

Cross-link density measurement of nitrile rubber vulcanizates using dynamic shear test^a

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Abstract

Cross-link density impacts most mechanical properties of rubber, therefore it is necessary to have a method to measure it. The most widely used method is via equilibrium swelling, however, it is time consuming and uses organic solvents. Dynamic Shear Test (DST) can be used to calculate both chemical and physical cross-links in rubber compounds in shorter times than by swelling equilibrium method, and without the use of solvents. In this work, equilibrium swelling using toluene and acetone was used to validate the dynamic shear tests for different nitrile rubber (NBR) compounds. The DST had a good correlation with the swelling equilibrium method using acetone, with a correlation coefficient of ~0,91, validating the use of DST. Moreover, the use of the Modified Guth-Gold equation (instead of Guth-Gold Equation with Medalia correction) also allowed to deduct the effect of carbon black on the cross-link density from the DST.

Keywords: *nitrile rubber, cross-link density, dynamic shear test, swelling equilibrium, solubility parameter*

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1. Introduction

Rubber compounds are designed as a complex mixture of components that includes vulcanization (curing) systems, reinforcement fillers, protective systems, and process aids. The choice of the vulcanization system is of extreme importance in the manufacturing and final properties of rubber products. The three-dimensional network formed during the vulcanization process is responsible for the high elasticity behavior and the reversible deformability of rubber materials, besides, it also affects their mechanical and thermal properties^[1,2]. Therefore, it is necessary to have suitable techniques for evaluating the cross-linking density (CLD).

Although there are several techniques in the literature that measure the CLD, it is unquestionable that Equilibrium swelling is the most used method^[2-3]. The Equilibrium swelling method is based on the Flory–Rehner theory of swollen networks. It quantifies the cross-link density, μ (mol.g⁻¹), which is proportional to the inverse of the average molecular weight between cross-links ($\mu \propto 1/2 Mc$, g.mol⁻¹)^[2,4,5]. Although it is widely used, the Equilibrium swelling method uses organic solvents, and it is a laborious and time-consuming technique. Furthermore, the results will directly depend on the solvent used.

Lee et al.^[6] presented a fast method for assessing the CLD from rheological properties of natural rubber (NR) and styrene butadiene rubber (SBR), using the Rubber Process Analyzer (RPA 2000). This dynamic shear test (DST) method allows the measurement of physical crosslink density, which is related to the chain's entanglements, and the measurement of total crosslink density, which also includes the contribution from chemical cross-links formed during the vulcanization process. The chemical cross-links can be calculated as the difference between total and physical crosslink densities^[6-9]. Silva et al.^[8] compared the crosslink density values of epoxidized natural rubber filled with hydrotalcite measured by equilibrium swelling and DST methods. The authors reported a good correlation between both methods and highlighted that DST is a fast and efficient alternative, with the advantage of not using any organic solvent^[8]. Ünügül and Karaagaç^[9], employed the dynamic shear test to study the effect of reactive silane on the vulcanization of the chlorinated polyethylene (CPE) and chloroprene rubber (CR) compounds. The authors reported that CPE showed a noticeable increase in physical

cross-link density and that amino silane compounds exhibit significantly higher chemical and total cross-link densities.

Despite its potential and its use in different rubbers, there are few reports in literature of the dynamic shear test and even less of this method applied to nitrile rubber. A more detailed understanding of the relationship of the DST with other, more conventionally used methods such as equilibrium swelling, will prove useful to attest the validity of the DST and to better understand rubber cross-link density.

Aiming at validating the applicability of the dynamic shear test (DST) in nitrile rubber, unfilled and carbon black filled NBR compounds were vulcanized at different times to generate different degrees of vulcanization, and their cross-link density was measured by equilibrium swelling (using both toluene and acetone) and DST.

2. Materials and Methods

2.1 Materials

Three different grades of poly(acrylonitrile-co-butadiene), also known as nitrile rubber or NBR, with different acrylonitrile (ACN) content were kindly donated by Nitriflex S/A Indústria e Comércio: N726 (28% of ACN), N615 (33% of ACN), and N206 (45% of ACN). Moreover, carbon black (N330), zinc oxide (ZnO), stearic acid, and n-tert-butyl-2-benzothiazolesulfenamide (TBBS) were used as received.

2.2 Rubber compounding and samples preparation

Unfilled (gum) and carbon black filled rubber formulations were designed according to Table 1, using ASTM D3187 as reference. The experimental coding used was **AA%/BB**, in which AA is the CAN content (28, 33, and 45%) and BB is the amount of carbon black. The compounds were prepared in an open mixing mill (Luxor, model BML 150) following the procedure described in ASTM D3187.

Rheometric curves were determined based on ASTM D5289 using the Rubber Process Analyzer (RPA 2000, Alpha Technologies). The test was performed at 160°C, oscillation amplitude of $\pm 0.5^\circ$ arc, and frequency of 1.67 Hz. For each rubber compound, four different vulcanization times, t_x , (ranged from t_{20} to t_{90} , Table 2) were established from the torque *versus* time curves with the purpose of producing different cross-link densities. “ t_x ” is the time needed to achieve a “ x ” % of vulcanization. The same specimen from DST was submitted to equilibrium swelling test method to compare the two methods.

2.3 Cross-link density characterization by Dynamic Shear Test (DST)

The dynamic shear test to calculate the compounds' CLD was conducted on an RPA 2000 (Alpha Technologies). The DST protocol was divided in four steps, following the parameters defined by Lee and Coran as to avoid sample shrinkage and degradation^[6]. In the first step, the test specimen was preconditioned during 2 min at 100°C, 0.2° of strain, and 0.5-Hz frequency. The second step consisted of measuring the elastic modulus at 5.0 Hz frequency (G'_{5Hz}), at 100°C of temperature and 0.25° of strain. In the third step, the test specimen was vulcanized at 160°C using the respective vulcanization times (Table 2). In the fourth step, the temperature was reduced to 100°C, and then the elastic modulus was measured at 0.5 Hz frequency (named as $G'_{0.5Hz}$), at 100°C of temperature and 0.25° of strain. At the end, the test specimen was removed from RPA and reserved for testing in the equilibrium swelling test.

For the unfilled rubber compounds, the physical $[\mu]_p$, total $[\mu]_T$, and chemical $[\mu]_C$ cross-link densities were calculated using Equations 1, 2, and 3, respectively, where R is the gas constant ($8.314 \text{ J.K}^{-1}\text{mol}^{-1}$) and T is the absolute temperature in Kelvin (K)^[6,7].

$$[\mu]_P = (G'_{5Hz}) / (2RT) \quad (1)$$

Table 1. Unfilled and filled nitrile rubber (NBR) formulations. Amounts in part per hundred parts of rubber (phr).

Component	28%/00	33%/00	45%/00	33%/40
NBR with 28% of acrylonitrile	100	-	-	-
NBR with 33% of acrylonitrile	-	100	-	100
NBR with 45% of acrylonitrile	-	-	100	-
ZnO	3	3	3	3
Stearic acid	1	1	1	1
Sulphur	1.5	1.5	1.5	1.5
TBBS ¹	0.7	0.7	0.7	0.7
N330 ²	-	-	-	40

1 – n-tert-butyl-2-benzothiazolesulfenamide; 2 – carbon black N330.

Table 2. The curing times of the compounds and their percentage of vulcanization*.

28%/00		33%/00		45%/00		33%/40	
t_{23}	6 min	t_{20}	7 min	t_{20}	5 min	t_{25}	4 min
t_{55}	7 min	t_{63}	9 min	t_{60}	7 min	t_{53}	5 min
t_{83}	9 min	t_{78}	11 min	t_{70}	11 min	t_{78}	7 min
t_{90}	11 min	t_{90}	15 min	t_{90}	20 min	t_{90}	11 min

*Based on time of $t(x)$ related to the $M(x) = ML + (MH - ML) \left(\frac{x}{100} \right)$, where x is the percentage of vulcanization (20 to 90%).

$$[\mu]_T = (G'_{0.5Hz}) / (2RT) \quad (2)$$

$$[\mu]_C = [\mu]_T - [\mu]_P \quad (3)$$

It is important to highlight that Equations 1, 2, and 3 were developed for unfilled rubber. Therefore, it is necessary to deduct the filler's contribution in the $G'_{0.5Hz}$ and $G'_{0.5Hz}$ values for filled rubber compounds, i.e., it is necessary to estimate the modulus values of the respective "gum-state". Therefore, it was used the Guth-Gold Equation with Medalia correction^[6,7] (Equation 4) and the modified Guth-Gold equation^[10] (Equation 5) developed for carbon black-filled rubbers^[5].

$$G'_{filled} = G'_{unfilled}(1 + 2.5\phi + 14.1\phi^2) \quad (4)$$

$$G'_{filled} = G'_{unfilled}(1 + 2.5\phi + 14.1\phi^2 + 0.20(\sqrt{S})^3 \phi^3) \quad (5)$$

Wherein G'_{filled} is the elastic modulus of filled samples, $G'_{unfilled}$ is the elastic modulus without filler contribution, ϕ is the volume fraction of the filler, and S is the BET nitrogen surface area (NSA) of carbon black. According to literature^[10], Equation 4 is recommended when the particles are dispersed from each other in a rubber matrix, behaving almost independently, while Equation 5 is applied to systems where particles or aggregates are connected to each other forming a network structure.

2.4 Cross-link Density characterization by Equilibrium swelling test

The equilibrium swelling test was assessed using toluene and acetone. Each test specimen from the DST test was cut in four pieces, being two tested with toluene and the other two with acetone. The test protocol consisted in weighing the test specimen in air and solvent to calculate their initial mass and density (according to Archimedes' principle). Then, each test specimen was swollen in the solvent until the system reached equilibrium. After this time, the test specimen was removed from the solvent and weighed. Lastly, the solvent inside the swollen test specimen was removed and the sample reweighed thereafter. The cross-link density was calculated by the equation developed by Flory-Rehner, shown in Equation 6. Wherein μ is cross-link density ($\text{mol}\cdot\text{cm}^{-3}$), v_r is the volume fraction of rubber in the swollen sample determined by Equation 7, V_0 is the molar volume of the solvent (toluene: $106.83 \text{ cm}^3\cdot\text{mol}^{-1}$ and acetone: $73.7 \text{ cm}^3\cdot\text{mol}^{-1}$) and χ is the Flory-Huggins interaction parameter for the solvent and the elastomer.

$$\mu = \frac{-\left[\ln(1-v_r) + v_r + \chi * v_r^2\right]}{\left[V_0 * \left(\frac{1}{v_r^3} - \frac{v_r}{2}\right)\right]} \quad (6)$$

$$v_r = \frac{\left(\frac{M1 - M1 * f_f}{\rho_c}\right)}{\left[\left(\frac{M1 - M1 * f_f}{\rho_c}\right) + \left(\frac{M2 - M3}{\rho_s}\right)\right]} \quad (7)$$

Wherein M_1 , M_2 , and M_3 are, respectively, the initial, the swollen, and the dried sample masses; f_f is the filler fraction in volume; ρ_c is the sample density, and ρ_s is the solvent density.

The interaction parameters (χ) of NBR/Acetone and NBR/toluene were calculated by using the Hildebrand model (Equation 8)^[11,12], wherein δ_{sol} ($(\text{cal}/\text{cm}^3)^{0.5}$) is the solubility parameter of solvent ($\delta_{toluene} = 8.90$; $\delta_{acetone} = 9.88$) and δ_{rub} ($(\text{cal}/\text{cm}^3)^{0.5}$) is the solubility parameter of rubber ($\delta_{NBR28\%} = 9.35$; $\delta_{NBR33\%} = 9.57$; $\delta_{NBR45\%} = 10.19$). The χ values are shown in Table 3.

$$\chi = 0.35 + \frac{V_0}{RT} (\delta_{sol} - \delta_{rub})^2 \quad (8)$$

2.5 Statistical analysis

Pearson product-moment correlation coefficient was used to assess the relationship between DST and equilibrium swelling methods. The Pearson correlation coefficients range between -1 and +1 and measure the strength of the linear relationship among the variables^[13]. As the correlation coefficients gets closer to +1 or -1, the more correlated the datasets will be, with a positive trend (+1) or negative trend (-1). When the correlation coefficient is close to zero, its linear relationship is poor. The p-value was used to evaluate the statistical significance of the correlation coefficient.

The Pearson product-moment correlation coefficient was preferred instead of the conventional coefficient of determination of a linear fit, R^2 , because it is a more accurate way to describe the strength of the linear relationship rather than R^2 because we are not evaluating the strength of a linear model.

The cross-link data were processed using the statistical software STATGRAPHICS Centurium 18 with 95,0% of confidence level. This analysis was conducted for the groups of variables: $[\mu]_C$, $[\mu]_T$, μ_{Tol} , and μ_{Acet} , using all data from unfilled NBR.

3. Results and Discussions

3.1 Cross-link density characterization by Dynamic Shear Test

Figure 1 shows the values of the physical ($[\mu]_p$), chemical ($[\mu]_C$) and total ($[\mu]_T = [\mu]_C + [\mu]_p$) cross-link densities measured from DST test for unfilled NBR.

The vulcanization times (from t_{20} to t_{90}) did not affect the values of $[\mu]_p$ for each of NBR sample. This behavior was expected, since the $[\mu]_p$ is mainly associated with the presence of physical entanglements for unfilled rubber. Moreover, the physical entanglements ($[\mu]_p$) vary according to the type of NBR, increasing from 28% to 45% of acrylonitrile content.

Table 3. Calculated rubber-solvent interaction parameter (χ) values based on Equation 8.

Solvent	NBR28%	NBR33%	NBR45%
Toluene	0.3760	0.4253	0.6482
Acetone	0.3945	0.3627	0.3618

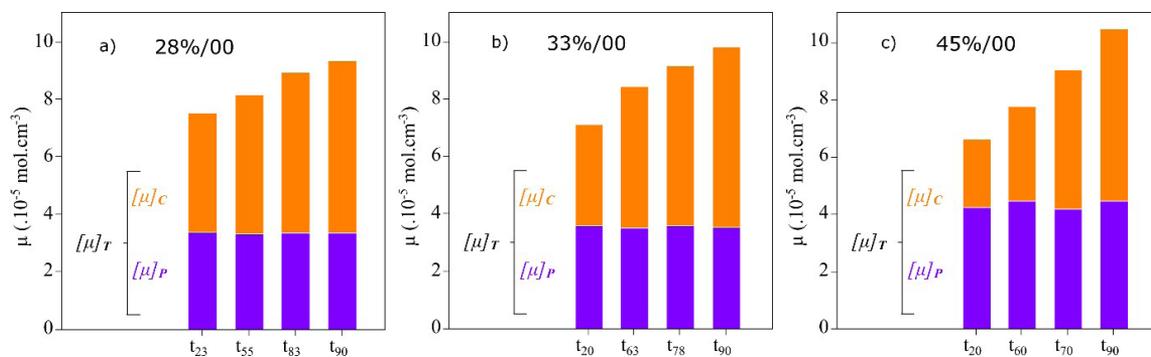


Figure 1. Physical ($[\mu]_P$), chemical ($[\mu]_C$) and Total ($[\mu]_T = ([\mu]_C + [\mu]_P)$) cross-link densities ($\cdot 10^{-5} \text{ mol.cm}^{-3}$) of unfilled rubber with acrylonitrile content of (a) 28%, (b) 33% and (c) 45%, cured at times related to specific vulcanization percentages.

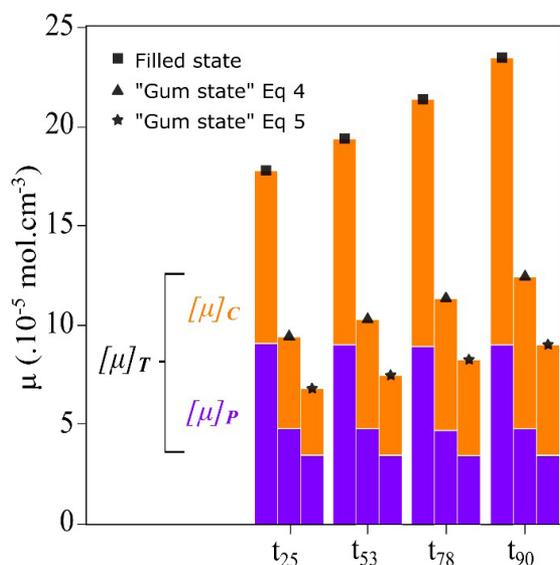


Figure 2. Physical ($[\mu]_P$), chemical ($[\mu]_C$) and Total ($[\mu]_T = ([\mu]_C + [\mu]_P)$) cross-link densities ($\cdot 10^{-5} \text{ mol.cm}^{-3}$) of filled rubber 33%/40 vulcanized at crescent times and deducting the filler content using Guth-Gold Equation with Medalia correction (Equation 4) and the modified Guth-Gold equation (Equation 5).

Regarding the chemical crosslink density ($[\mu]_C$), as expected, there is an increase in $[\mu]_C$ values as the vulcanization time increases, and at t_{90} vulcanization time the three NBR compounds presented similar $[\mu]_C$ values ($\sim 6 \cdot 10^{-5} \text{ mol.cm}^{-3}$). This behavior is reasonable since the same vulcanization system (Table 1) was used for all NBR compounds. Therefore, the difference of $[\mu]_T$ values at t_{90} ($28\%/00 > 33\%/00 > 45\%/00$) is directly related to the different physical crosslinks of each sample.

Figure 2 shows the values of $[\mu]_P$, $[\mu]_C$, and $[\mu]_T$ cross-link densities for the 33%/40 compound, whose calculation was done considering two conditions: (i) “filled-state”, i.e., with the contribution of carbon black in the result, and (ii) “gum-state”, in which the carbon black contribution was discounted using Guth-Gold Equation with Medalia correction^[6,7] (Equation 4) and the modified Guth-Gold equation^[10] (Equation 5).

A noticeable increase in $[\mu]_P$ values of 33%/40 is observed for the “filled-state” compared to unfilled NBR (33%/00, Figure 1b). A similar behavior was observed with carbon black filled natural rubber (NR) compounds^[14] using ¹H-NMR method. Higher values of physical crosslink density for carbon black filled NR was observed than to the unfilled one. This is because carbon black restricts the rubber chains’ mobility, besides the inherent rubber chains’ entanglements.

The comparison between the results of 33%/40 (Figure 2) and 33%/00 (Figure 1b) shows that the correction of modulus made with modified Guth-Gold Equation (Equation 5) produced values of $[\mu]_P$ “gum-state” close to the unfilled $[\mu]_P$ of 33%/00. Therefore, this result indicates that modified Guth-Gold equation (Equation 5) was more effective deducting the filler’s contribution from moduli values.

Regarding the higher values observed of values of $[\mu]_P$ “gum-state” using Equation 4, the Guth-Gold Equation with Medalia correction only accounts for the amplification of the modulus caused by rigid particles that do not deform; but does not consider the amplification of the modulus caused by the interaction of rigid particles, as in the formation of a network structure. Fukahori et al.^[10] indicates that the modulus increase caused by carbon black network is better described using the modified Guth-Gold equation (Equation 5).

Furthermore, as expected, the chemical crosslink ($[\mu]_C$) values of “filled-state” are higher than “gum-state” ones (Equation 4 and 5). Comparing the 33%/40 $[\mu]_C$ “gum-state” from Guth-Gold equation to the 33%/00 $[\mu]_C$, one can infer that carbon black affected negatively in the chemical cross-links. However, there is no major consensus in the literature on carbon black/cross-link density effect. Some studies^[15] suggest carbon black increases the formation of cross-links, whereas others^[16,17] indicates carbon black does not affect the cross-link density.

3.2 Comparison of cross-link densities between Equilibrium swelling and DST

Figure 3(a), (b) and (c) shows the cross-link densities values of **unfilled** NBR measured from equilibrium swelling method using two different solvents: toluene (μTol) and acetone (μAcet). Regardless of the solvent type, all crosslink densities increased with the vulcanization time. Similar values were observed when the compounds were vulcanized at respective t_{90} , with a small tendency of a lower

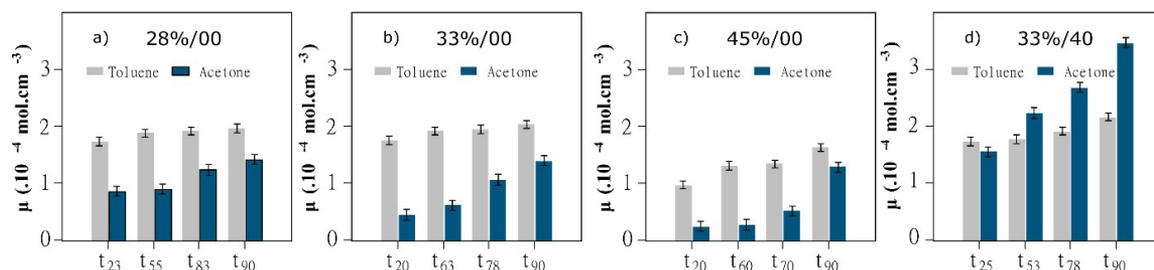


Figure 3. Cross-link densities ($10^{-4} \text{ mol.cm}^{-3}$) of unfilled NBR, (a) 28%/00, (b) 33%/00 and (c) 45%/00, and filled NBR, (d) 33%/40, cured at different times determined from Equilibrium swelling data.

value for 45%/00. The cross-link density for the different NBR samples were similar, as expected, because the same vulcanization system was employed. The same trend was also observed on the results from DST.

Figure 4a shows the scatterplot matrix with a scatterplot for each pair of the variables $[\mu]_C$, $[\mu]_T$, μ_{Tol} , and μ_{Acet} (using data from unfilled NBR) plotted against each other. Figure 4b shows the Pearson product-moment correlation coefficient plot, corr-plot, which consists of cells with the correlation coefficient of each pair of variables, as well as the p-value of each correlation coefficient in parenthesis. This was done to assess the relationship between DST and equilibrium swelling methods: as the correlation coefficient gets closer to +1 or -1 (straight line in the scatterplot), the correlation between variables gets stronger^[13]. It is important that the cross-link densities obtained with any method are correlated, because in principle they are measuring the same property. The scatterplot and the correlation plot of the variables $[\mu]_C$ and $[\mu]_T$ were not shown because they are linearly dependent by definition ($[\mu]_T = [\mu]_C + [\mu]_P$).

As shown in Figure 4b, there are strong positive linear correlation (color from orange to red) for all pairs of variables, except for “ $[\mu]_T \times \mu_{Tol}$ ”. Regarding the equilibrium swelling with toluene and acetone, μ_{Acet} produced higher correlation than μ_{Tol} , being the strongest correlation found for “ $[\mu]_C \times \mu_{Acet}$ ”. These findings are interesting for showing an agreement between the techniques and showing the importance of solvent type. It has been shown that “good” solvents, which have a better interaction with the rubber and subsequent lower interaction parameters, give more accurate results of cross-link density when using the Hildebrand equation than “bad” solvents^[2]. As the interaction parameters of NBR/acetone are lower than the NBR/toluene ones (Table 3), the use of acetone is more appropriate for NBR samples.

As for the DST, the use of $[\mu]_C$ produced higher correlation than $[\mu]_T$ with the equilibrium swelling with acetone, with correlation coefficients of approximately 0.91 for the pairs “ $[\mu]_C \times \mu_{Acet}$ ” against 0.80 for “ $[\mu]_T \times \mu_{Acet}$ ”. This shows that best variable from DST to compare the cross-link density with the equilibrium swelling is the $[\mu]_C$ and confirms the validity of using the dynamic shear method.

Figure 3(d) and (b) shows the cross-link density comparison between 33%/40 (filled rubber) and 33%/00 measured by equilibrium swelling data.

The test performed with toluene indicated that there was no appreciable difference in cross-link densities between 33%/40 and 33%/00, while the test with acetone resulted in

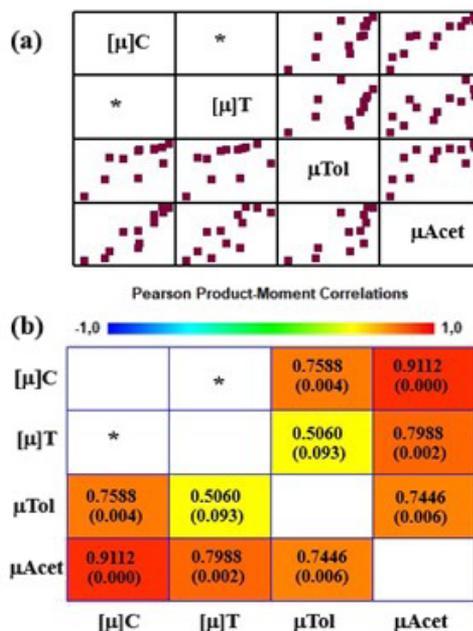


Figure 4. Correlation of variables $[\mu]_C$, $[\mu]_T$, μ_{Tol} , and μ_{Acet} by (a) Scatterplot matrix, with each variable plotted against each other; (b) Correlation plot, with each cell with the corresponding pair correlation coefficient and the p-value in parenthesis. (*) correlation between “ $[\mu]_C \times [\mu]_T$ ” was not considered because they are linearly dependent by definition ($[\mu]_T = [\mu]_C + [\mu]_P$).

higher values of CLD for 33%/40. Literature shows that the calculated CLD from carbon black filled rubber is higher than unfilled, given that the immobilized rubber next to the filler acts as a cross-link (bound rubber)^[16-20].

4. Conclusions

The cross-link density of the three grades of unfilled NBR was successfully determined using both the Dynamic Shear Test and the Equilibrium swelling method. Based on the results obtained, we could conclude:

- 1) Both dynamic shear test (DST) and the equilibrium swelling method have good correlation (correlation coefficient of ~0.91) for NBR, when using the chemical cross-link density, $[\mu]_C$, for DST and when swelling acetone instead of toluene as solvent;

- 2) Acetone as solvent for equilibrium swelling method for NBR compounds gives better results than toluene as solvent when using the Hildebrand solubility parameter to calculate the interaction parameter;
- 3) Vulcanization times did not affect the physical cross-links of the NBR compounds;
- 4) Modified Guth-Gold equation gives better results deducting carbon black effect on cross-link density than Guth-Gold Equation with Medalia correction;
- 5) Dynamic shear test method is a reliable, solventless method for calculating cross-link densities for both filled and unfilled rubber compounds, and it conducted faster than equilibrium swelling method.

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