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Cross-Linked Density Determination of Natural Rubber Compounds by Different Analytical Techniques

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This paper investigated the formation of crosslinks in natural rubber compounds in the vulcanization systems: conventional (CV), semi-efficient (SEV), and efficient (EV), processed with three types of accelerators: MBTS (dibenzothiazole disulfide), TMTD (tetramethylthiuram disulfide) and CBS (n-cyclohexyl 2-benzothiazole sulfenamide). The cross-linked densities were determined by organic solvent swelling, dynamic mechanical analysis (DMA), stress *vs* strain, and low-field nuclear magnetic resonance, the latter being the reference technique for comparison with the other results. It was found that the choice of accelerator type influences the processing time and the cross-linked density of the vulcanizate. The four techniques showed close values of cross-linked density for natural rubber compounds, demonstrating that the analytical techniques studied can be applied to determine cross-linked density.

Keywords: *Natural rubber, cross-linked density, Flory-Rehner, Mooney-Rivlin, NMR.*

1. Introduction

Natural rubber (NR) compounds can be cross-linked by sulfur (vulcanization), peroxides (cure), or sulfur donor accelerators, such as tetramethylthiuram (TMTD). The most used curing agent in the rubber industry is sulfur[1,2], because it offers advantages such as low cost, good compatibility with other additives, and also the predictable properties of vulcanized rubber[3,4]. The degree of cross-linked density or amount of cross-linked per material volume is associated with the number of sulfur atoms bonded between two carbon atoms of two adjacent chains in the polymer structure. These bonds can be of the mono-, di- and polysulfide types[5] and are predominant according to the vulcanization system (conventional, semi-efficient, and efficient) used[6]. Cross-linked density can be determined by several methods[7] including balance swelling using an organic solvent. Furthermore, they can also be calculated using the Flory-Rehner equation[8,9], nuclear magnetic resonance[10], dynamic mechanical analysis (DMA)[11], and stress *vs* strain using the Mooney-Rivlin method[12-14]. The accelerator used in the curing process must have adequate safety time and reaction rate that is compatible with the vulcanization process. It must additionally have adequate vulcanization time and must assist in obtaining the desired final properties of the rubber compound[15-17]. Aside from the choice of the vulcanization system and the characteristics of the accelerator, it is further possible to improve the chemical resistance as regards the degradation and the mechanical properties of the compound with the incorporation of fillers[18,19]. Currently, several studies are being carried out with elastomers — particularly the innovation of formulations[20,21], such as adding fillers[22], various crosslinking systems[23-25] and finding new applications[26]. Several methodologies are also being developed to determine cross-linked densities[27,28] and their thermal[29,30] and mechanical behavior[31]. Honorato et al.[32] investigated vulcanized NR compounds using various combinations of accelerators (TMTD / MBT / and Sulfenamide) in an EV curing system. Among the curing systems used, those that contain the highest amount of free sulfur seemingly showed the best mechanical

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performance, before and after aging. The composition with the least number of crosslinks demonstrated superior performance, in relation to the dynamic properties after aging. Howse[33] determined the amount and distribution of chemical crosslinks in both unaged and aged NR using different TMTD compositions by means of rheometry, hardness, dynamic mechanical properties, stress-strain (Mooney-Rivlin), equilibrium solvent swelling (Flory-Rhener), and low-field nuclear magnetic resonance (NMR) using the double quantum technique (DQ). The degree of crosslinking increased proportionally with TMTD concentration and the reaction rate of three TMTD molecules for crosslinking formation was maintained.

Given the above, it is evident how important it is to study cross-linked density, as well as the techniques used to determine the degree of crosslinking in rubber compounds. This paper thereby aims to compare the techniques used to determine the cross-linked densities of natural rubber compounds in conventional, semi-efficient, and efficient vulcanization systems using three types of accelerators. The four techniques compared in this work for determining cross-linked densities were swelling in organic solvent using the Flory-Rehner equation, dynamic mechanical analysis, stress *vs* strain using the Mooney-Rivlin equation, and nuclear magnetic resonance by hydrogen in low field.

2. Experimental Process

2.1. Materials

The materials used in this study were: Natural rubber (Brazilian light crepe, DLP Indústria e Comércio de Borrachas e Artefatos Ltda-ME, Brazil), zinc oxide (99.8%, PA, neon), stearic acid (95%, PA, Scientific Exotic), sulfur (99.5% Scientific Exotic), accelerators (MasterBor Indústria e Comércio de Produtos Químicos LTDA, São Paulo, Brazil): dibenzothiazole disulfide (MBTS), tetramethyltiuram disulfide (TMTD), n-cyclohexyl 2-benzothiazole sulfenamide (CBS). All reagents were both used and purchased without any treatment.

2.2. Preparation of rubber compounds

The rubber compounds were made from formulations based on the accelerator/sulfur ratio. Plasticizer oil, antioxidants, fillers, or binary accelerators were not added to avoid affecting the results. Three compounds were prepared for each type of accelerator in each vulcanization system (CV, SEV, and EV). The different compositions are shown in Table 1. An open roller mixer with a friction ratio of 1:1.25 according to ASTM D3182[34] was used.

The compounds obtained were then subjected to rheometric tests (ASTM D2084-17)[35] using an oscillating disk rheometer (Team Equipment) and a 1° arc at a temperature of 150 °C. The rheometric parameters determined were: M_L (minimum torque), M_H (maximum torque), ts_1 (scorch time), t_{90} (optimum cure time) obtained from Equation 1, and CRI (cure rate index) obtained from Equation 2.

$$t_{90} = \left(M_H - M_L\right)x0.9 + M_L \tag{1}$$

$$CRI = \frac{100}{t_{90} - t_{s1}} \tag{2}$$

where:
CRI: cure rate index (min^{-1});
t_{90}: optimal cure time (min);
ts_1: scorch time (min).

The molding of the NR compounds was formed by compression in a hydraulic press with heating at a temperature of 150 °C, under a pressure of 210 kgf cm^{-2} in a mold measuring 150 x 150 x 2 mm.

2.3. Methodology

2.3.1. Cross-linked density by swelling in an organic solvent (Flory-Rehner)

The determination of the cross-linked density of the compounds was obtained according to the ASTM D297-15(2019) standard[36] using ethyl alcohol with a density of 0.79 g cm^{-3} and calculated using Equation 3.

$$\rho = \frac{\rho_L \; .m_A}{m_A - m_B} \tag{3}$$

Where:
ρ = sample density (g cm^{-3});
ρ_L = ethanol density at analysis temperature (g cm^{-3});
m_A = mass of the wireless sample in air (g);
m_B = mass of the wireless sample in liquid (g).

Table 1. Formulations and vulcanization properties for rubber compounds produced with various accelerators.

MATERIALS	CV (phr)			SEV (phr)			EV (phr)		
	CV1	CV2	CV3	SEV1	SEV2	SEV3	EV1	EV2	EV3
Natural rubber	100	100	100	100	100	100	100	100	100
Zinc oxide	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
Stearic acid	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Sulfur	2.0	2.0	2.0	1.5	1.5	1.5	0.8	0.8	0.8
MBTS[a]	0.4	---	---	1.1	---	---	2.0	---	---
TMTD[b]	---	0.4	---	---	1.1	---	---	2.0	---
CBS[c]	---	---	0.4	---	---	1.1	---	---	2.0
Ratio used: Accelerator/Sulfur	0.2			0.7			2.5		
Ratio range: Accelerator/Sulfur[82]	0.1 - 0.6			0.7 - 2.5			2.5 - 12		

[a]benzothiazole disulfide. [b]tetramethyltiuram disulfide. [c]n-cyclohexyl 2-benzothiazole sulfenamide.

The samples were weighed to a mass of approximately 0.25 ± 0.05 g and immersed in toluene in a dark environment for 5 days until equilibrium was reached. The samples were then removed, dried to remove excess solvent, and weighed. The samples were then placed in the oven at a temperature of 80 ºC for 24 hours and weighed. These mass values were used to determine the cross-linked density using Equation 4 developed by Flory-Rehner[8,9]. The values used for the molar volume of toluene (V_0) and for the Flory-Huggins interaction parameter (χ) were 106.4 $cm^3\ mol^{-1}$ and 0.39, respectively[37].

$$v = \frac{-(\ln(1-V_B)+V_B+\chi\ .\ (V_B)^2)}{(\rho_B)\ .(V_0).\left(V_B^{\frac{1}{3}}-\frac{V_B}{2}\right)} \tag{4}$$

Where:

v : Cross-linked density (mol cm^{-3});

χ: polymer-solvent interaction parameter (Flory parameter);

ρ_B: rubber density;

V_0: molar volume of the solvent;

V_B: rubber volume fraction of the swollen form, determined from the increase in weight by swelling.

2.3.2. *Cross-linked density by dynamic mechanical analysis (DMA)*

The DMA tests were performed on a Netzsch model DMTA 242C, in traction mode with a frequency of 3 Hz, at a heating rate of 5 °C min^{-1} and a temperature range of -100 °C to 150 °C, in test specimens measuring 10 x 5 x 0.25 mm. The cross-linked density was determined with the values of the storage module (E') obtained in the DMA test at a temperature of approximately 25 ± 2 °C (room temperature) and calculated using Equation 5[38,39,40]:

$$\eta = \frac{E'}{6\ .R\ .T} \tag{5}$$

where:

η = cross-linked density (mol cm^{-3});

E' = elastic storage modulus of the polymer;

R = universal gas constant (J mol^{-1} K^{-1});

T = absolute temperature (K).

2.3.3. *Cross-linked density by the Mooney-Rivlin method*

Stress *vs* strain tests were performed in an Instron traction testing machine at a speed of 50 mm min^{-1} with a 1,000 N load cell and an internal strain transducer. Quintuplets of test specimens cut into a C-binder format were used to perform the mechanical testing.

The evaluation of the cross-linked density of rubber compounds was based on the Mooney-Rivlin equation[41], which has been widely used[42] to correlate the behavior of the network deformation with the crosslinking properties of the polymeric network[43]. This theory is derived from the elastic deformation energy in ideal rubbers[44]. The Mooney-Rivlin theory works well at low to moderate stress levels[45] and the general expression is shown in Equation 6[46]:

$$\frac{\sigma}{\left(\lambda-\lambda^{-2}\right)} = 2\ .C_1 + \frac{2\ .C_2}{\lambda} \tag{6}$$

where:

σ = actual stress calculated from the stress x strain curve (MPa);

λ = elongation rate;

C_1 = parameter related to network structures;

C_2 = parameter related to intermolecular forces.

Equation 7 shows the relationship between the cross-linked density obtained by physical means (η) and the constant C_1 to estimate the cross-linked density of the vulcanized rubber[47]:

$$\eta = \frac{2\ .C_1}{R\ .T} \tag{7}$$

where:

η = cross-linked density (mol cm^{-3});

R = universal gas constant;

T = absolute temperature (K).

Equation 7 was used to accurately determine the cross-linked density at deformations in the uniaxial direction between 30 to 150% ($\lambda^{-1} \approx 0.4 - 0.7$)[48,49].

2.3.4. *Low-field nuclear magnetic resonance cross-linked density using hydrogen*

NMR measurements were performed on a Bruker Mini-spec NMR spectrometer at a frequency of 20 MHz for ^1H under 40 ºC. For the determination of double quantum (DQ), the conditions were: Pulses of 90 º at 3.1 μs, pulses of 180 º at 6 μs and time between scans of 2 s with the number of scans being equal to 32. The double quantum ^1H (DQ^1H) or multiple-quantum ^1H (MQ^1H) is considered one of the most versatile, robust, and non-invasive NMR analysis techniques. This technique provides a reliable estimate of the cross-linked regions and their distribution, characterized by the representation of a residual dipolar coupling (RDC)[50,51]. The average intensity of the RDC is inversely related to the average molecular mass between dynamically restricted regions and is thus directly related to the cross-linked density in the polymer network[52,53].

3. Results and Discussion

3.1. *Rheometry*

The minimum torque values (M_L) are obtained in the pre-cure phase (t_{S1}) where the NR compounds are not yet vulcanized. The M_L values are associated with the viscosity of the compound that depends on the degree of processability of the materials that compose it[54]. The values of maximum torque (M_H) for compounds without fillers depend on the degree of crosslinking[55,56]. The curing characteristic is shown in Table 2 based on the NR rheometric parameters in their respective crosslinking systems.

Table 2. Rheometric parameters of NR compounds vulcanized and accelerated by: MBTS, TMTD and CBS in their respective crosslinking systems.

Crosslinking systems		Accelerators	M_L	M_H	ΔM	ts_1	t_{90}	CRI
			(dN.m)	(dN.m)	(dN.m)	(min)	(min)	(min^{-1})
CV	CV_1	MBTS	0.95	12.03	11.08	4.02	11.45	13.49
	CV_2	TMTD	0.89	19.75	18.86	3.32	4.82	66.33
	CV_3	CBS	0.99	17.27	16.28	4.62	10.35	17.48
SEV	SEV_1	MBTS	1.00	14.75	13.75	5.07	9.15	24.55
	SEV_2	TMTD	0.87	19.92	19.05	3.75	4.65	110.31
	SEV_3	CBS	0.84	18.92	18.08	5.25	7.65	41.83
EV	EV_1	MBTS	0.79	11.56	10.77	6.58	9.90	30.05
	EV_2	TMTD	0.93	18.07	17.14	3.83	5.57	58.36
	EV_3	CBS	0.79	15.17	14.38	6.12	8.17	49.38

The systems vulcanized with TMTD showed higher values of maximum torque and thus a higher degree of crosslinking. This behavior is due to the fact that this accelerator is a sulfur donor, able to donate up to 13% sulfur from its own structure[57].

The semi-efficient vulcanization system (SEV) has a medium sulfur quantity when compared to the conventional system (CV) with a regular sulfur quantity and the efficient system (EV) with a low sulfur quantity[58,59]. The difference between the maximum and minimum torques (ΔM) indicates the degree of crosslinking in the polymer matrix. As can be seen in Table 2, the compounds with TMTD accelerator were those that exhibited the highest degree of reinforcement[60,61]. The optimal cure time values were lower for TMTD, which also affected the CRI due to its sulfur donor character[62].

3.2. Stress vs strain

Figure 1 shows the curves obtained in the stress *vs* strain tests. Materials vulcanized with TMTD tend to produce short monosulfide bonds, which are more rigid and thus more susceptible to breakage[63,64]. MBTS compounds showed greater elasticity due to longer crosslinks compared to polysulfide and disulfide types, which are more elastic and flexible and therefore promote greater elongation to failure[65]. Table 3 shows the stress *vs* strain data. The Semi-Efficient system exhibited the best stress-strain for the three types of accelerators. In this system, the ratio of sulfur to accelerator is close to 1, likely forming lattices with a predominance of polysulfide and disulfide bonds, resulting in superior stress-strain[66].

3.3. Mechanical dynamic analysis (DMA)

The all-natural rubber compounds had storage modules close to 1,000 MPa at a temperature of -100 °C in their respective crosslinking systems. These values are related to the limitations on the relative movements of the polymer chains attributed to the glassy state of the rubber. For values above the glass transition temperature, between -60 °C to -40 °C, all compounds showed an abrupt reduction in the storage module due to the movement of the chains, particularly the longest polymer chains, and the dissipation of mechanical energy attributed to the relaxation of the said chains. The curves of the storage module (E') are shown in Figure 2.

Table 3. Data obtained from the stress versus strain tests of vulcanized and accelerated NR compounds by: MBTS, TMTD and CBS in their respective crosslinking systems.

Accelerator	Crosslinking System	Maximum stress	Maximum strain
		(MPa)	(%)
MBTS	CV	14.6 ± 0.6	1241.7 ± 6.6
	SEV	16.0 ± 1.5	1170.0 ± 19.5
	EV	14.4 ± 2.2	1291.7 ± 27.3
TMTD	CV	19.2 ± 1.7	1136.7 ± 27.7
	SEV	21.7 ± 3.9	1100.0 ± 35.3
	EV	17.4 ± 2.1	1051.7 ± 28.1
CBS	CV	17.4 ± 1.5	1140.0 ± 28.0
	SEV	21.0 ± 3.2	1325.0 ± 22.7
	EV	17.2 ± 2.3	1128.4 ± 30.7

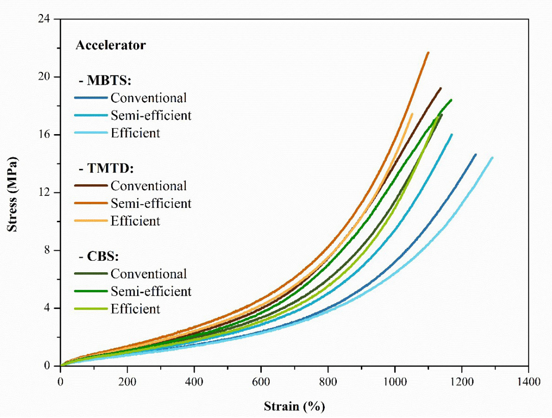

Figure 1. Stress vs. strain curves of NR compounds vulcanized and accelerated by: MBTS, TMTD and CBS in their respective vulcanization systems.

The curves of Tan δ as a function of temperature are shown in Figure 3. It further illustrates the relaxation of the chains and the maximum dissipation of the system energy[67]. For all compounds, this event occurs with greater intensity at the temperature of around -40 °C, as shown by the peaks of the Tan δ curves.

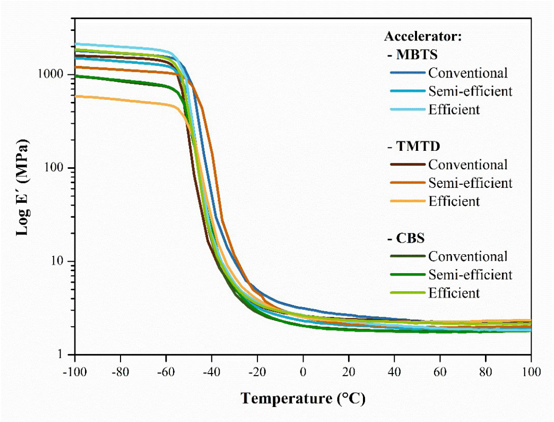

Figure 2. Storage module curves (E') of NR compounds vulcanized and accelerated by: MBTS, TMTD and CBS in their respective vulcanization systems.

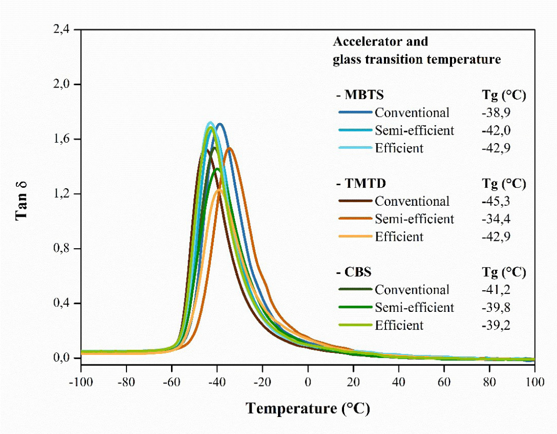

Figure 3. Delta tangent curves (Tan δ) of NR compounds vulcanized and accelerated by: MBTS, TMTD and CBS in their respective crosslinking systems.

3.4. *Cross-linked density with NMR*

Analysis of the NMR results has shown that elastomeric networks are far from ideal, so it is important to consider the spatial distribution of crosslinks[68,69]. Figures 4, 5, 6 illustrate the accumulation of magnetization for NR compounds in their respective crosslinking systems, obtained from normalizing the double quantum intensity (I_{DQ}).

The accumulation of magnetization represents only chemical crosslinks, and the higher the normalized I_{DQ} intensity of the accumulation curve, the greater the number of crosslinks present[70]. In Figure 4, the conventional MBTS accelerator system presents more crosslinks in relation to the semi-efficient and efficient systems. In Figure 5, the semi-efficient and efficient TMTD accelerator systems show the same number of crosslinks.

Figure 6 also shows the magnetization accumulation curves for the semi-efficient and efficient CBS accelerator systems, which are virtually the same and have the same number of crosslinks. Figure 7 shows the distributions of average molecular weight (1/2Mc) associated with chain size and crosslinks present.

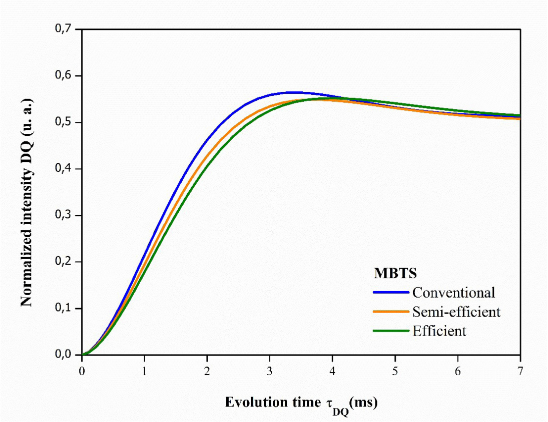

Figure 4. Normalized magnetization accumulation curves for vulcanized NR compounds and those accelerated by MBTS in their respective crosslinking systems.

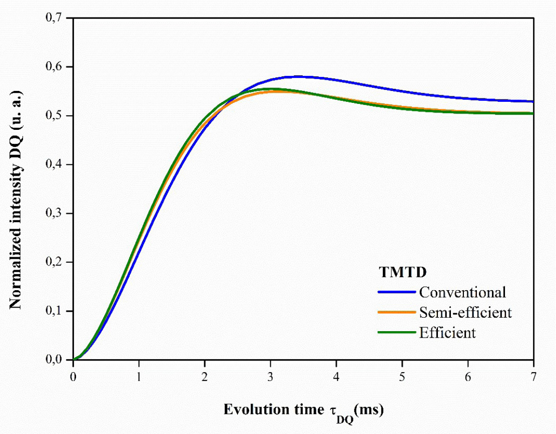

Figure 5. Normalized magnetization accumulation curves for NR compounds vulcanized and accelerated by TMTD in their respective crosslinking systems.

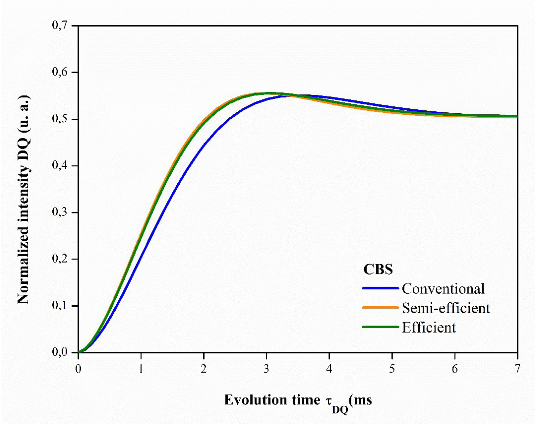

Figure 6. Normalized magnetization accumulation curves for vulcanized NR compounds and those accelerated by MBTS in their respective crosslinking systems.

The mechanical properties of vulcanized elastomers are influenced by the distribution and heterogeneity of crosslinks in the polymeric network[71]. It can be observed that the SEV and EV vulcanization systems had chains with closer molecular weights and therefore with a more homogeneous distribution, except for the cross-linked compounds in the

Table 4. Cross-linked densities of vulcanized NR compounds determined by the Swelling, DMA, Stress x Strain and ^{1}H NMR techniques in respective crosslinking systems.

Accelerators	Crosslinking systems	Swelling cross-linked density by Flory Rehner	Cross-linked density by DMA	Cross-linked density by Mooney Rivlin	Cross-linked density by ^{1}H NMR
		(10^{-4} mol cm^{-3})	(10^{-4} mol cm^{-3})	(10^{-4} mol cm^{-3})	(10^{-4} mol cm^{-3})
MBTS	CV1	1.36 ± 0.01	1.74 ± 0.03	1.97 ± 0.02	1.81 ± 0.01
	SEV1	1.20 ± 0.02	1.37 ± 0.02	1.93 ± 0.01	1.70 ± 0.05
	EV1	0.86 ± 0.01	1.49 ± 0.02	1.44 ± 0.01	1.56 ± 0.01
TMTD	CV2	1.29 ± 0.01	1.59 ± 0.02	3.10 ± 0.02	1.78 ± 0.01
	SEV2	1.28 ± 0.01	1.41 ± 0.03	3.30 ± 0.04	2.07 ± 0.01
	EV2	1.40 ± 0.03	1.53 ± 0.01	2.84 ± 0.04	2.01 ± 0.01
CBS	CV3	1.33 ± 0.01	1.25 ± 0.01	2.73 ± 0.02	1.73 ± 0.01
	SEV3	1.42 ± 0.01	1.23 ± 0.03	2.81 ± 0.02	2.02 ± 0.01
	EV3	1.35 ± 0.01	1.54 ± 0.02	2.32 ± 0.03	1.97 ± 0.01

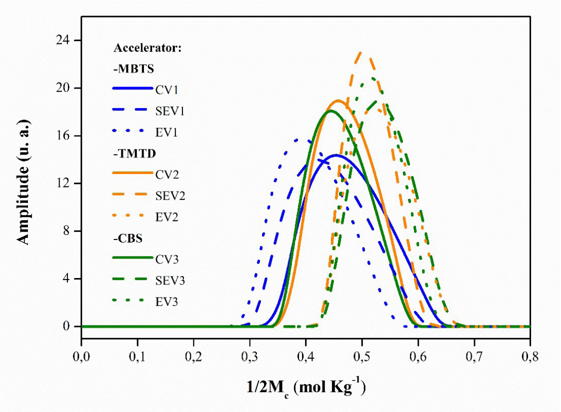

Figure 7. Distribution curves of the average molecular weight of the NR compounds vulcanized and accelerated by: MBTS, TMTD and CBS in their respective crosslinking systems.

presence of MBTS. As the amount of accelerator increased and the amount of sulfur decreased, the distribution of the average molecular weight of the polymer chains shifted to higher values and with more homogeneity.

3.5. Comparison of cross-linked densities of NR compounds as determined by swelling, DMA, stress vs strain, and NMR techniques

The results of the cross-linked densities obtained by the Swelling, DMA, Stress x Strain, and ^{1}H NMR techniques are on the order of 10^{-4} mol cm^{-3}, indicating that the four techniques showed relatively coherent results for determining the cross-linked densities. The results obtained with the four techniques are shown in Table 4.

Therefore, the crosslink density determined by physical means such as DMA, stress x strain (obtained from the elastic regions) and ^{1}H NMR has higher values compared to the solvent swelling.

NMR experiments are done in a relaxed state. While the tests of stress-strain, DMA and swelling correspond to deformations of large amplitude. In Table 4, the results of different techniques are correlated. The values differ slightly between the techniques, due to defects (topological restrictions, entanglements, etc.) acting differently in the different techniques besides the stable cross-links[72]. Furthermore, in determining the crosslink density, each technique uses different nature information of vulcanized rubber. For example, in the hydrogen NMR at low magnetic field the hydrogen protons were studied, being possible to determine the number of each of the different types of non-equivalent protons, as well as obtain similar information regarding the nature of the immediate environment by a simplified dynamic model of network chain characterization[73]. The uniaxial stress-strain test was used to obtain the crosslink density, the data were obtained from the curves in the range of strains between 30 to 150%, with a rate of 50 mm min^{-1} in a quasi-equilibrium deformation system The theories by which this can be done differ mainly in the way in which topological interactions between network chains are taken into account. The network model used was the affine applied in the Mooney-Rivlin equation[74]. The determination of crosslinked densities by dynamic mechanical analysis was determined experimentally by measuring the elastic storage module in the rubber plateau region at room temperature. In this technique, the effects of chain ends, main chain splitting and entangled chain entanglements acting as crosslinking were not taken into account, which can result in a quantitative error in the crosslinking density determinations[75]. An alternative is the analysis of the swelling equilibrium in a suitable solvent, it has been widely used to characterize network structures of elastomeric. The Flory-Rehner equation, based on the elastic response to the osmotic stress of the solvent, directly relates the rubber volume fraction at swelling equilibrium to the average molecular weight between cross-links. Thus, the average molecular weight between the cross-links can be determined in a simple way[76].

Several works in the literature have shown that increasing the sulfur content favors the crosslinking degree, which in turn increases the cross-linked densities[77-79]. However, as shown in the studies in this paper, only the MBTS met this condition in the CV, SEV, and EV systems when swelling, stress x strain, and NMR were used. So, the exception is the MBTS with EV system when DMA was used.

The NMR results are more sensitive and accurate compared to the other techniques mentioned because it examines the structure of the network at the molecular level and identifies all types of defects that restrict the movement of the polymer chains[80]. When comparing the results in

Table 4, the results from the NMR technique were those that showed the least variation. Valentin and Saalwachter compared the swelling techniques in solvent and NMR for determining crosslinks and questioned the results obtained by swelling. In their work, they identified possible errors associated with the Flory-Rehner equation in determining the volumetric fraction of the rubber, with the Flory-Huggins parameter for polymer-solvent interaction, and with the applied model of rubber elasticity.

The highest values of crosslinking densities were obtained in the stress-strain tests, as shown in Table 4. Hagen and co-authors showed that the crosslink density depends on the time scale of the method used, which means that there is not sufficient time to disentangle before the direction of deformation is reversed during dynamic mechanical tests. The lowest crosslink densities are obtained from equilibrium swelling data, where all entanglements that are not trapped have enough time to untangle themselves.

The rubbers have complex parameters and properties that are difficult to predict and require further study. Some of these parameters and properties are the length distribution of the main polymer chain, network defects (free ends of the chain, cyclic links, and entanglement of the chains), and limited chain extensibility (applicable in the elastic ranges between 30 to 150% of the chain length deformation)[81].

4. Conclusions

In this work, we investigated the cross-linked density using different techniques, in three crosslinking systems: conventional, semi-efficient, and efficient in the presence of three accelerators: MBTS, TMTD, and CBS. The solvent swelling tests are the most commonly used by researchers today and their results are unanimously accepted. However, the results showed that the other methods for determining the cross-linked densities are consistent and provide satisfactory results for studying the mechanical properties of natural rubber compounds. Using the NMR technique as a reference, since it is a more accurate method for determining the cross-linked density among the other techniques, the results showed that the stress *vs* strain and DMA techniques are suitable for estimating the cross-linked density within a small margin of error. The stress *vs* strain and DMA techniques are simpler and less expensive compared to the NMR technique. Thus, new opportunities are created to measure crosslinks using alternative methods that provide adequate, simple, and rapid tools for studying cross-linked density, in addition to choosing a crosslinking system with accelerators suitable for the desired applications of natural rubber compounds.

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