

Determination of the Crosslink Density of Silica Filled Styrene Butadiene Rubber Compounds by different Analytical Methods

Pilar Bernal-Ortega, Rafal Anyszka, Anke Blume

University of Twente, Department of Mechanics of Solids, Surfaces & Systems (MS3), Chair of Elastomer Technology & Engineering, Faculty of Engineering Technology, 7500 AE Enschede, The Netherlands;

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ABSTRACT

The crosslink density (CLD) of rubber compounds has a great effect on the properties of the final product. For this reason, a suitable characterization method is required to understand and optimize the final performance of rubber materials. Four different experimental techniques were used to determine the crosslink density of silica filled Styrene Butadiene Rubber (SBR) composites: equilibrium swelling experiments, stress-strain measurements using the Mooney Rivlin theory, freezing point depression temperature tests and Temperature Scanning Stress Relaxation (TSSR) measurements. The evaluation of these different techniques shows that the results obtained follow a similar trend for all four methods. The results from the Mooney Rivlin and TSSR measurements correlate the best. These two techniques are the least affected by the presence of fillers and are the less time consuming ones. Furthermore, they also show the best correlation with the mechanical properties of the studied compounds.

Introduction

Rubber is characterized by its high elasticity, being capable of recover its original shape after being stretched.[1–3] This elasticity of rubber is a unique phenomenon to which many researchers have tried to find an explanation. Many models and theories have been developed in the elastomer field in order to understand the behavior of the elastomeric networks.[4–8] This unique elasticity of rubber is obtained after a curing process. In this process a three-dimensional network of crosslinks is created by loosely connecting the polymeric chains. The crosslink density mainly influences the final performance of rubber products, being a key property of rubber compounds.[9,10] There are different methods to obtain and study crosslink density. Each method has its advantages and disadvantages such as lower or higher costs or longer or shorter measurement times. However, it is important to evaluate which methods are the most reliable ones and which show the best correlation with in-rubber properties. For this reason, a detailed study and understanding of the different techniques to measure crosslink density (CLD) is of great importance.

The crosslink density (ν) is defined as the number of crosslinks per unit of volume of rubber. It is usually expressed in (number of crosslinks)/(cm³) of rubber. This parameter can be expressed also as the average molecular weight between cross-linking points (M_c). These two parameters are inversely proportional.

$$\nu \propto \frac{\rho}{M_c} \quad [\text{eq. 1}]$$

Where ρ is the rubber density.

Depending on their structure, crosslinks can be classified into carbon-carbon or sulfidic crosslinks. In the case of sulfidic crosslinks, they are classified as monosulfidic (C-S-C), disulfidic (C-S₂-C) and polysulfidic (C-S_x-C, x≥3). The type of crosslink also has a great influence on the final properties of the material.[11]

There are different techniques and methodologies to quantify and analyze the crosslink density of rubber compounds. The most common techniques used for the determination of this parameter are equilibrium swelling experiments based on the Flory-Rehner model [12] and stress-strain tests using the Mooney Rivlin approach [13,14]. However, the last few years has brought up some novel techniques such as dielectric measurements[15], low field NMR[16], differential scanning calorimetry [17–19] or temperature scanning stress relaxation (TSSR).[20–23]

The aim of this work is the comparison of different experimental techniques to determine the crosslink density of rubber compounds with the purpose to identify which method correlates in the best way with in-rubber properties. For this reason, four different techniques to obtain CLD were studied and compared, analyzing the obtained results and also their advantages and disadvantages such as price or time of the experiment. The following four approaches were chosen: equilibrium swelling experiments, stress-strain tests based on the Mooney Rivlin approach, freezing point depression temperature method and temperature scanning stress relaxation measurements. In order to analyze the effect of different silanization processes on the rubber network, different compounds were prepared using in-situ and ex-situ silanization of the silica. These compounds were compared to an unmodified silica-filled compound. In general, the crosslink density of silica filled compounds is affected by several factors: the filler-filler network, the polymer-polymer network and silica/silane/polymer coupling.

Experimental

Equilibrium swelling

The crosslink density by equilibrium swelling experiments was obtained using the Flory-Rehner equation (eq. 2) [12]. The samples were previously extracted with acetone for 24 hours. The extraction with acetone removes low molecular, non-rubber soluble substances, such as zinc salt of the accelerator and its decomposition products, zinc fatty acid soaps, antioxidants, polymerization aids, oils, etc. [24] Five vulcanized samples (~0.25 g) of each compound were swollen in 150 ml of toluene at room temperature for a period of 7 days, changing the solvent on a regular basis.

$$\nu = - \frac{\ln(1 - V_r) + V_r + \chi V_r^2}{V_0 \left(V_r^{\frac{1}{3}} - \frac{2V_r}{f} \right)} \quad [\text{eq. 2}]$$

Where ν is the crosslink density in mol/cm³, V_r is the volume fraction of rubber in a swollen sample, V_0 is the solvent molar volume, f the functionality of crosslinks ($f = 4$, assuming the formation of tetra functional crosslinks) and χ is the Flory-Huggins interaction parameter. In this work, χ was calculated by using eq. 3 [25]:

$$\chi_{12} = \frac{[V(\delta_1 - \delta_2)^2]}{RT} + 0.34 \quad [\text{eq. 3}]$$

Where V is the molar volume of the solvent, δ_1 is the solubility parameter of the rubber, δ_2 is the solubility parameter of the solvent, R is the ideal gas constant, T the temperature.

Freezing point depression

The determination of the freezing point depression temperature was carried out using a Differential Scanning Calorimetry DSC 214 Polyma, from Netzsch-Gerätebau (Selb, Germany). Small pieces of the vulcanized rubber (previously acetone-extracted), around 2x2x1.5 mm, were swollen in ~150 ml of cyclohexane for 3 days to reach the equilibrium swelling. The swollen samples were then placed into DSC pans with an excess of cyclohexane to ensure that the solvent is trapped inside the polymer network. Cyclohexane was used as solvent because it shows a clear crystallization peak in DSC and it is a good swelling solvent for SBR.[26,27,28,29] The samples were cooled until -30 °C, then the temperature was maintained for 5 min and afterwards increased until 20 °C. The cooling/heating rate was 5 °C/min under nitrogen atmosphere.

Mooney Rivlin

The determination of the crosslink density by Mooney Rivlin approach, was carried out by stress-strain essays performed in a universal testing machine Zwick Z010 (Zwick, Germany). Test specimens were 2 mm thick, with a test length of 20±0.5 mm and a width of the narrow portion of 4±0.1 mm, according to the ISO 37 (dye type 2) standard. The stress-strain essays consisted in two different steps:

- i) In the first step, the samples were pre-cycled 10 times until 200% strain at a crosshead speed of 500 mm/min. This first step is performed in order to destroy the filler network.
- ii) In the second step the specimens were stretched until a strain of 200 % at a crosshead speed of 10 mm/min.

Temperature Scanning Stress Relaxation (TSSR)

The crosslink density obtained by Temperature Scanning Stress Relaxation experiments, was measured using a TSSR instrument from Brabender Messtechnik (Duisburg, Germany). Test specimens were 2 mm thick, with a test length of 20 ± 0.5 mm and a width of the narrow portion of 4 ± 0.1 mm, according to the ISO 37 (dye type 2) standard. The experiments were performed in two steps (**Error! Reference source not found.**):

- i) In the first step the sample was placed in a heating chamber at room temperature ($T_0 = 23^\circ\text{C}$). A strain of 50% ($\varepsilon = 50\%$) was applied for 2 hours. In this first step a short time relaxation process occurs reaching a quasi-equilibrium state for the sample.
- ii) The second step starts directly after the isothermal relaxation: The 50% strained sample was heated with a constant rate of 2 K/min until reaching 100°C .

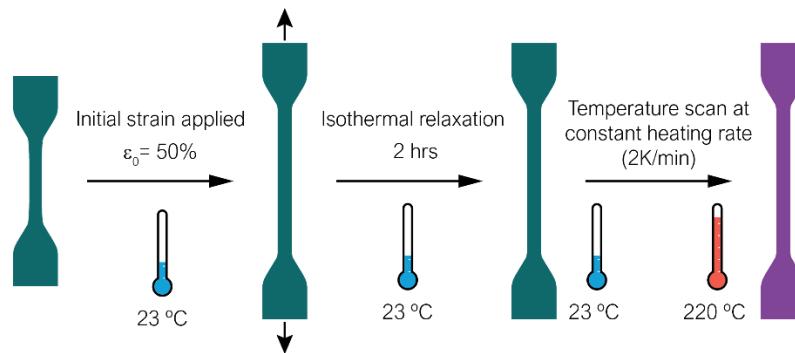


Figure 1. Schematic representation of the TSSR procedure.

Results

Expected crosslink density

According to the different interactions present in each compound (silica-rubber and silica-silane coupling and filler-filler interactions) an estimation of which samples will have a higher or a lower crosslink density was done (Table 1).

Table 1. Different interactions present in the studied rubber compounds.

Sample	Silica-rubber coupling	Silica-silane coupling	Filler -filler interactions
R1	None	None	High
R2	Medium	Medium	Medium
R3	None	Low	High
R4	Medium	Medium	Medium
R5	None	High	Low
R6	High	High	Low
R7	High	High	Low
R8	None	High	Low

Summarizing, the order of the expected CLD of the compounds from high to low is: $R6 > R7 > R4 > R2 > R8 > R5 > R3 > R1$.

Freezing point depression

The DSC freezing curves and the freezing point depression of the swollen rubber compounds are shown in Figure 2. In all DSC curves two different peaks can be observed: the peak of the free solvent and the peak of the solvent trapped in the rubber network. (Figure 2a) The depression of the freezing temperature of the solvent is clearly visible for all samples.

The sample R1 (unmodified silica) shows a relatively high freezing depression point, just lower than the compounds containing TESPD in the formulation. The lower CLD compared to these compounds (R2, R6 and R7) is caused by the absence of a bi-functional silane in R1, and therefore the non-existence of a coupling between the silica and the rubber. The covalent bonds formed due to the presence of TESPD increase the crosslink density of these compounds (R2, R4, R6 and R7) leading to a smaller mesh size. As a consequence, the crystallization of the solvent is hindered and the freezing point depression is larger. Furthermore, it can be noticed that the intensity of the peak of the trapped solvent in these samples is lower. As explained above this is caused by the smaller amount of solvent trapped in the network. However, the CLD for the sample R1 is significantly higher than expected, reaching similar values than the ones obtained for sample R4 (pre-modified with TESPD). The high freezing point depression can be explained by the presence of a mechanical or physical three-dimensional mesh formed by the strong filler-filler interactions in R1.[28,30] This mesh restricts the swelling, leading to a higher freezing point depression which assumes a higher value of crosslink density for this compound. This behavior could also explain why R4 has a lower CLD than R2. The pre-modification of the silica with TESPD in R4, led to a more effective silanization of the silica surface and consequently to a decrease in the filler-filler interactions.[27]

As expected, the samples that present the largest freezing point depression are R6 and R7, both pre-modified with TESPD and with the supplementary addition of TESPD (R6) or CA (R7) during mixing. As explained above, this result is caused by the extra addition of TESPD and CA during mixing in these compounds. This principle was followed in the sample R6: the addition of TESPD during the mixing process can cover the freshly created silica surface and couple to the polymer which results in additional covalent bonds, indicated by the highest crosslink density. For the compound R7, the addition of the covering agent during mixing covers the freshly created silica surface as well but does not couple to the rubber resulting in a lower CLD than R6.

Regarding the samples which contain covering agent (R3, R5 and R8), they present the lowest values of the freezing point depression. These results can be explained by the absence of a polymer-filler coupling and a weak filler network. The sample R8 presents an extremely low crosslink density. This result is explained by the additional covering agent added during the mixing process. As previously before, when additional covering agent is incorporated, it can cover the new freshly created silica surface reducing the interaction between particles in a higher degree. [27] In the case of R3, the small addition of CA during mixing is not sufficient to avoid filler-filler interactions. For this reason, it presents a higher CLD than R5 and R8.

Analyzing the obtained results for this method and comparing with the interactions present in each compound (Table 1), it can be concluded that the silica-rubber coupling is the interaction which has the highest impact on the CLD. This is observed in the results obtained for samples R6 and R7, that present the highest filler-rubber interactions and the highest values of CLD of all samples. However, it also can be noticed that these measurements are influenced by the filler network. This is observed in samples R1 and R3. These two samples show an extremely strong filler network and also an unexpected high CLD.

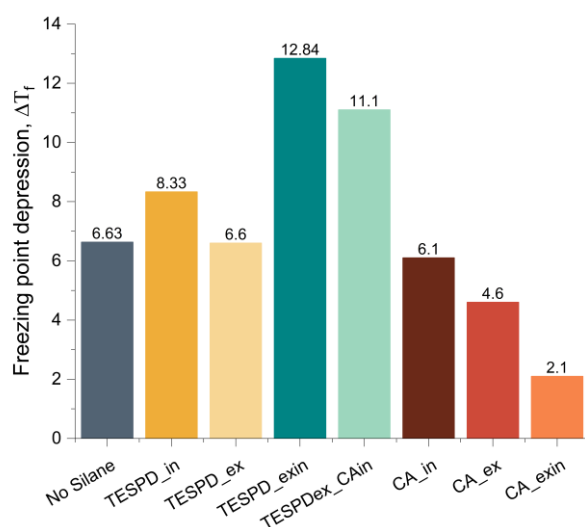


Figure 2. Freezing point depression of the compounds.

Equilibrium swelling experiments

The crosslink density of the studied compounds obtained by equilibrium swelling is shown in Figure 3. As observed in the DSC results, the sample R1 shows a higher CLD than expected, just lower than the compounds with TESPd. However, in this method the difference between R1 and R2 and R4 is much higher. This result could be caused by the filler effects on the equilibrium swelling experiments. Several investigations claimed that the presence of particles in the rubber compounds, that are non-swelling elements, can lead to a miscalculation of the crosslink density.[28, 31–33] The presence of fillers causes a restriction on the swelling behavior of rubber compounds leading to an overestimated calculated CLD. For this reason, R1 (with a strong filler network) presents a higher CLD than expected, but also R2 and R4. For compounds R2 and R4, the combination of a medium level of particle-particle interactions plus the presence of a polymer -filler coupling leads to a much higher CLD than R1. Moreover, these two samples show similar values than R6 and are superior to R7, which have an extra addition of coupling agent during mixing and therefore lower filler-filler interactions. This behavior is especially evident in sample R7, that presents the lowest value of the compounds containing TESPd. This can be explained by the much better shielding effect of the long alkyl chain of the CA compared to the TESPd. As a result, the filler-filler interactions are reduced in a higher degree in this sample.

As already observed with the freezing point depression study, samples with covering agent (R3, R5 and R8) show the lowest CLD. Again, some differences are there. R8 shows a much higher crosslink density than R5. A possible explanation for this result could be that in sample R5, the accelerators may be absorbed by the new silica surface created during mixing causing a decrease of the CLD. In sample R8 this situation is avoided by the addition of covering agent during mixing.

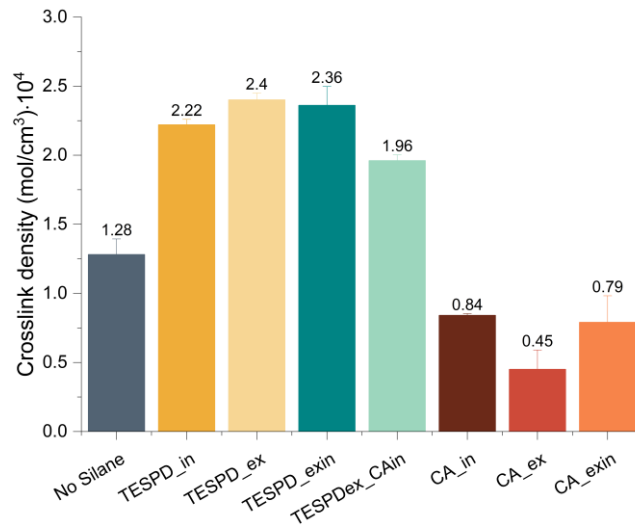


Figure 3. Crosslink density measured by equilibrium swelling experiments

Correlating the results obtained for equilibrium swelling and the interactions present in the samples (Table 1), it can be concluded that the filler-filler interactions dominate the results obtained by this swelling measurement. The samples in which these interactions are reduced (R5 and R8) have the lowest values of CLD. Furthermore, the filler effects also cause that samples R1, R2 and R4 show a higher CLD than expected. In this measurement, sample R2 and R4 reach a similar value of CLD than R6 and superior to the value obtained for sample R7.

Mooney Rivlin

The results obtained by stress-strain experiments based on the Mooney Rivlin theory are depicted in Figure 4. As observed before for DSC and swelling experiments, sample R1 shows a much higher CLD than expected. However, this result is more similar to the one obtained in the freezing point depression. Sample R1 reaches CLD values similar to R4 and R7 and just lower than R2 and R6. As discussed already for the other analyzed techniques, this result could be explained by the strong filler-filler interactions due to the absence of a coupling agent in this sample. It might be that the cyclical stretching sequence performed to destroy the filler network before the measuring of the final polymer network took place, was not sufficient in this compound or that there was a re-forming of the filler network caused by the long duration of the measurements. If this strong filler network might not be fully destroyed by the application of the stress-strain pre-cycles to the samples it can be the cause of this high value of CLD obtained for R1.

Regarding samples R2,R4,R6 and R7 (containing TESPd), they present the highest values of CLD due to the presence of covalent bonds between the silica and the rubber. Once again, sample R6 (pre-modified with TESPd + addition of TESPd during mixing) shows the highest CLD of all samples. As already explained, this is due to the new covalent bonds formed by the addition of extra TESPd during mixing. However, some differences with the other techniques can be noticed. In this Mooney Rivlin method, the results of samples R4 and R7 are approximately the same. The main difference between these samples is that R7 has lower filler-filler interactions caused by the extra addition of CA during mixing. Therefore, a possible explanation is that the CLD calculated for R4 is overestimated due to the filler effects. For this reason, sample R4 with the same level of polymer filler interactions but with a stronger filler network, reaches similar values than sample R7.

As for the samples with CA, they show the lowest crosslink density. Again, the Mooney Rivlin results for these compounds are more similar to the ones obtained by the freezing point depression.

Sample R3 shows a much higher CLD than R5 and R8, which have significantly less filler-filler interactions due to the larger content added of CA in these compounds.

As already observed for the freezing point depression and the equilibrium swelling experiments, the stress-strain experiments are also affected by the different interactions present in the compounds. The results obtained are mainly influenced by the filler-filler interactions and the presence or absence of a filler-polymer coupling. However, the filler effects seem to have here a lower impact than in the swelling experiments. In this method the interactions that seem to dominate the obtained results are the silica-rubber bonds, as it is observed by the higher CLD obtained for sample R6 (Table 1).

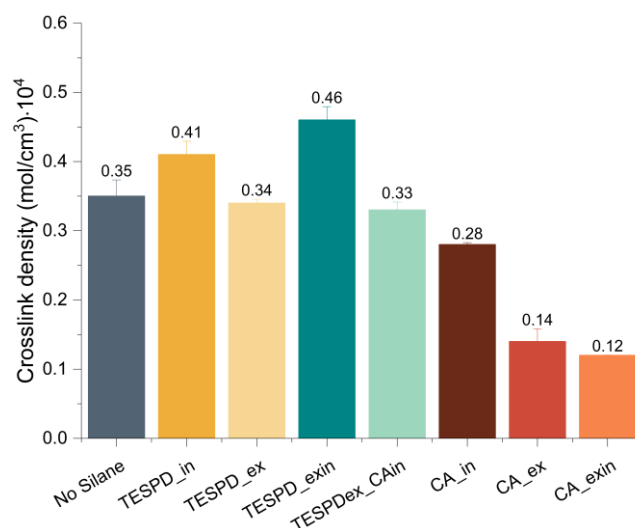


Figure 4. Crosslink density measured by stress-strain experiments using the Mooney Rivlin approach.

Temperature Scanning Stress Relaxation (TSSR)

The values of the crosslink density calculated using the data obtained from TSSR measurements are shown in Figure 5 5. It is clearly revealed that the results of this technique present similarities with the ones obtained with the other three methods. Starting with sample R1 (unmodified silica), once more a higher value of CLD than expected is reached. With this technique sample R1 presents almost the same crosslink density than sample R2 and R4, and lower than R4 and R6. As previously discussed, this behavior can be associated to the strong filler network being present in this compound that can lead to the assumption of a higher crosslink density.

Regarding the samples containing TESP (R2,R4,R6 and R7), they show the highest values of CLD. Moreover, R6 presents again the highest CLD of the studied compounds. This was observed in all studied techniques. However, again some differences can be noticed. In the TSSR results, the CLD of sample R4 is higher than those in R7 and R2. As discussed before, this outcome is the result of the effects of the different interactions present in this sample in the calculation of CLD. The sum of the influence of the filler-polymer and filler-filler interactions leads to a higher CLD than sample R7, where the filler-filler interactions are lower.

From the samples with covering agent, sample R8 presents the lowest CLD, due to the further reduction of the filler-filler interactions due to the addition of CA during mixing and the absence of a silica-rubber coupling. Sample R3 presents an unexpected high value, in this case the small amount of CA added in this compound is not sufficient enough to avoid the formation of a strong filler network.

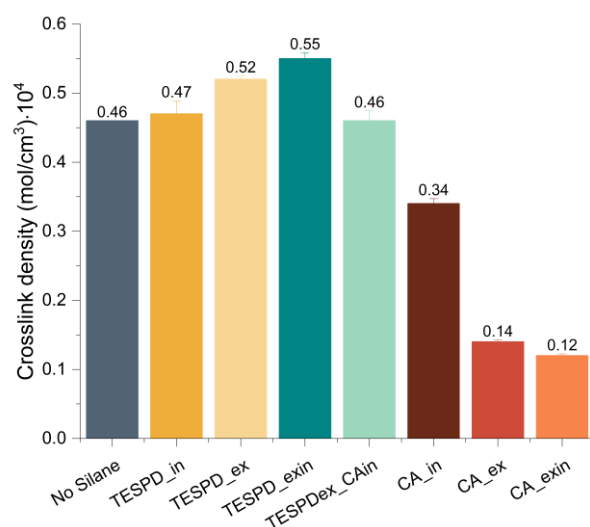


Figure 5. Crosslink density measured by TSSR experiments.

Correlation of the different techniques with in-rubber properties

In order to determine if the results of CLD calculated with each technique are in agreement with other in-rubber properties, a correlation with the modulus at 300% strain ($M_{300\%}$) and the hardness of the compounds was made. The values of R^2 obtained for each correlation are shown in Table 2.

On the one hand, the results of CLD obtained with TSSR and Mooney Rivlin show the best correlation with the hardness and the $M_{300\%}$ of the studied compounds. This outcome indicates that the CLD obtained by TSSR or Mooney Rivlin can be used as a reliable tool to predict other in-rubber properties. On the other hand, as expected, the freezing point depression and equilibrium swelling experiments results present a lower correlation to the analyzed in-rubber properties.

Table 2. Correlation of the crosslink density obtained with the different techniques with the hardness and the modulus at 300 % strain of the studied compounds.

Correlation with Hardness	R²	Correlation with M_{300%}	R²
Equilibrium swelling	0.69	Equilibrium swelling	0.77
Freezing point depression	0.53	Freezing point depression	0.59
TSSR	0.96	TSSR	0.87
Mooney Rivlin	0.83	Mooney Rivlin	0.90

Conclusions

In this work four types of experimental methods to measure the crosslink density were evaluated: equilibrium swelling, stress-strain measurements based on the Mooney Rivlin theory, freezing point depression temperature and TSSR experiments. The study of the crosslink density was performed on SBR/silica compounds prepared using in-situ and ex-situ silanization.

The analysis of this study showed that all the investigated methods are appropriate for the determination of the crosslink density of rubber compounds. It also was observed that CLD in silica

filled compounds is highly affected by different factors such as the filler-filler interactions or the type of modifying agent used. The results from all the methods present high consistency in the obtained trends for crosslink density. For all of them higher values of this parameter were obtained for the samples containing TESP in the formulation. It was also noticed that the compounds with mono-functional silane present the lower values of CLD. Moreover, in all four techniques revealed that the sample filled with unmodified silica (R1) showed a surprisingly high crosslink density. This result could indicate that the filler network has a strong influence on the calculation of this parameter.

This study also revealed some limitations in the determination of crosslink density for filled compounds. As observed by the results obtained for sample R1 (unmodified silica), all techniques were affected by the presence of strong filler network in this compound. However, this effect was more evident in the case of equilibrium swelling experiments and freezing point depression. There are some uncertainties in the experiments and calculations of the results that are related to the presence of fillers. The restriction of the swelling behavior of the samples due to the presence of particles (non-swelling elements) leads to an overestimation of the CLD using these methods. As a consequence, the values of CLD obtained with these techniques are significantly higher for samples with a strong filler network than the ones achieved with the Mooney Rivlin theory or the TSSR measurements.

Comparing the results of CLD between each technique, TSSR and Mooney Rivlin show the best correlation between each other. Moreover, they also show a good correspondence with in-rubber properties of the studied compounds. For all these reasons, it could be concluded that equilibrium swelling and freezing point depression temperature are good qualitative methods that can be used in order to compare samples with the same filler loading. For a more accurate quantitative analysis and less time consuming, stress-strain experiments using the Mooney Rivlin theory or TSSR measurements are more appropriate.

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