Probing small network differences in sulfur-cured rubber compounds by combining nuclear magnetic resonance and swelling methods

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ABSTRACT: We studied the network structure of elastomers based on polyisoprene, polybutadiene, and their blends in the narrow range of formulations compatible with actual use in the automotive tyre industry. Cross-link density (CLD) was quantified comparatively by low-field ^{1}H multiple quantum time domain nuclear magnetic resonance (MQ TD-NMR) and by equilibrium swelling technique. The robustness and agreement of the two methods was demonstrated in measuring minute alterations of unfilled vulcanizates beyond the optimum cure time. Comparison with samples where polysulfidic bonds were selectively cleaved also demonstrates that the length of the sulfur chain constituting the cross-link does not significantly affect residual dipolar coupling. Kraus, Lorenz, and Parks correction for filler restriction on swelling is validated by MQ TD-NMR, which also allows extracting information on cross-link distribution not provided by swelling measurement. Cross-link distributions in the blends were demonstrated to be significantly different from the weighted average of the pure samples, while average proton–proton residual dipolar coupling values correspond. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42700.

INTRODUCTION

The elastic and mechanical properties of rubbers are regulated by cross-links between highly mobile long polymer chains, formed in a complex chemical process called vulcanization. A full understanding of the resulting three-dimensional network structure–property relationship is still the subject of vigorous research.[1] In fact, mechanical and thermal properties of vulcanizates are influenced by the amount and distribution of cross-links[2] that in turn may depend[3] on the vulcanization system, backbone structure of the polymer, concentration of curing agents, cure temperature, etc.

Moreover, addition of fillers and blending between different polymers are commonly used in industry to fine tune the properties of materials, further complicating their analysis. Different grades of carbon black are the most commonly used fillers in tyre industries,[4,5] alone or combined with nonblack fillers.[6,7] Further opportunities are provided by the emerging class of nanofillers: nanoparticles,[8] carbon nanotubes,[9] and graphene.[10] The interaction between filler and rubber and the influence of fillers on the vulcanization reaction itself are aspects that still attract attention of researchers from both academia and indus-

try. Blending between different polymers, including natural rubber (NR), polyisoprene (IR), polybutadiene (BR), and various grades of styrene–butadiene rubber (SBR), is also widely employed to combine desired features of different polymers.[11] Properties of the blends often differ from the weighted average of component rubbers, due to the formation of different but interconnected phases[12] and to distribution of fillers and additives within them.[13] Diffusion of curatives and reaction rates are also different at different cure temperatures in BR and IR. For example, in a given blend, different cure conditions can favor the cross-linking of one polymer rather than other.[14] As a result, cross-link distribution also varies, making the characterization of cured blends particularly challenging.[15] Further options are provided by the use of compatibilizing agents[16] or by the interaction of a filler with a blend, where the partition of the particles between different phases is a factor influencing the macroscopic properties.[17]

In the presence of so many different parameters, whose control in an industrial context is subject to time and cost constraints, variations in the final properties of the material are easily introduced. Thus, there is increasing need of faster and more precise

Additional Supporting Information may be found in the online version of this article.

characterization techniques to assist the production or postproduction.

The single most important parameter for structure–property correlation is the molecular weight between cross-link junctions (M_c), which is inversely proportional to cross-link density (CLD). The most commonly used methods for the estimation of the CLD are equilibrium swelling,[18] mechanical measurements,[19] high-resolution NMR,[20] and low-resolution TD-NMR at high[21] and low field.[22] Instruments were also developed for measurement in inhomogeneous magnetic field, allowing applications also on finished products.[23]

Rheometry can analyze rubber compounds at the macroscopic level, and is thus used to determine cure parameters phenomenologically. For example, rheometric analysis of vulcanization is based on the assumption that measured torque during vulcanization reaction is proportional to the effective cross-linking.[9]

Equilibrium swelling is a widely applied technique to determine CLD of elastomer networks. This method is based on the Flory–Rehner theory of network models developed from the ideal network assumptions. These models are derived for any deformation in the network including swelling[24] caused by the absorption of solvent. The quantitative results obtained from this method always depend on the choice of model and of the thermodynamic parameters related to the polymer–solvent interaction. Erman[18] reviewed the molecular foundation of affine and phantom models in detail by comparison of several experimental techniques with theoretical predictions of real networks. Equilibrium swelling method qualitatively agrees well with any other independent method in characterizing unfilled ("gum") vulcanizates, but in case of practically important filler-reinforced rubbers, such direct agreements could not be established, especially with methods investigating the molecular level.

Even in absence of a comprehensive theoretical model on the issue of filler restrictions on swelling, Lorenz and Parks,[25] and later Kraus,[26] were able to assess the filler restriction on swelling. According to their observations on filled vulcanizates, at constant loading of given filler, the apparent number of network chains is approximately a constant multiple of the number of cross-links in the unfilled vulcanizates. This approximation is independent of network cross-link density in the unfilled vulcanizates. The constant multiple depends on the volume fraction of loaded filler and filler type. This relationship helps in evaluating physical cross-links or swelling restrictions caused by the filler in the filled vulcanizates.

NMR spectroscopy is a powerful tool for studying the structure and dynamics of a variety of polymer systems such as elastomers,[27] filled rubbers,[28] polymer melts,[29] and block copolymers.[30] The traditional transverse ^{1}H-NMR relaxation[21] was recently complemented by multiple quantum nuclear magnetic resonance method (MQ NMR), whose application to unfilled and filled rubbers was extensively described by Valentin.[31,32] The existence of cross-links or any topological constraints in the rubber matrices causes anisotropic fluctuations in the semilocal segmental level of polymer chains and generates residual dipolar couplings. The magnitude of residual dipolar coupling constant (D_{res}) can be measured by MQ NMR and is related to network microscopic parameters such as CLD, entanglement length, and the presence of other topological constraints,[33] and can be used to follow in detail the evolution of a polymer network, for example, when cross-linking is induced by radiation.[34]

The primary aim of this work is the precise determination of the CLD in sulfur-cured polyisoprene and polybutadiene networks and their blends. This was performed by applying TD-NMR to challenging tasks like following minute network evolution during over-cure period. The technique has been previously[31] tested on samples with much larger range of CLD, obtained through different amounts of sulfur rather than by modification of the same network. The effects of fillers on same compounds were also studied. Results were compared with swelling measurements, demonstrating MQ NMR can provide equivalent data with higher precision and less experimental time. Moreover, TD-NMR can provide data on cross-link distribution that are inaccessible by swelling.[35] To the authors' knowledge, there are no reports available on studying blend CLD and distribution at the microscopic level using MQ NMR. Here we took advantage of NMR for studying polyisoprene/polybutadiene blends cross-link densities compared to pure polyisoprene and polybutadiene networks prepared in similar conditions.

EXPERIMENTAL

Sample Preparation

Polyisoprene (IR) and polybutadiene (BR) rubber samples were kindly supplied by Pirelli Tyre. The label IR indicates high cis-polyisoprene (cis-1,4 content 97% min) low viscosity (Mooney viscosity (ML (1 + 4) 100°C) 70 ± 5 MU) obtained by solution polymerization with Ziegler/Natta catalyst. BR samples were high cis-polybutadiene (cis-1,4 content 97% min) low viscosity (Mooney viscosity (ML (1 + 4) 100°C) 43 ± 3 MU) polymerized by Neodymium catalysts.

Details of the sulfur-based cure recipes, including the type of carbon black (N234) used for filled samples, are given in Table I.

Compounds were prepared in an open two-roll mill using standard mixing procedure and vulcanized in pneumatic double plate press at a temperature of 170 and 150°C for unfilled and carbon black filled samples, respectively. The optimum cure time (t_{95}) was deduced from the rheometric curves (Supporting Information, Table S1).

Samples were prepared with varying cure time, starting from 7 min, which was slightly below optimal cure time for carbon black filled compounds, up to 50 min.

Rheometry

Rheometry analysis was performed on a Monsanto MDR (Moving Die Rheometer) 2000E. Cure curves were recorded for 50 min (shown in Supporting Information, Figure S1).

Equilibrium Swelling

The vulcanized rubber network CLD was determined by equilibrium swelling measurements performed in toluene solvent at temperature of 20°C. Experiments were performed also on samples

Table I. Formulation of BR and IR Compounds and Blends (Quantities are Expressed in Parts per Hundred (phr))

Sample	Polyisoprene (phr)	Polybutadiene (phr)	Carbon black N234 (phr)	Sulfur (phr)	ZnO (phr)	Stearic acid (phr)	CBS[a] (phr)
BR	–	100	–	1.2	2.5	2	2.8
IR+BR	50	50	–	1.2	2.5	2	2.8
IR	100	–	–	1.2	2.5	2	2.8
BR (CB)	–	100	50	1.2	2.5	2	2.8
IR+BR (CB)	50	50	50	1.2	2.5	2	2.8
IR (CB)	100	–	50	1.2	2.5	2	2.8

[a] N-cyclohexyl-2-benzothiazole sulfonamide, a curing accelerator.

treated with cleaving agents that break polysulfidic links, following established literature procedures.[36]

The modified Flory–Rehner equation was used to calculate the network CLD by adopting phantom model according to the eq. (1).

$$\ln(1-\Phi_r) + \Phi_r + \chi\Phi_r^2 = -\frac{\phi}{M_c}V_s(1-\frac{2}{f})\Phi_r^{\frac{1}{3}} \quad (1)$$

In this equation, M_c is the molecular weight between cross-link junctions, inversely proportional to the CLD, and Φ_r is the experimentally measured volume fraction of rubber in the swollen gel. χ = polymer–solvent (Flory–Huggins) interaction parameter depends on the volume fraction of rubber; however, in literature it is usually considered as a constant without introducing a significant error. ρ_r = density of rubber network depends on the quantity of curatives used, i.e., sulfur content, which is constant in our sulfur cured networks since the same recipe has been used for all the samples. V_s = molar volume of solvent; f=cross-link functionality. We used the values of χ=0.39 for toluene–polyisoprene rubber pair, χ=0.36 for toluene–polybutadiene,[37] $\rho_r = 0.92$ g/cm^3, $V_s = 107$ mL/mol. Cross-link functionality f was equal to 4, implying the formation of tetrafunctional cross-links.

In reporting CLD values, we considered both the statistical error of the measurement and the error due to differences in samples from different batches produced with the same nominal parameters. This last aspect is important since it was verified by forensics studies on rubber gloves of commercial origin that NMR results can vary significantly even within a single batch.[38] Thus, statistical error was evaluated by five measurements on samples prepared at the same time from the same compound, resulting in a standard deviation ±2.2% in the measured CLD. By measuring five separately cured samples with the same nominal recipe and cure time, an error of ±7% was instead determined.

In filled vulcanizates, filler particles adsorb elastomer chains and act as physical cross-links and create swelling restrictions, thus increasing the apparent CLD. In order to obtain actual chemical cross-link number, it was necessary to make the following correction (known as the Lorenz–Parks and Kraus empirical correction)[39] according to the type and volume fraction of the loaded filler:

$$\text{Actual CLD=Apparent CLD}/(1+K\emptyset) \quad (2)$$

$\emptyset$ is the volume fraction of filler in the compound, and K is the constant for given filler ($K = 4.53$ for N234 carbon black) and K is an empirical constant obtained from dibutyl phthalate

absorption (DBPA). Dibutyl phthalate absorption measures the relative structure of carbon black by determining the amount of DBP a given mass of carbon black can absorb before the so obtained DBP/CB paste reaches a specified viscosity.

TD-NMR Spectroscopy
Solid-state ^{1}H MQ NMR experiments were carried out on a Bruker Minispec mq20 system operating at a resonance frequency of 19.65 MHz with a 90° pulse length of 2.2 µs. Two rubber discs of 7 mm diameter and 3 mm height were centered in an 8 mm inner diameter glass tube. All experiments were performed at 353 K temperature, well above the glass transition, to obtain temperature-independent structural information.[31] The instrument was set to the required temperature at least 6 h prior to experiments in order to stabilize the magnetic unit temperature and reduce thermal gradients in the sample surroundings. Each sample was thermalized 10 min inside the instrument before measurement. By accumulating 128 scans and setting the recycle delay to 1 s, each MQ NMR experiment was performed in 2.5 h.

The molecular weight between cross-links junctions M_c was measured using a recent version[22] of the Baum and Pines MQ experiment.[40] Experimental data were analyzed using fast Tikhonov regularization (ftikreg) procedure[41] to obtain the average residual dipolar coupling constant (D_{res}) and its distribution. Statistical error on D_{res} was evaluated at ±0.8% on the basis of five measurements, while the error associated to measuring five separately cured samples with the same nominal recipe and cure time was estimated at ±2%.

The residual dipolar coupling constant is related to M_c according to the eq. (3).

$$M_c = \frac{A}{D_{res}/2\pi} \quad (3)$$

The constant A depends on the polymer repeating unit, and following the treatment of Ref 22 takes the values A_{BR}, A_{IR}=617, 000 $Hz \cdot g \cdot mol^{-1}$ for polybutadiene (BR) and polyisoprene (IR) networks, respectively. The defined cross-link density can be obtained from M_c from the expression $CLD = \frac{1}{2M_c}$.

RESULTS AND DISCUSSION

Cross-Link Density and Network Structure
CLD was calculated from swelling data by applying the phantom network model (eq. (1)). For all unfilled samples not
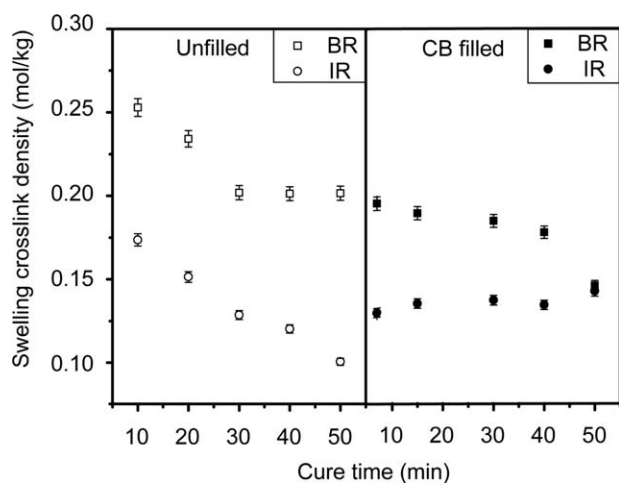
Figure 1. Cross-link density of unfilled (left) and filled (right) vulcanizates evaluated by equilibrium swelling method, and thus comprehensive of both mono, di, and poly sulfidic links. CLD in filled compounds are plotted after subtracting the filler restrictions on swelling. Since all the samples were prepared from the same compound and then cured for different times, for the error bars we used the statistical error of $\pm 2.2\%$. CLD decrease is immediately seen in unfilled samples, while filled samples have a less definite trend.

treated with cleaving agents, CLD is plotted against curing time in Figure 1. For ease of comparison, the correction indicated in eq. (2) was applied on the filled samples, which are also plotted in Figure 1.

The same calculation was performed on filled and unfilled samples treated with cleaving agents, obtaining lower cross-link values. Since cleaving agents are selective, the reduction of CLD corresponds to the quantity of polysulfidic cross-links in the pristine rubbers, as reported in Figure 2.

During cure time, both the breaking and reformation of cross-links are active (the reaction mechanism is shown in Supporting
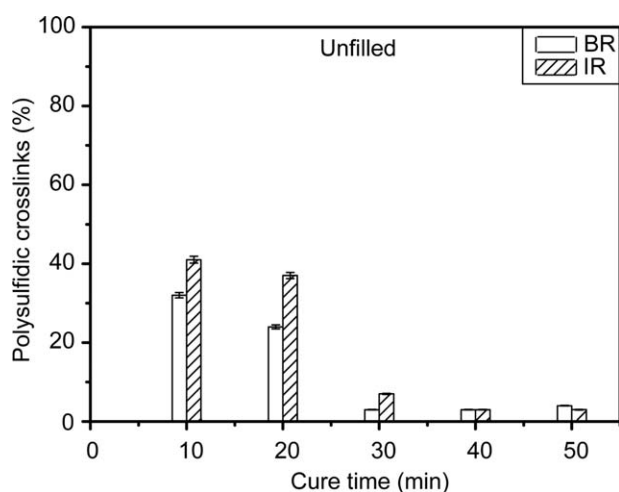

Figure 2. Percentage of cross-link density attributed to polysulfidic bonds in unfilled polybutadiene (BR) and polyisoprene (IR) vulcanizates as function of cure time. They were evaluated by difference between the swelling data of untreated and thiol/piperidine-treated samples.

Information, Figures S6 and S7). Thus, the evolution of the systems can be described as continuous breaking of less stable[1] polysulfidic links, partially or totally compensated by reforming of shorter sulfidic bridges. For example, unfilled polybutadiene network total CLD is decreasing with cure time up to 30 min, and is then almost constant up to 50 min. Polysulfidic links in the same system also decrease from a starting value of 30% to <5% within the first 30 min. Unfilled polyisoprene networks contain a higher proportion of polysulfidic cross-links relative to polybutadiene networks. Those cross-links decay from the starting value of more than 40% measured at 10 min of cure time to values of 7% at 30 min and 3% at 40 min. The overall CLD of polyisoprene networks instead decreases with cure time up to 50 min.

Thus, in BR, the evolution of CLD is dominated by breakdown of the polysulfidic bonds. When they are depleted, at 30 min, further reduction of the total CLD is difficult. In IR, the evolution of total CLD is also initially dominated by polysulfidic degradation like in polybutadiene samples. After they are depleted, lower degree polysulfidic links are also breaking.

Filled networks exhibiting higher amount of polysulfidic links at all cure times compared to corresponding unfilled compounds are shown in Figure 3. The amount of total CLD variation is minute in polyisoprene network and continuous decay is observed in polybutadiene network shown in Figure 1 (right). The constant overall CLD and at the same time decaying of polysulfidic links indicates that both the mechanisms of breaking and reformation of sulfidic links are competing in carbon black filled polyisoprene network.

TD-NMR Results and Comparison with Swelling
MQ TD-NMR measured CLD of unfilled and carbon black filled polybutadiene and polyisoprene network are shown in Figure 4 (calculation from MQ NMR raw data, performed following Ref. 41, is also exemplified step-by-step for one sample in the Supporting Information).

The values and their evolution with cure time are in agreement with equilibrium swelling method. Unfilled polybutadiene CLD is decreasing with cure time up to 30 min, and remains constant during further cure due to the presence of more stable mono–di sulfidic bridges, in agreement with Figure 2. Polyisoprene networks CLD display a trend of continuous decay. Filled polybutadiene network CLD decays throughout the range of cure time due to the predominance of breaking of sulfidic bridges over the repartication of broken sulfidic chains in cure. In filled polyisoprene compounds, the two mechanisms compete with each other, thus there is no clear tendency of decay or growth, as shown in Figure 1 (right).

A comparison between CLD measured with the two methods in unfilled polyisoprene and polybutadiene networks is shown in Figure 5.

Data are interpolated with linear functions, where slopes of polyisoprene and polybutadiene samples are 0.44 ($R^2 = 0.93$) and 0.59 ($R^2 = 0.96$), respectively. Intercepts are 0.11 and 0.09, values that differ from zero since NMR is measuring not only chemical cross-link restrictions but also physical restrictions imposed by
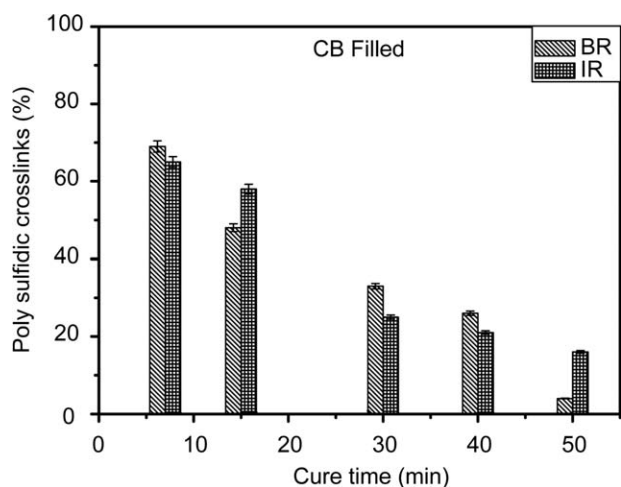
Figure 3. Percentage of polysulfidic cross-links in carbon black filled polybutadiene and polyisoprene vulcanizates as a function of cure time .They were evaluated by comparing swelling data of untreated and thiol/piperidine-treated samples.

Figure 5. Polybutadiene and polyisoprene vulcanizates cross-link density measured by equilibrium swelling and MQ TD-NMR (arrow indicates progress of cure time). The good correspondence between the two methods is indicated by the linear fitting.

entanglements that are partially released at equilibrium swelling state. This is summarized by the following relation:[31]

$$\frac{1}{M_C(\text{NMR})} + \frac{1}{M_e} \approx \frac{1}{M_c(\text{swelling})} + \frac{1}{M_{te}} \tag{4}$$

Where the mass M_e of polymer chains entanglements is less than or equal to the M_{te} (trapped entanglement).[42–44] Therefore, the y-intercept indicates a difference between total entanglements measured by the NMR and trapped entanglements present in swollen state.

This points out that mono and disulfidic links are the same in NMR point of view, despite the fact that mono and poly sulfide links can have different effects on the macroscopic mechanical properties.[45,46]

For a discussion of the validity of the correction proposed in eq. (2), uncorrected equilibrium swelling against NMR CLD of carbon black filled networks are shown in Figure 6.
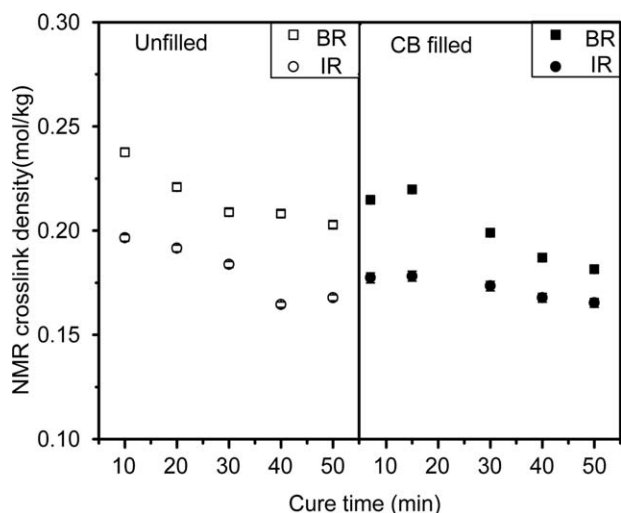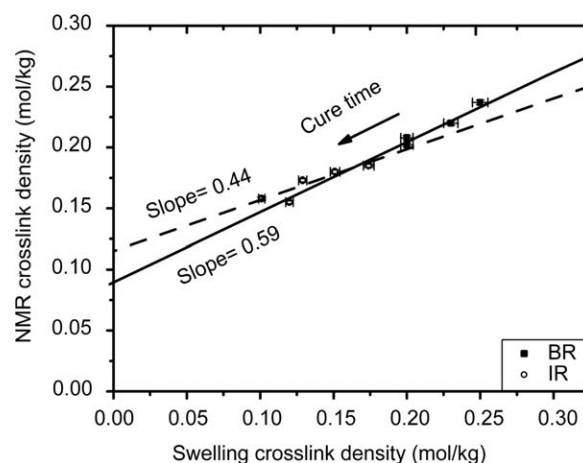

Figure 4. Cross-link density of unfilled (left) and filled (right) vulcanizates evaluated by multiple quantum NMR method and plotted versus cure time.

In filled compounds, a substantial reduction of network swelling was observed compared to corresponding unfilled networks. The reason is the adsorption of polymer chains by the filler or by meshes of filler particles glued together, as described in literature.[32] Filled samples shown in Figure 6 presented higher swelling CLD compared to corresponding unfilled sample. After subtraction of filler restrictions according to eq. (2), swelling results are in better agreement with NMR. In filled networks, the linear correlation between successive data points is absent, indicating a limitation in the estimation of very minute network differences in presence of fillers. Note that filled samples in this work actually span an even smaller range of CLD than unfilled samples. Still, corrected values are much closer to MQ TD-NMR results, corroborating the Lorenz, Parks, and Kraus relation for filler restrictions on swelling.[39] However, it should be pointed out that the Lorenz–Parks and Kraus empirical correction (eq. (2)) for filler restriction on swelling is validated with MQ-NMR measurements only for polyisoprene and polybutadiene cross-linked networks. It may not be fully valid for other elastomers.

In conclusion, linearity between swelling and NMR is obtained in unfilled networks whereas in filled networks, filler restrictions has to be subtracted to obtain better matching of the data.

Network Cross-Link Density and Distribution by TD-NMR in Blends

The calculation of CLD from the D_{res} proposed in eq. (3) is applicable to the case of single polymers with a known A parameter. For a model-free discussion of the IR/BR blend network, direct comparison of the MQ TD-NMR D_{res} is presented in Figure 7 for the blend and the component rubbers. The weighted average of the D_{res} values of the two components, calculated considering the proton % associated to each polymer, is also presented. D_{res} values are also presented in Supporting Information (Table S2 and S3). Polybutadiene displays higher residual dipolar coupling constant than the corresponding polyisoprene network. Unfilled blend D_{res} constants are very close, but always lower than the weighted average of pure
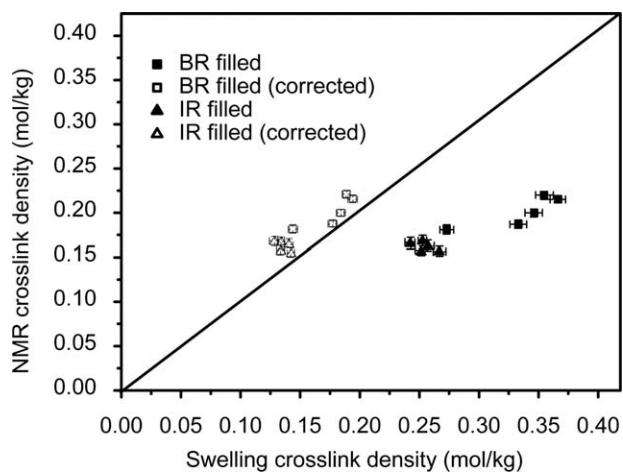
Figure 6. Carbon black filled polybutadiene and polyisoprene vulcanizates CLD measured by equilibrium swelling and MQ TD-NMR. A straight line passing through the origin having unity slope and zero intercept is displayed as guide for the eye, indicating how the filler corrected results more closely match NMR results after the correction.

components. This difference, while only marginally greater than the experimental error, can indicate preferential solubility of curatives in the polyisoprene, since the final D_{res} is shifted in the direction of the IR value. This was further validated by verifying that the D_{res} value associated to a mechanical mixture of IR and BR chunks with equivalent quantities is undistinguishable from the weighted average of the two components.

This tendency is even less pronounced in filled blends since filler influence on cure kinetics and filler adsorption affinity also differs between polymers.[35]

Analysis of MQ NMR data also provides a distribution of D_{res} values, and thus an experimental approach to measuring cross-link distribution that can be more informative on the network structure than a simple average, for example, by detecting the presence of local inhomogeneities.[47]
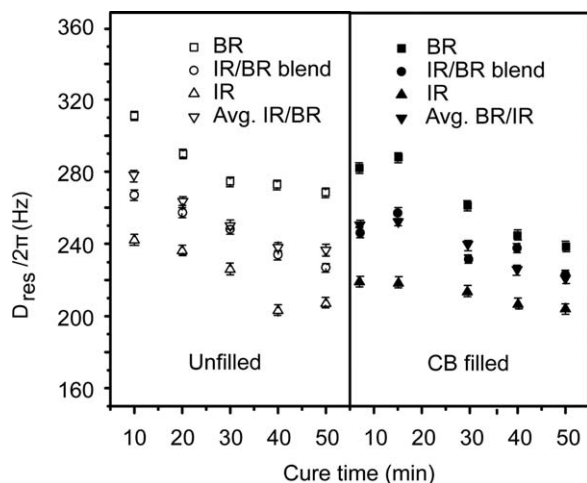

Figure 7. MQ TD-NMR measured D_{res} constants of polybutadiene (BR), polyisoprene (IR), blend (IR/BR), and weighted average of IR, BR vulcanizates networks at variable cure time. Values for blends are mostly close to the weighted average of the component rubbers.
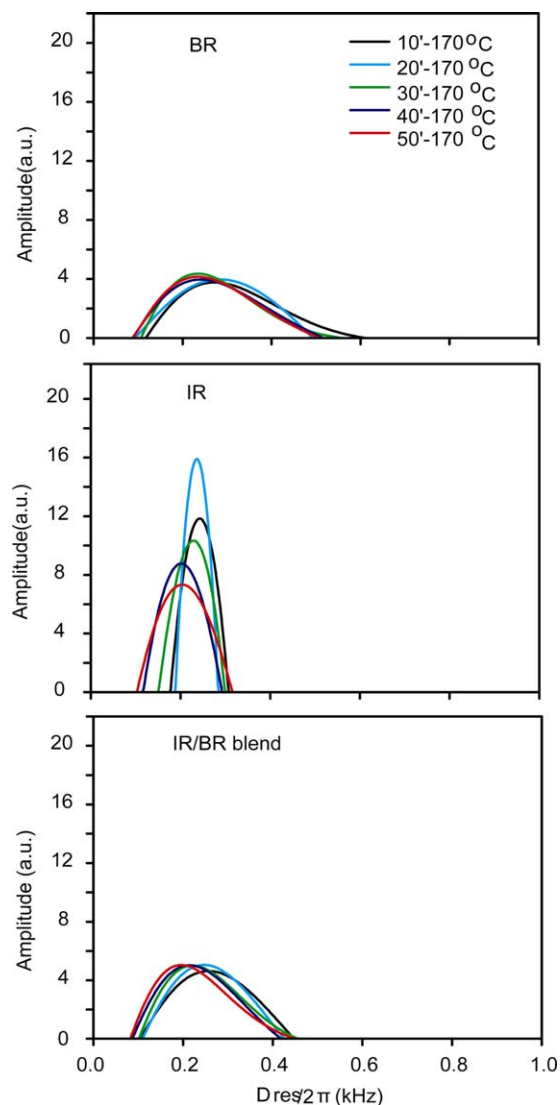

Figure 8. Over-cure effect on cross-link density distribution in unfilled polybutadiene (BR), polyisoprene (IR), and blend (IR/BR) networks. Numbers in the image legend indicate cure time and temperature, respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Sulfur-cured polyisoprene networks near the optimal cure time exhibit a narrower distribution than the corresponding polybutadiene networks under the same cure conditions as shown in Figure 8. The D_{res} distribution in blend networks is different from both pure polymer networks, with an apparently intermediate behavior.

Upon over-curing, unfilled polyisoprene changes drastically, probably due to the extensive restructuring of the greater number of polysulfidic links present. Its network D_{res} distribution becomes broader with cure time progress. The increased amplitude at low D_{res} values is evidence of chain scission, while increased amplitude at higher values is a sign of the formation of additional cross-links. Since the average is moving toward low D_{res} values, the dominant phenomenon is chain scission in agreement with the decrease of total and polysulfidic cross-links during over-cure period as shown in Figures 1 and 2,
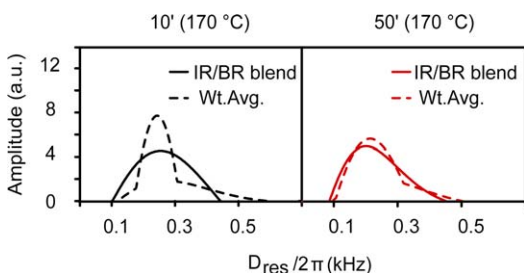
Figure 9. Over-cure effect on cross-link density distribution in blend (IR/BR) network compared with weighted average of constituting polymer networks. The cure time and temperatures are presented in the image. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

respectively. In polybutadiene rubber networks, D_{res} distribution is less affected by cure time, also in agreement with the CLD change observed by NMR and swelling methods. Filled compounds (reported in Supporting Information, Figure S2) display a slightly narrower D_{res} distribution compared to corresponding unfilled vulcanizates. Their evolution over time follows the same trends discussed for unfilled vulcanizates.

For unfilled rubbers, a direct comparison between the D_{res} distribution of the blend and the weighted average of the two components is presented in Figure 9. It is apparent that the system cannot be considered a simple juxtaposition of two separate rubbers, even though the IR/BR blend is known to present phase separation in the range of hundreds of nanometers,[48] much greater than the scale probed by MQ NMR.

A possible explanation for this observed behavior and for the average D_{res} values observed in Figure 7 involves the effect of different solubility and reactivity of curing agents in the two phases, resulting in much greater inhomogeneities even within the IR phase at low curing time.

CONCLUSIONS

In this work, we detected minute differences in network structure by TD-NMR with high precision. Errors associated to those measurements are much smaller than the corresponding values measured with swelling experiments. Moreover, the experimental time is significantly reduced, thus demonstrating the feasibility of MQ NMR as a technique for quality control in industrial context. In line with the analytical nature of this work, we set a relatively high number of accumulations. Even in these conditions, the required experimental time for cross-link measurement is limited to few hours: for actual quality-control applications, the experimental time could be further reduced by a factor of 2 or 4. Quantitatively good linear relation between two methods were observed in unfilled compounds whereas higher swelling measured CLD values are observed in carbon black filled samples, due to filler restrictions on swelling that have no equivalent at the microscopic level probed by NMR. After subtracting the filler-related restrictions on swelling results, both methods strongly agreed, thus validating the current approaches for filler correction at least in the case of conventional CB fillers. Changes occurring in the sulfur networks

beyond the optimum cure time and the distribution of cross-links are also discussed together with the effect of carbon black filler. Cross-link distribution in IR/BR polymer blends is studied by MQ TD-NMR for the first time. The comparison of residual dipolar coupling constants of blends and their distributions with those of pure components provides qualitative clues about different solubility/reactivity of curatives in the two rubbers composing the blend.

In conclusion TD-NMR is interesting in the perspective of extending the application of inexpensive, fast, and solvent-free (green) technique to quality control and day-to-day R&D purpose.

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