</i>							
$\Delta T$ , dNm	4.46	5.30	6.07	6.77	7.24	8.15	10.16
$t_{97}$ , min	31.8	31.4	31.2	31.1	30.1	30.3	31.8
Crosslink density, $\nu \cdot 10^5$ mol/cm <sup>3</sup>	4.91	6.24	7.01	8.84	10.06	10.68	15.40

**TABLE III**  
Compound Formulations, Cure Characteristics, and Mechanical Properties of NR Compounds Cured with Different Curing Systems

Natural rubber (NR)	100 <sup>a</sup>	100 <sup>b</sup>	100 <sup>b</sup>
Zinc oxide	—	5	5
Stearic acid	—	1	1
DCP	1.64	—	—
DPTT	—	3	—
CBS/Sulphur	—	—	1.22/1.22
<i>Properties of curing compounds</i>			
$\Delta$ Torque, dNm	6.07	5.88	6.0
$t_{97}$ , min	31.2	3.3	18.5
Crosslink density, $\nu \cdot 10^5$ mol/cm <sup>3</sup>	7.01	6.88	7.0
Tensile strength, MPa	12.4	34.0	21.5
Elongation at break, %	730	750	780

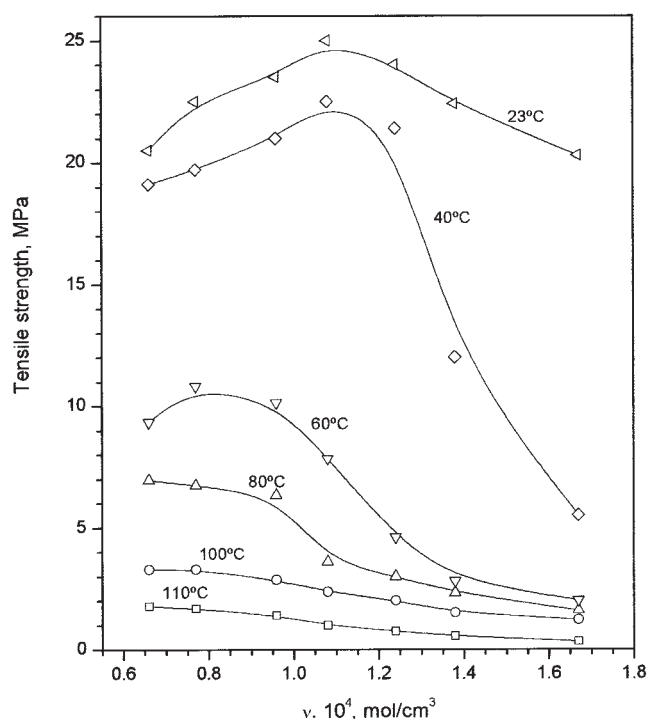
<sup>a</sup> cured at 160°C.

<sup>b</sup> cured at 150°C.

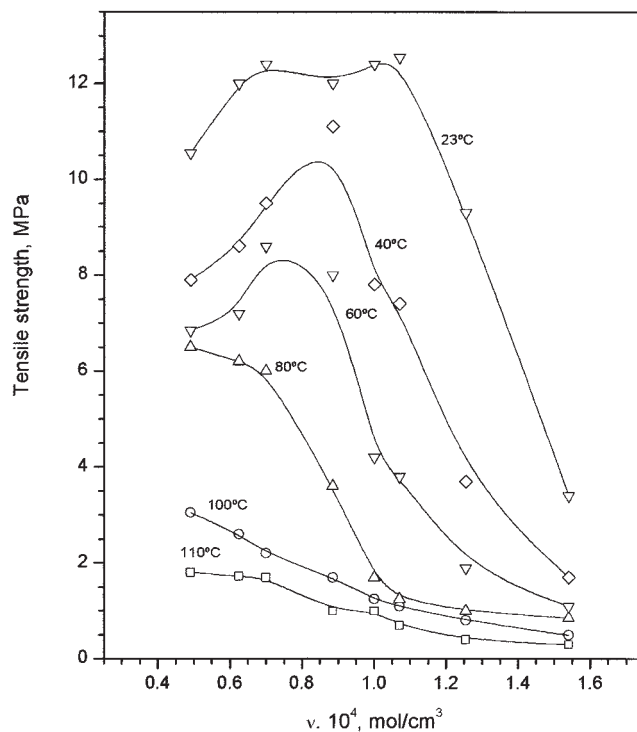
temperature of the test ranged from room temperature to 110°C. The test pieces were allowed to equilibrate in the oven for 15 min before testing.

## RESULTS AND DISCUSSION

In Tables I and II, the formulations for NR compounds with CBS/sulfur and DCP cure systems are shown. The variations in tensile strength with the temperature are plotted against crosslink density in Figures 1 and

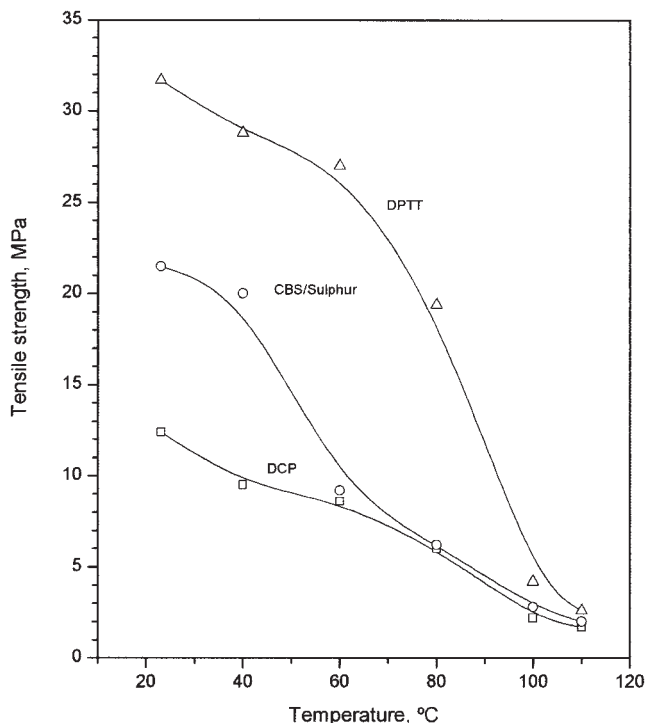


**Figure 1** Tensile strength versus crosslink density at different temperatures for NR vulcanized with various amounts of CBS/sulfur.



**Figure 2** Tensile strength versus crosslink density at different temperatures for NR vulcanized with various amounts of DCP.

2. The tensile strength obtained at room temperature (23°C) of the compounds cured with CBS/sulfur shows the usual behavior: with increasing crosslink density, the strength goes through a maximum. The samples cured with DCP present similar behavior, but with values much lower than the sample cured with accelerated sulfur. However, both series present similar crosslink density. The tensile strength results in both series decreased steadily when the test temperature was increased up to 110°C, phenomena attributed to a lesser amount of strain induced crystallinity. These data seem to be consistent with those found in literature, where tensile strength depends on whether the crosslinks are sulfidic or carbon-carbon type. As the decrease in the tensile strength with the temperature is attributed to the hindrance of strain induced crystallization, it could be this hindrance that causes the drop of mechanical properties with the increase on the crosslink density. Therefore, not only crosslink nature, but also type, number, and spatial distribution of these crosslinks, the so called network topology in the literature,<sup>12</sup> must be considered to explain phenomena such as: (a) the slight decrease on properties measured at room temperature on CBS/S compounds after the maximum, compared with the abrupt drop in the DCP cured compounds; (b) the shift of tensile strength maximum towards lower crosslink density on samples cured with DCP; (c) the drastic drop in tensile strength of CBS/S compounds when measured



**Figure 3** Tensile strength versus temperature for NR compounds vulcanized with the cure systems listed in Table III.

at 60°C; and (d) samples with higher crosslink density showing similar tensile strength values when measured at higher temperatures.

The next step was to use a sulfurating agent, dipentamethylene tiuram tetrasulfide (DPTT), as the curing system, including ZnO and stearic acid as activators,<sup>13,14</sup> to obtain a different chemical crosslink type in a comparable content to the compound cured with CBS/S. Table III shows the formulations for NR compounds with DPTT, DCP, and CBS/sulfur in suitable proportions to obtain cured samples with the same crosslink density. The values of tensile strength are plotted against temperature in Figure 3. At room temperature, the result was very different in the three samples. When the test temperature was increased, a rather sharp drop in strength took place over a narrow temperature range. However, the transition temperature, or more exactly, the temperature at which the samples do not crystallize on stretching, is not due to the increase in the crosslinking degree as in the compounds previously studied. This behavior might be attributed to effects or variations in the network topology, or heterogeneity in the spatial distribution of the crosslinks in the vulcanizates.

It is reasonably demonstrated that in an NR gum vulcanizate, the important property of tensile strength is a function of the capacity of the rubber to crystallize. However, there exist different factors that might affect the strain induced crystallization: defects introduced during the process of vulcanization, such as defects of

topological nature, the network chain density, the chemical nature of the crosslink, and other factors.

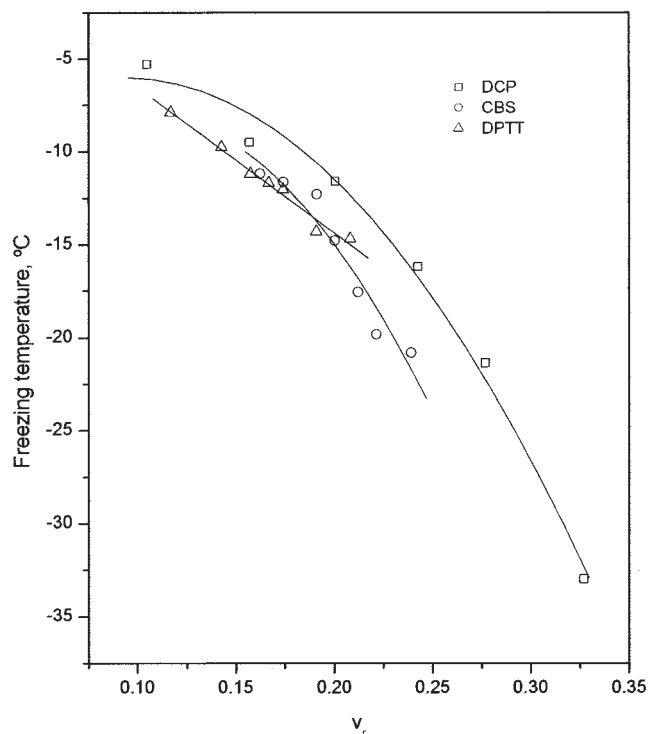
Greensmith and coworkers<sup>15</sup> reported that the tensile strength of an NR gum decreased with the system of vulcanization, in the following order: accelerated sulfur > TMTD-sulfurless > peroxide > high energy radiation. Afterwards, the elaboration of this observation allowed Mullins<sup>16</sup> to conclude that the tensile strength depends on the type of crosslink present, decreasing in the order polysulphidic > monosulphidic > carbon-carbon. However, some evidence is not in agreement with this hypothesis. Lal<sup>17</sup> treated NR gum vulcanizates to change polysulphide links to monosulphide links and did not observe any dependence on strength with the nature of the crosslink.

Regarding DCP compounds, the low level of tensile strength can be explained in terms of changes in the spatial arrangement of the crosslinks, the topology of the network. The crosslinking reaction of NR with peroxide radicals can follow two mechanisms, namely, the recombination of macroradicals and the "polymerization" of double bonds.<sup>18-20</sup> This last route gives rise to a relatively small volume of densely crosslinked polymer (cluster). As a result, the cluster will be embedded in the less firmly crosslinked polymer.<sup>21</sup> Obviously, when such a heterogeneous network is subjected to strain, a consequential non uniform stress distribution may induce anticipated material rupture.

On the other hand, the freezing point of cyclohexane imbibed by the samples versus  $v$ , can be observed in Figure 4. The DCP compounds show a nonlinear behavior, indicative of network heterogeneity. A non-uniform distribution of crosslinks with densely crosslinked cluster formation would thus generate stress accumulation responsible for the lower tensile strength obtained. In this sense, DCP vulcanizates do not show an abrupt drop in tensile strength with the temperature, so strain induced crystallization contribution to the tensile strength must be small.

NR compounds cured with DPTT, on the contrary, show the linear behavior predicted for a uniform network. In fact, this compound, with 3 phr of DPTT, presents a tensile strength (34 MPa) very elevated and difficult to obtain with dry unfilled rubber, and usually only attainable with vulcanized latex films. The network must be homogeneous and the different crosslink types present ( $S_x$ ,  $S_2$ , and  $S_1$ ) should be homogeneously distributed in the rubber matrix, as the MacGill and colleagues theory predicts. These samples also showed higher tensile strength values in a wide temperature range. Therefore, it can be said that a homogeneous network presents the higher capacity of strain induced crystallization, being inhibited only at higher temperatures.

The compounds vulcanized with CBS/sulfur show a nonlinear relationship for the freezing point of cy-



**Figure 4** Cyclohexane freezing point versus volume fraction of rubber ( $v_r$ ) in swollen NR vulcanized with various amounts of DCP (○), CBS/sulfur (△) and DPTT (□).

clohexane versus the volume fraction of rubber in the swollen gel (Fig. 4). Therefore, they must be considered as a heterogeneous network. However, the tensile strength obtained with this cure system always is very superior to compounds cured with DCP, but inferior to compounds cured with DPTT, in the absence of free sulfur. The relative content of the different chemical crosslink types are similar for the compounds cured with DPTT and CBS/sulfur, and according to Lal<sup>17</sup> there is no dependence of strength on the degree of sulfuration of the crosslinks in the network. Perhaps the presence of free sulfur in the system CBS/sulfur increases the complexity of the process with topological changes in the network, but always to a lesser degree than for the compounds cured with DCP.

## CONCLUSIONS

Just as the tensile strength of unfilled NR compounds vulcanized with different systems depends on the temperature because strain induced crystallization is inhibited, tensile strength of NR compounds vulcanized with CBS/sulfur and DCP varies with the crosslink density because of crystallization inhibition.

The tensile strength of unfilled NR compounds at a given crosslink density depends on the vulcanization system chosen. It was found that the temperature at which a sharp drop in tensile strength takes place is different for the three vulcanization systems, following the order: DPTT (sulfurless) > CBS/S > DCP, despite having virtually the same crosslink density. It is necessary to conclude that network topology effects explain the tensile strength behavior with the temperature.

Analysis of the freezing temperature of cyclohexane imbibed in the network predicted a homogeneous network for DPTT, while a heterogeneous network was predicted for CBS/S and DCP samples, since the heterogeneity was higher for DCP vulcanizates. This finding is consistent with tensile strength results. Therefore, strain induced crystallization showed by NR samples depends on both the nature and the spatial distribution of crosslinks.

The authors thank the CICYT for partial support of this research (MAT 2001/1634).

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