



**HAL**  
open science

## Solid-state NMR of vulcanized natural rubber / butadiene rubber blends: Local organization and cross-linking heterogeneities

Pierre Daniel, Cristina Coelho-Diogo, Valérie Gaucher, Grégory Stoclet, Clément Robin, Cédric Lorthioir

### ► To cite this version:

Pierre Daniel, Cristina Coelho-Diogo, Valérie Gaucher, Grégory Stoclet, Clément Robin, et al.. Solid-state NMR of vulcanized natural rubber / butadiene rubber blends: Local organization and cross-linking heterogeneities. *Magnetic Resonance Letters*, 2024, pp.200155. 10.1016/j.mrl.2024.200155 . hal-04733851

HAL Id: hal-04733851

<https://hal.sorbonne-universite.fr/hal-04733851v1>

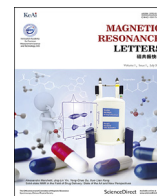
Submitted on 13 Oct 2024

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial - NoDerivatives 4.0 International License



## Research Article

# Solid-state NMR of vulcanized natural rubber / butadiene rubber blends: Local organization and cross-linking heterogeneities

Pierre Daniel <sup>a</sup>, Cristina Coelho-Diogo <sup>b</sup>, Valérie Gaucher <sup>c</sup>, Grégory Stoclet <sup>c</sup>, Clément Robin <sup>d, \*\*</sup>, Cédric Lorthioir <sup>a, \*</sup>

<sup>a</sup> Sorbonne Université, CNRS, Laboratoire de Chimie de la Matière Condensée de Paris, LCMCP, UMR 7574, 75005 Paris, France

<sup>b</sup> Sorbonne Université, CNRS, Fédération Chimie et Matériaux de Paris-Centre, FR 2482, 75005 Paris, France

<sup>c</sup> Univ. Lille, CNRS, INRAE, Centrale Lille, Unité Matériaux et Transformations, UMET, UMR 8207, 59000 Lille, France

<sup>d</sup> Hutchinson Research and Innovation Center, 45120 Châtelet-sur-Loing, France

## ARTICLE INFO

## Article history:

Received 31 July 2024

Received in revised form 26 August 2024

Accepted 3 September 2024

Available online xxx

## Keywords:

Rubbers

Blends

Cross-linking

<sup>1</sup>H solid-state NMR

Relaxation

Double-quantum NMR

Dipolar recoupling

## ABSTRACT

Elastomer blends, among which natural rubber (NR) and butadiene rubber (BR), are involved in many components of the automotive/tire industry. A comprehensive understanding of their mechanical behavior requires, among other features, a detailed description of the cross-link density in these mixtures. In the case of vulcanized immiscible blends, the distribution of the cross-link density within each of the NR- and BR-rich domains is key information, but difficult to determine using the conventional approaches used for one-component cross-linked elastomers. In this study, the vulcanization within NR/BR blends is investigated using a robust <sup>1</sup>H double-quantum (DQ) MAS recoupling experiment, BaBa-xy16. Two kinds of cross-linked NR/BR blends were considered with two different microstructures for the BR component. The bulk organization of the resulting blends was first probed by analyzing the <sup>1</sup>H spin-lattice relaxation behavior. In a second step, BaBa-xy16 was used to investigate, in a selective way, the cross-link heterogeneities within NR/BR blends. In particular, for immiscible NR/BR mixtures, the distribution of the cross-link density between both phases was compared and the observed differences were discussed.

© 2024 The Authors. Publishing services by Elsevier B.V. on behalf of KeAi Communications Co. Ltd. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

## 1. Introduction

Blending technologies have always been playing a very important role in the rubber industry [1]. Blends composed of natural rubber (NR) and butadiene rubber (BR), which stand among the most widely used blends in the rubber industry, are key components in the automotive/tire industry, including the design of tire treads and anti-vibration components displaying high mechanical performances. Blending NR with BR, this latter being introduced as a minor component, allows to improve

\* Corresponding author.

\*\* Corresponding author.

E-mail addresses: [clement.robin@hutchinson.com](mailto:clement.robin@hutchinson.com) (C. Robin), [cedric.lorthioir@sorbonne-universite.fr](mailto:cedric.lorthioir@sorbonne-universite.fr) (C. Lorthioir).

Peer review under the responsibility of Innovation Academy for Precision Measurement Science and Technology (APM), CAS.

<https://doi.org/10.1016/j.mrl.2024.200155>

2772-5162/© 2024 The Authors. Publishing services by Elsevier B.V. on behalf of KeAi Communications Co. Ltd. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

Please cite this article as: P. Daniel, C. Coelho-Diogo, V. Gaucher et al., Solid-state NMR of vulcanized natural rubber / butadiene rubber blends: Local organization and cross-linking heterogeneities, Magnetic Resonance Letters, <https://doi.org/10.1016/j.mrl.2024.200155>

both thermo-oxidative aging behavior and abrasion resistance of NR [2]. The process of materials based on elastomer blends mostly involves a vulcanization step, generally carried out using sulphur or peroxide [3,4], which allows to form covalent links between elastomer chains. The BR chain microstructure is a crucial parameter that governs the uncross-linked NR/BR blend morphology at equilibrium. *Cis*-1,4-poly(isoprene) is reported to be miscible with 1,2-poly(butadiene), due to a negative value of the Flory interaction parameter  $\chi$  [5], whereas it is considered as totally immiscible with 1,4-poly(butadiene) [6]. The situation is more complex with poly(butadiene) chains composed of *cis*-1,4-, *trans*-1,4- and 1,2-units. In this case, as the content of the poly(butadiene) chains in 1,2-units is raised up, a large increase of miscibility with *cis*-1,4-poly(isoprene) is observed, with the occurrence of a LCST phase behavior for intermediate compositions [7].

The distribution of the cross-link density is a particularly important feature of elastomer-based materials since it partly governs their elastic behavior, above their glass-transition temperature. Several experimental approaches have been proposed to determine the average cross-link density  $\bar{\nu}$  of neat vulcanized elastomers. Swelling measurements in a good solvent for the considered elastomer are one of these conventional methods. The Flory-Rehner equation may then be applied to unfilled, cross-linked elastomers to derive  $\bar{\nu}$  [8]. Another possibility relies on the use of uniaxial tensile testing. The stress-strain curves may be analyzed through the classical Mooney-Rivlin equation and the average cross-link density may be derived [9,10]. Lastly, the measurement of the storage modulus within the rubbery plateau region through dynamic mechanical analysis is also widely used since the plateau modulus is a linear function of  $\bar{\nu}$  [11].

Nevertheless, it is worth remarking that all these approaches provide the average value of the cross-link density,  $\bar{\nu}$ . Yet, for most of the vulcanization systems used industrially, cross-link heterogeneities occur within the resulting rubber materials. In such cases, the distribution of  $\nu$ , and not only its average value, is key information since it affects not only the storage modulus at rubbery plateau, but also other mechanical properties of the cross-linked elastomers, such as tensile strength and deformation at break.

In this respect, an original and robust solid-state NMR approach was developed by Saalwächter et al. in 2003 [12]. It relies on  $^1\text{H}$  multiple-quantum (MQ) NMR measurements, performed without any spinning of the sample at the magic angle (static conditions). Under appropriate temperature conditions, the analysis of the  $^1\text{H}$  double-quantum (DQ) coherence build-up curve recorded for one-component cross-linked elastomers allows to investigate the distribution of the  $^1\text{H}$  dipolar coupling,  $D_{\text{HH}}$ . In a first approach, one may consider that  $D_{\text{HH}}$  is proportional to  $\nu$  so that these measurements are a way to detect whether vulcanized rubbers exhibit a wide distribution of the cross-link density or not. If this is so, the corresponding distribution can be derived [13]. This NMR experiment is essential in the field of elastomers since it allows get a better understanding of the relationships between the network topology, probed at the macromolecular length scale, and the elastic behavior of elastomers at the macroscopic level [14,15]. Unfortunately, when applied to vulcanized mixtures of immiscible elastomers, such a  $^1\text{H}$  MQ experiment cannot lead to the distribution of the cross-link density within each of the blend phases since the  $^1\text{H}$  NMR peaks related to both kinds of chains cannot be distinguished, due to the absence of magic-angle spinning (MAS) of the sample.

In this context, the determination of the distribution of  $\nu$  in each domain of cross-linked immiscible blends requires a homonuclear DQ MAS recoupling pulse sequence [16]. In particular, the BaBa-xy16 experiment, introduced in 2011 in the literature [17], offers a robust recoupling scheme. It may be seen as a pseudo-2D NMR experiment with the  $^1\text{H}$  MAS NMR spectrum along the direct dimension and the  $^1\text{H}$  double-quantum build-up curves along the indirect dimension. The analysis of such data is conceptually similar to the one that was reported for one-component elastomers, without sample spinning [13,15], except that these build-up curves are determined for the different kinds of protons that may be distinguished in the  $^1\text{H}$  MAS NMR spectrum. In the context of vulcanized elastomer blends, one may realize that BaBa-xy16 provides a unique pathway to derive the distribution of the cross-link density, with a possible distinction between chemically distinct species and thus, between both blend phases. Such information is crucial to get a deeper knowledge of rubber mixtures. Since 2011, two reports have taken advantage of BaBa-xy16 to investigate a vulcanized blend composed of NR and styrene-butadiene rubber (SBR), with a SBR content of 50 wt % [18,19]. One of the aims of these studies was to monitor the evolution of each elastomer component under thermo-oxidative ageing and also, under artificial weathering.

In the present study, we take advantage of the  $^1\text{H}$  DQ MAS recoupling experiment, BaBa-xy16, to investigate the extent of cross-linking within NR/BR blends. The influence of the microstructure of the BR chains will be considered. Prior to these measurements, the bulk organization of the studied sulphur-cured NR/BR blends will be probed by analyzing their  $^1\text{H}$  spin-lattice relaxation functions.

## 2. Experimental section

### 2.1. Materials

The natural rubber used in this work, denoted as NR in the following, was purchased from SAPH, under the reference TSR 10CV60. Two poly(butadiene) homopolymers, characterized by two significantly different chain microstructures, were selected: Buna® CB 22 (Arlanxco), denoted as BR1, and Europrene® BR HV80 (Versalis, ENI Group), denoted as BR2. The percentage of *cis*-1,4-, *trans*-1,4- and 1,2-units for these three homopolymers was determined by  $^1\text{H}$  and  $^{13}\text{C}$  solution-state NMR ( $^1\text{H}$  single-pulse and  $^{13}\text{C}\{^1\text{H}\}$  inverse-gated-decoupling experiments). The corresponding results are gathered in Table 1.

**Table 1**

Content of *cis*-1,4-, *trans*-1,4- and 1,2-units, derived from solution-state NMR, molecular characteristics (weight-average molecular weight  $M_w$  and polydispersity  $I_p$ ), determined by size-exclusion chromatography (SEC), and glass-transition temperature  $T_g$ , obtained by differential scanning calorimetry (DSC), for NR, BR1 and BR2. The  $T_g$  values were determined using the second heating scan following a cooling step from 333 K to 123 K. Two heating/cooling rates, 20 K min<sup>-1</sup> and 100 K min<sup>-1</sup>, were used, the highest rate allowing to preventing the crystallization of BR1 during both cooling and heating ramps.

	NR	BR1	BR2
<i>cis</i> -1,4 units (mol %)	97 %	96 %	9 %
<i>trans</i> -1,4 units (mol %)	3 %	3 %	15 %
1,2 units (mol %)	0 %	1 %	76 %
$M_w$ (g.mol <sup>-1</sup> )	–	590 300	484 800
$I_p$	–	2.2	1.9
$T_g$ (K), heating rate of +100 K min <sup>-1</sup>	233 K	191 K	–
$T_g$ (K), heating rate of +20 K min <sup>-1</sup>	213 K	170 K	248 K

Blends of NR and BR1 as well as blends of NR and BR2, both composed of 30 wt % of NR, were prepared under the same processing conditions. NR and BR1 (BR2) were first mixed for 1 min at 323 K and 40 rpm, using a 390 mL net volume Haake internal mixer equipped with tangential rotors. 2,2,4-Trimethyl-1,2-dihydroquinoline antioxidant (TMQ, 2 phr), stearic acid (1 phr) and ZnO (3 phr) were then incorporated and the blend components were mixed for 3 additional minutes. Here, phr means “parts for hundred rubber” and corresponds to the weight of a given compound introduced in 100 g of rubber. In a second step, the samples were mixed at 313 K on a two-roll mill, using a 1.2:1 friction ratio with the front cylinder speed set to 12 rpm. A sulphur/*N*-cyclohexyl-2-benzothiazolesulfenamide (S/CBS) cure package was progressively incorporated and dispersed. The ratio S/CBS was set to 2/1 with a CBS content of 2 phr. Lastly, rubber blend sheets were cross-linked at 433 K, using a hydraulic press and a pressure of 180 bar. The curing time was set equal to the  $t'_{95}$  value, the specific time taken for the cure to be 95 % completed, independently measured by monitoring the time evolution of the torque during cross-linking through dynamic shear rheology.

## 2.2. <sup>1</sup>H solid-state NMR spectroscopy

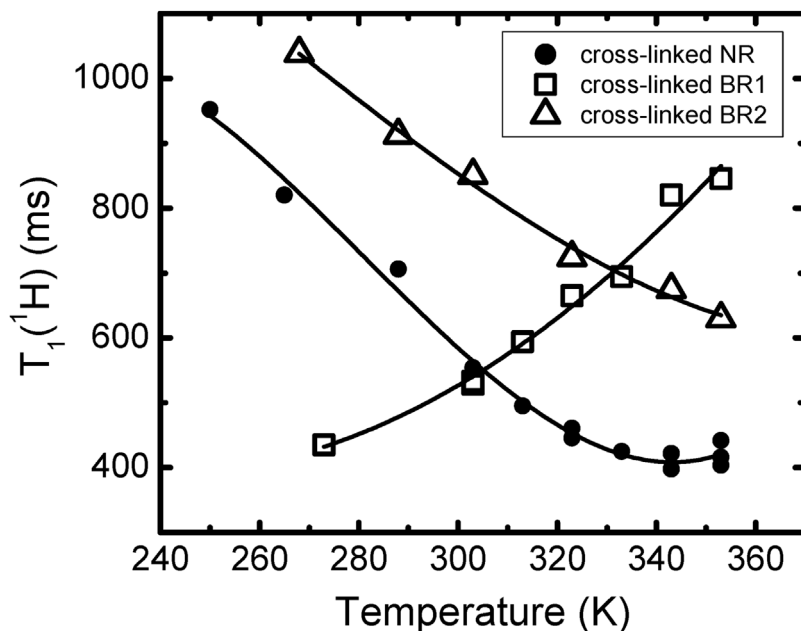
<sup>1</sup>H spin-lattice relaxation signals were measured with a 400 MHz Bruker Avance I solid-state NMR spectrometer, coupled to a NMR magnetic field of 9.4 T, and a 3.2 mm double-resonance MAS probe. The inversion-recovery pulse sequence was used to determine the  $T_1$  relaxation functions. These experiments were carried out under static conditions while the volume of the samples, collected on the sheets of vulcanized elastomer blends, was restricted to about 0.05 cm<sup>3</sup> and centered with respect to the RF coil. The 90°(<sup>1</sup>H) pulse length was equal to 4 μs and the recycle delay ranged between 4 s and 6 s, depending on the temperature between 250 K and 343 K.

<sup>1</sup>H double-quantum build-up curves were recorded under fast MAS using BaBa-xy16 as a homonuclear dipolar recoupling pulse sequence. Such measurements were carried out with a Bruker Avance III solid-state NMR spectrometer and an NMR magnetic field of 16.4 T. A 3.2 mm double-resonance MAS probe was used, allowing a sample spinning at a frequency of 20 kHz. The 90°(<sup>1</sup>H) pulse length was equal to 3.5 μs and the recycle delay was set to 6 s at 353 K. It is worth noting that the samples investigated were cryo-grinded prior to the BaBa-xy16 experiments. The <sup>1</sup>H chemical shift values were calibrated by considering adamantane as an external standard.

## 3. Results and discussion

### 3.1. Morphology of cross-linked NR/BR blends

The bulk organization of vulcanized NR/BR blends was investigated through <sup>1</sup>H solid-state NMR, more precisely, through the analysis of the <sup>1</sup>H spin-lattice relaxation in the laboratory frame. In the first step, the <sup>1</sup>H  $T_1$  relaxation function was measured, under static conditions, between 250 K and 353 K for neat NR, neat BR1 and neat BR2, these three elastomers being cross-linked using the same conditions as for the blends. For each temperature, the <sup>1</sup>H  $T_1$  decay is found to be mono-exponential and may be described by a single relaxation time,  $T_{1, NR}$ ,  $T_{1, BR1}$  or  $T_{1, BR2}$ . The temperature dependence of  $T_{1, NR}$ ,  $T_{1, BR1}$  and  $T_{1, BR2}$  for the neat cross-linked NR, BR1 or BR2, reported in Fig. 1, shows the expected evolution. In contrast to the evolution of <sup>13</sup>C  $T_1$  with temperature  $T$ , the <sup>1</sup>H  $T_1(T)$  curves cannot be described using motional models describing the local dynamics, such as the Dejean-Lauprêtre-Monnerie model [20]. Nevertheless, from a qualitative point of view, the temperature  $T_{min}$  corresponding to the minimum of the <sup>1</sup>H  $T_1(T)$ -dependence (343 K for cross-linked NR, lower than 273 K for cross-linked BR1 and higher than 353 K for cross-linked BR2) is somehow related to the temperature at which the characteristic frequency of the segmental motions matches with the <sup>1</sup>H Larmor frequency (400 MHz in the present case). As a result, the difference of  $T_{min}$  between both cross-linked elastomers NR and BR1 observed in Fig. 1 is consistent with the higher glass-transition temperature for the NR network compared to the one of the BR1 network ( $T_{g, NR}$  (DSC) = 233 K,  $T_{g, BR1}$  (DSC) = 191 K, as measured by DSC on a heating ramp at 100 K min<sup>-1</sup>). In a similar way, the  $T_1$ (<sup>1</sup>H)-data related to cross-linked NR and cross-linked BR2 are in qualitative agreement with their respective glass-transition temperature ( $T_{g, NR}$  (DSC) = 213 K,  $T_{g, BR2}$



**Fig. 1.** Evolution of the spin-lattice relaxation time  $T_1(^1\text{H})$  with temperature for cross-linked natural rubber NR, cross-linked poly(butadiene) BR1 and cross-linked poly(butadiene) BR2.

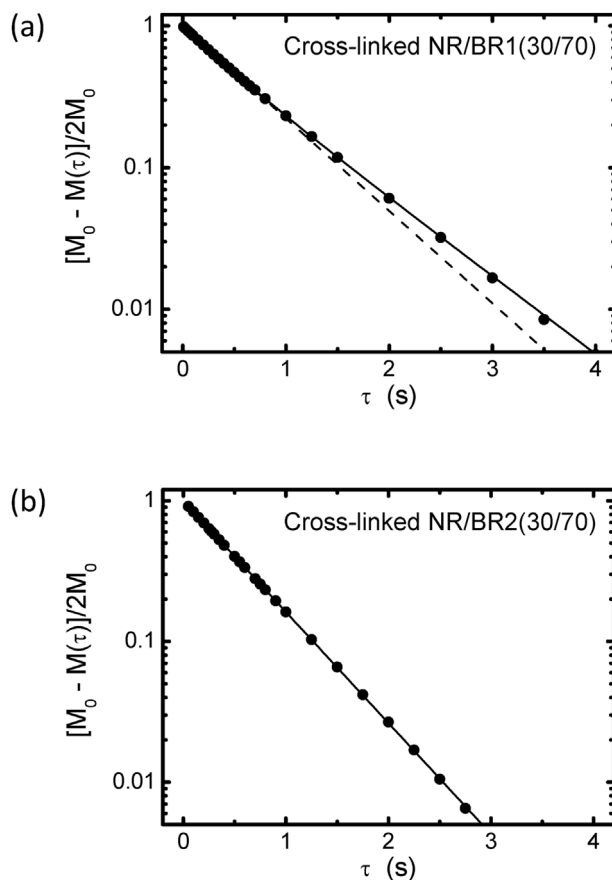
(DSC) = 248 K, as measured by DSC on a heating ramp at  $20 \text{ K min}^{-1}$ ). Lastly, Fig. 1 also shows that the high-temperature regime of the  $^1\text{H}$   $T_1(T)$  evolution is achieved between 250 K and 353 K for cross-linked BR1 while in the same temperature range, cross-linked BR2 still stands in the low-temperature regime of  $T_1(T)$ . Such an increase of  $T_{\min}$  for the BR2 network compared to the vulcanized BR1 is consistent with the higher content of 1,2-units for BR2. In the following, the  $^1\text{H}$  spin-lattice relaxation signal for a cross-linked NR/BR1 blend will be determined at the temperature corresponding to the highest difference between  $T_{1,\text{NR}}$  and  $T_{1,\text{BR1}}$ , that is to say 353 K.

The  $^1\text{H}$  spin-lattice relaxation function measured at 353 K for the vulcanized blend NR/BR1 (30/70), again under static conditions, is shown in Fig. 2(a). A deviation from a mono-exponential decay is detected and two exponential decays may be observed. This result indicates that the magnetization from the NR protons is not fully equilibrated with the one from the BR1 protons by  $^1\text{H}$ -driven spin diffusion. Therefore, the cross-linked blend NR/BR1 (30/70) should be composed of two kinds of domains characterized by a typical size higher than the length scale  $\ell$  over which  $^1\text{H}$  spin diffusion occurs during the  $^1\text{H}$   $T_1$  relaxation. The order of magnitude of  $\ell$  will be determined in the following.

For NR/BR1 (30/70), the fraction of protons from the NR (BR1, respectively) component may be estimated to 0.25 (0.75, respectively). The relaxation data reported in Fig. 2(a) were thus fitted using a bi-exponential function,  $A_S \times \exp(-\tau/T_{1,S}) + A_L \times \exp(-\tau/T_{1,L})$ , while  $A_S$  ( $A_L$ ) were constrained to the estimated fraction of NR and BR1 protons ( $A_S = 0.25$ ,  $A_L = 0.75$ ). The best fitting curve, depicted in Fig. 2(a), provides an accurate description of the experimental data and the two free parameters,  $T_{1,S}$  and  $T_{1,L}$ , were found to be about 397 ms and 794 ms, that is to say close to the values measured at the same temperature for the neat cross-linked NR and the neat cross-linked BR1. This analysis suggests that both kinds of domains evidenced by  $^1\text{H}$   $T_1$  measurements are mostly composed of NR cross-linked chains on the one hand and BR1 cross-linked chains on the other hand. This result is somehow in agreement with the fact that NR and poly(butadiene) chains with a high content of 1,4-units are considered incompatible [6,7].

The  $^1\text{H}$  spin diffusion coefficient for the NR phase,  $D_{\text{NR}}$ , may be estimated using the approach proposed by Mellinger et al. [21]. The  $^1\text{H}$  transverse relaxation signal for the cross-linked NR was recorded at 353 K using the Hahn echo experiment. As suggested in Ref. [21], this signal may be described using three relaxation components characterized by a fraction of protons  $f_i$  and a relaxation time  $T_{2,i}$ . The average  $\sum_{i=1}^3 \left( \frac{f_i}{T_{2,i}} \right)$  was then computed and led to a value of about  $0.03\text{--}0.04 \text{ nm}^2 \text{ ms}^{-1}$  for  $D_{\text{NR}}$  at 353 K. Using a similar approach,  $D_{\text{BR1}}$  was found to be approximately equal to  $0.04 \text{ nm}^2 \text{ ms}^{-1}$ . Considering the  $^1\text{H}$   $T_1$  values measured for NR/BR1, the lower limit for the characteristic size of NR (BR1) domains in the sulphur-cured blend is about  $\ell = 9\text{--}14 \text{ nm}$ .

The  $^1\text{H}$   $T_1$  relaxation was investigated for another cross-linked blend, NR/BR2 (30/70), prepared with poly(butadiene) chains displaying a different microstructure from BR1. In contrast to NR/BR1, the observed decay,  $[M_0 - M(t)]/2M_0$ , can be described at 343 K by a single exponential component (Fig. 2(b)) and, in other words, a single relaxation time  $T_1(^1\text{H})$  equal to 550 ms. This feature shows that for this sulphur-cured blend, full equilibration between the magnetization from the NR protons and the one from the BR2 protons occurs. From this point of view, this vulcanized blend may be considered miscible at a length scale given by  $\ell = (6 \times D \times T_1)^{1/2}$ ,  $D$  denoting the effective spin diffusion coefficient. As  $D_{\text{NR}} \approx 0.03\text{--}0.04 \text{ nm}^2 \text{ ms}^{-1}$



**Fig. 2.** (a)  $^1\text{H}$  spin-lattice relaxation function measured for the cross-linked blend NR/BR1 (30/70) at 353 K. The dashed line serves to illustrate the deviation from a mono-exponential decay. The solid line corresponds to the fit of the experimental data using a bi-exponential decay, performed by fixing the amplitude of both relaxation components to the proton fraction related to the NR and BR blend components. (b)  $^1\text{H}$  spin-lattice relaxation function determined for the vulcanized blend NR/BR2 (30/70) at 343 K and the corresponding fit using a mono-exponential decay (solid line).

and  $D_{\text{BR2}}$  amounts to  $0.03 \text{ nm}^2 \text{ ms}^{-1}$ , again according to Reference [21], one may consider that  $D \approx 0.03 \text{ nm}^2 \text{ ms}^{-1}$  and with  $T_1 = 550 \text{ ms}$ ,  $\ell$  is found to be of the order of 10 nm. This result is consistent with the fact that the extent of miscibility between *cis*-1,4-poly(isoprene) and poly(butadiene) gets higher as the fraction of 1,2-units along the poly(butadiene) chains increases [7]. Besides, as expected, due to spin diffusion, the unique  $^1\text{H}$   $T_1$  value should range between the relaxation time  $T_1$  determined on the neat cross-linked NR and the one obtained for the neat cross-linked BR2. More quantitatively, it should be given by the following mixing rule:

$$\frac{1}{T_1} = \frac{\phi_{\text{NR}}}{T_{1, \text{NR}}} + \frac{\phi_{\text{BR2}}}{T_{1, \text{BR2}}} \quad (1)$$

$\phi_{\text{NR}}$  ( $=1 - \phi_{\text{BR2}}$ ) standing for the fraction of protons related to the NR component in the blend. With  $\phi_{\text{NR}} = 0.25$ ,  $T_{1, \text{NR}} = 398 \text{ ms}$  and  $T_{1, \text{BR2}} = 675 \text{ ms}$  at 343 K, Equ. (1) leads to  $T_1 = 574 \text{ ms}$ , which is consistent with the value deduced experimentally for NR/BR2.

### 3.2. Cross-linking in immiscible NR/BR1 blends

The homogeneity or the heterogeneity of the cross-linking within neat elastomers may be efficiently assessed by means of  $^1\text{H}$  solid-state NMR, more precisely, using the static multiple-quantum experiment developed by Saalwächter et al. [13]. Provided significant cross-link heterogeneities occur, the distribution of the cross-link density may be additionally derived through this NMR approach. Although such an experimental approach may be applied to cured immiscible NR/BR1 blends, the assignment of the components displayed by the distribution of  $^1\text{H}$ - $^1\text{H}$  dipolar couplings  $D_{\text{HH}}$  to NR or BR1 is not possible. Indeed, despite the high extent of motional averaging, the  $^1\text{H}$  NMR single-pulse spectra of vulcanized NR/BR1 blends recorded under static conditions do not allow to resolve the contributions from the NR component and the ones from BR1. Such a



feature is illustrated in Fig. 3(a), showing the  $^1\text{H}$  NMR spectrum of NR/BR1 (30/70) obtained with a NMR magnet corresponding to a Larmor frequency of 700 MHz, without MAS. Therefore, in the case of sulphur-cured NR/BR1 blends, the analysis of the  $^1\text{H}$  multiple-quantum build-up curves recorded in the absence of Magic-Angle Spinning of the sample does not allow a selective investigation of the cross-link heterogeneities within NR-rich and BR-rich domains. As anticipated,  $^1\text{H}$  MAS NMR spectra of NR/BR1 (30/70), determined at 700 MHz and at a MAS spinning frequency of 20 kHz (Fig. 3(b)), leads to a clear resolution between the peaks related to the NR  $\text{CH}_3$  protons ( $\delta = 1.64$  ppm) and both NR and BR1  $\text{CH}_2$  protons ( $\delta = 2.06$  ppm). Moreover, under these conditions, the peaks assigned to the NR CH proton ( $\delta = 5.10$  ppm) and the BR1 CH protons ( $\delta = 5.35$  ppm) are also well-resolved. The  $^1\text{H}$ - $^1\text{H}$  dipolar couplings  $D_{\text{HH}}$  related to the NR and BR cross-linked elastomers are quite weak (a few hundreds of Hz) which are easily averaged out to zero by MAS. In this context, a double-quantum (DQ) homonuclear recoupling MAS NMR technique should be used to record the  $^1\text{H}$  DQ build-up curves for the protons related to NR and BR1 domains, in a selective manner. Here, the BaBa-xy16 pulse sequence, proposed by Saalwächter et al. in 2011 [17], was selected. Indeed, beyond the distribution of the  $D_{\text{HH}}$  values, leading to the distribution of the cross-link density, this approach allows the fraction of repeat units involved in the elastically-active chains to be quantified. Such a possibility relies on the measurement of the evolution of the reference signal,  $S_{\text{Ref}}$ , with the  $^1\text{H}$  DQ excitation time,  $t_{\text{DQ}}$ , in addition to the  $^1\text{H}$  DQ build-up curve,  $S_{\text{DQ}}(t_{\text{DQ}})$ , where  $S_{\text{Ref}}$  corresponds to all the magnetization which has not evolved into  $(4n + 2)$ -quantum coherences.

Representative  $S_{\text{DQ}}(t_{\text{DQ}})$  and  $S_{\text{Ref}}(t_{\text{DQ}})$  evolutions collected at  $\delta(^1\text{H}) = 5.10$  ppm (CH, NR component) and  $\delta(^1\text{H}) = 5.35$  ppm (CH, BR component) for NR/BR1 (30/70) using the BaBa-xy16 pulse sequence are shown in Figure S1. These experiments were carried out at 353 K. For both kinds of methine groups, the contribution to  $S_{\text{Ref}}(t_{\text{DQ}})$  from CH protons characterized by  $D_{\text{HH}} = 0$  Hz was identified as a slow-relaxing mono-exponential decay that may be observed on  $[S_{\text{Ref}}(t_{\text{DQ}}) - S_{\text{DQ}}(t_{\text{DQ}})]$  for long  $t_{\text{DQ}}$  values. Such a component was then subtracted from  $S_{\text{Ref}}(t_{\text{DQ}})$ , thus leading to the corrected  $S_{\text{Ref, corrected}}(t_{\text{DQ}})$ . From a physical point of view, such protons related to  $D_{\text{HH}} = 0$  Hz correspond to extractables and chain portions with a free extremity. The fraction of repeat units involved in elastically-active chain portions may thus be deduced from the ratio  $f_{\text{EAC}} = [S_{\text{Ref}}(0) - S_{\text{Ref, corrected}}(0)]/[S_{\text{DQ}}(0) + S_{\text{Ref}}(0)]$ . Besides, the distribution of the  $^1\text{H}$  dipolar coupling  $D_{\text{HH}}$ ,  $P(D_{\text{HH}})$ , may be derived from the normalized DQ build-up curve,  $I_{\text{DQ}}(t_{\text{DQ}})$ , defined as the ratio  $S_{\text{DQ}}(t_{\text{DQ}})/S_{\text{Ref, corrected}}(t_{\text{DQ}})$ , aimed at removing the  $^1\text{H}$  relaxation effects affecting  $S_{\text{DQ}}(t_{\text{DQ}})$ . Following the correction of  $S_{\text{Ref}}(t_{\text{DQ}})$  from the isotropic contribution and the normalization of  $S_{\text{DQ}}(t_{\text{DQ}})$  (Figure S1), the  $I_{\text{DQ}}(t_{\text{DQ}})$  curves reported in Fig. 4 were obtained at 353 K for the CH protons from the NR phase and the ones from the BR-rich domains. Under these conditions,  $f_{\text{EAC}}$  was found to be equal to 95 % for the NR component and 97 % for the BR one.

Before analyzing the cross-linking in both kinds of blend domains, the BaBa-xy16 experiment was performed at various temperatures between 303 K and 353 K. As NR/BR1 (30/70) was found to be immiscible (see section 3.1), these experiments were performed on neat cross-linked BR1 and neat cross-linked NR. The corresponding raw data  $S_{\text{DQ}}(t_{\text{DQ}})$  and  $S_{\text{Ref}}(t_{\text{DQ}})$ , shown in Figure S2(a), were processed as described above and the comparison of the resulting  $I_{\text{DQ}}(t_{\text{DQ}})$ -curves is shown in

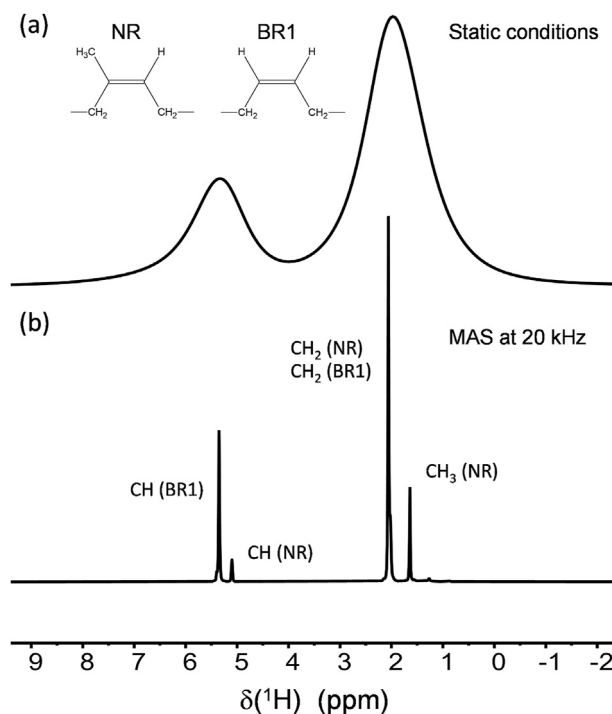
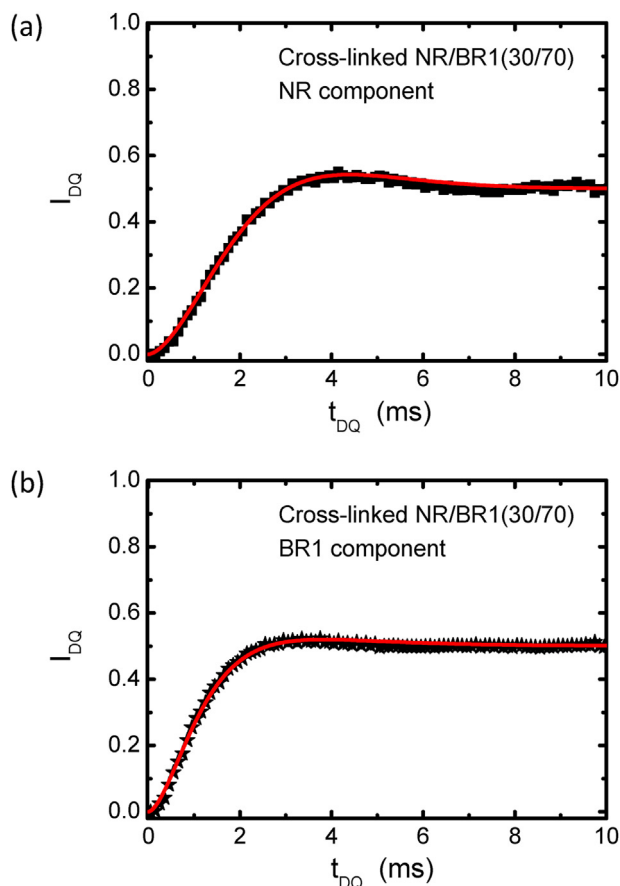


Fig. 3.  $^1\text{H}$  NMR single-pulse spectrum (700 MHz) obtained for NR/BR1 (30/70) at 323 K: (a) under static conditions; (b) at a MAS spinning frequency of 20 kHz.



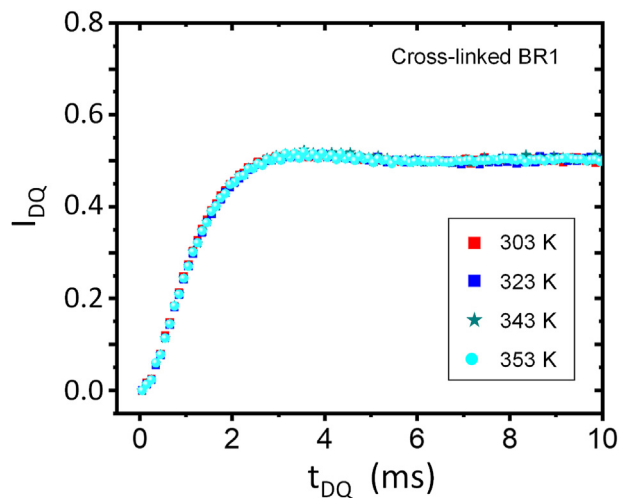
**Fig. 4.**  $^1\text{H}$  normalized DQ build-up curves,  $I_{\text{DQ}}(t_{\text{DQ}})$ , derived from the BaBa-xy16 pulse sequence carried out at 353 K for the cross-linked blend NR/BR1 (30/70). The data were collected at the  $^1\text{H}$  NMR peak at (a)  $\delta(^1\text{H}) = 5.10$  ppm (CH, NR), (b)  $\delta(^1\text{H}) = 5.35$  ppm (CH, BR1). The MAS spinning rate was set to 20 kHz. The solid line stands for the fit of the experimental data based on equation (2) combined with a log-normal distribution of  $D_{\text{HH}}$ .

Fig. 5 for the BR1 network. All the normalized growths of the  $^1\text{H}$  DQ coherences are found to be superimposed in the considered temperature range. The same behavior was obtained for the NR network prepared under the process conditions described in section 2.1. The corresponding results, obtained with BaBa-xy16, are depicted in Figure S2(b) and Figure S3. This feature indicates that for both elastomers, the reorientational motions related to their  $\alpha$ -relaxation are characterized by short correlation times compared to the  $t_{\text{DQ}}$  values. At the same time, it also implies that the fluctuations of the vectors connecting the chain portion extremities, defined by cross-links or entanglements, may be considered as frozen over the  $t_{\text{DQ}}$  time scale, between 303 K and 353 K. These data are in agreement with  $^1\text{H}$  MQ NMR measurements reported in the literature, which evidenced that  $I_{\text{DQ}}(t_{\text{DQ}})$  does not vary any longer with temperature being 50 K above the glass-transition  $T_g$  for cross-linked natural rubber and cross-linked poly(butadiene) with 98 % of *cis*-1,4 units [22]. As the vulcanized NR/BR1 blends considered in this study are composed of NR-rich and BR1-rich phases, the evolution of  $I_{\text{DQ}}$  with  $t_{\text{DQ}}$  is also expected to be unchanged around 353 K and thus, may be interpreted in terms of the extent of cross-linking within the blend domains.

At this stage, it is worth noting that despite the BaBa-xy16 experiments were performed at a MAS spinning frequency of 20 kHz, the  $I_{\text{DQ}}(t_{\text{DQ}})$  curves display the expected plateau value at 0.5 for long excitation times  $t_{\text{DQ}}$ . Such a feature might suggest that under the experimental conditions used, the influence of sample deformation induced by MAS on the normalized  $^1\text{H}$  DQ build-up curves may be neglected, in a first approximation [18]. This behavior was observed for the neat vulcanized elastomers NR, BR1 and BR2 (Figure S3, Fig. 5 and Figure S4) and for the cured blend NR/BR1 (30/70) (Fig. 4). Moreover, for this later, the  $I_{\text{DQ}}(t_{\text{DQ}})$  variations recorded using BaBa-xy16 experiments performed at two different MAS spinning frequencies, 20 kHz and 10 kHz, were found to be very similar (Figure S5), again indicating that deformations of the cross-linked NR/BR1 (30/70) blend by fast MAS does not play a major role in the shape of  $I_{\text{DQ}}(t_{\text{DQ}})$ , derived for both NR and BR components.

The  $^1\text{H}$  DQ build-up curve  $I_{\text{DQ}}(t_{\text{DQ}})$  related to the NR domains of the NR/BR1 (30/70) could not be satisfactorily fitted using the following expression [17]:





**Fig. 5.** Temperature evolution of  $I_{DQ}(t_{DQ})$  monitored for cross-linked BR1, using BaBa-xy16, between 303 K and 353 K. The data were collected at  $\delta(^1\text{H}) = 5.35$  ppm, assigned to the BR1 CH proton.

$$I_{DQ}(t_{DQ}) = \frac{1}{2} \left\{ 1 - \exp \left[ - (0.295 D_{HH} t_{DQ})^{1.5} \right] \times \cos(0.455 D_{HH} t_{DQ}) \right\} \quad (2)$$

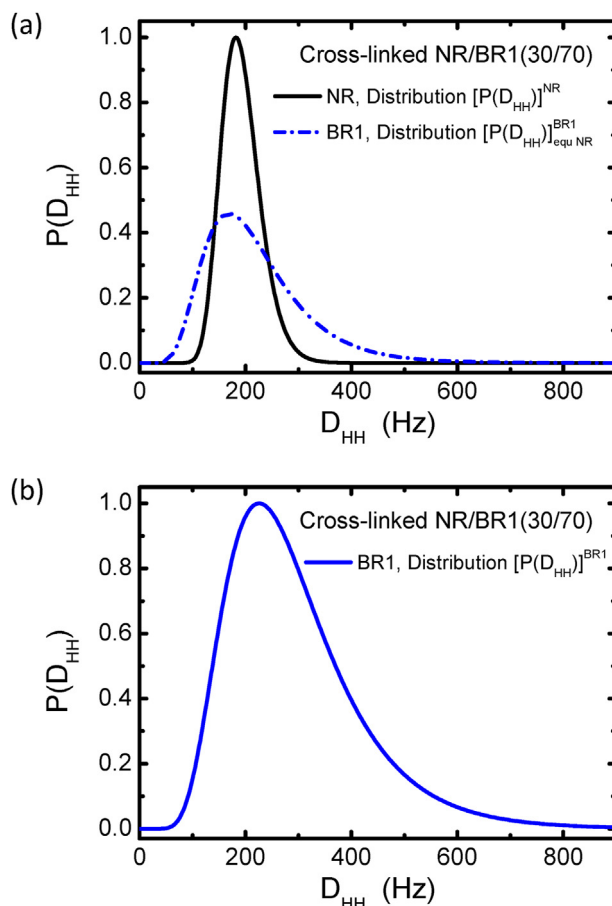
which assumes a very narrow distribution of the  $^1\text{H}$  dipolar coupling  $D_{HH}$ . A distribution of  $D_{HH}$ ,  $P(D_{HH})$ , and thus, of the cross-link density  $\nu \propto D_{HH}$  should be introduced. A log-normal  $P(D_{HH})$ :

$$P(D_{HH}) = \frac{1}{\sigma\sqrt{2\pi}} \frac{1}{D_{HH}} \exp \left[ - \frac{(\ln D_{HH} - \ln D_{HH,0})^2}{2\sigma^2} \right] \quad (3)$$

with  $D_{HH,0} = 189$  Hz and  $\sigma = 0.19$  is found to provide an accurate description of  $I_{DQ}(t_{DQ})$  recorded for the NR protons, as shown in Fig. 4(a). The corresponding distribution, depicted in Fig. 6(a), is characterized by a mean  $D_{HH}$  value of 192 Hz and displays a nearly-symmetric shape. From another point of view, as for the NR domains of NR/BR1 (30/70), equation (2) fails to fit the normalized  $^1\text{H}$  DQ build-up curve of the protons from the BR1 domains of the same blend. As for the NR blend component, a distribution  $P(D_{HH})$  is required and again, a log-normal distribution of  $D_{HH}$  with  $D_{HH,0} = 269$  Hz (mean  $D_{HH}$  value of 294 Hz) and  $\sigma = 0.42$ , shown in Fig. 6(b), allows to account for the  $I_{DQ}(t_{DQ})$  measured for the BR1 domains of the vulcanized blend. In contrast to the NR component, the use of a symmetric shape for  $P(D_{HH})$  does not lead, in this case, to a satisfactory description of the experimental data. These results indicate that the sulphur-based cross-linking leads to heterogeneous networks within both kinds of blend domains, NR-rich phase and BR1-rich phase. In order to go further into the comparison of the distribution of the cross-link density between both components, the difference in the constant of proportionality  $K$  between  $D_{HH}$  and the molecular weight between cross-links  $M_c$  for NR and BR1 should be taken into account. Previous reports in the literature [13,22] showed that  $K$  was estimated to  $K_{NR} = 617$  Hz kg mol $^{-1}$  for natural rubber and to  $K_{BR} = 656$  Hz kg mol $^{-1}$  for *cis*-1,4-poly(butadiene). The  $D_{HH}$  components ( $D_{HH}^{BR1}$ ) involved in the distribution  $[P(D_{HH})]^{BR1}$  determined for the cross-linked BR1 domains were converted according to the following equation:

$$\left( D_{HH}^{BR1} \right)_{\text{equ NR}} = \left( D_{HH}^{BR1} \right) \times \frac{K_{NR}}{K_{BR}} \times \frac{M_{ru}^{BR1}}{M_{ru}^{NR}} \quad (4)$$

$M_{ru}^{NR}(M_{ru}^{BR1})$  corresponds to the molecular weight of the NR (BR1) repeat unit.  $K_{BR}$  was used here since BR1 is composed of 96 mol % *cis*-1,4-units. Such a scaling allows to replace any  $D_{HH}^{BR1}$  value related to a BR1 elastically-active chain by the equivalent  $D_{HH}$ , denoted as  $(D_{HH}^{BR1})_{\text{equ NR}}$ , that would be measured for a NR network chain having the same number of repeat units between the cross-links/entanglements at its extremities. Therefore, equation (4) may be considered as a way to plot the distribution of the  $^1\text{H}$  dipolar coupling that would be obtained for cross-linked NR domains with the same network topology as the one determined for the BR1-rich phase,  $[P(D_{HH})]^{BR1}$ . The resulting  $[P(D_{HH})]_{\text{equ NR}}^{BR1}$ , depicted in Fig. 6(a), displays differences with the symmetric distribution  $[P(D_{HH})]^{NR}$  experimentally derived for the NR component of NR/BR1 (30/70). In particular, the average  $D_{HH}$  value for  $[P(D_{HH})]_{\text{equ NR}}^{BR1}$  (220 Hz) is somehow higher than the one obtained for  $[P(D_{HH})]^{NR}$  (192 Hz). More importantly,  $[P(D_{HH})]_{\text{equ NR}}^{BR1}$  is much broader than  $[P(D_{HH})]^{NR}$  and in particular, displays an extension towards the high  $D_{HH}$  values.



**Fig. 6.** Distribution of the  $^1\text{H}$  dipolar coupling,  $P(D_{HH})$ , determined for the NR-rich (a) and BR-rich (b) domains of NR/BR1 (30/70). In (a), the dash-dotted line corresponds to  $[P(D_{HH})]^{BR1}_{equ NR}$  (see text for more details).

Here, it should be reminded that sample deformation effects under MAS, which were reported to result in a possible broadening of the distribution of the  $^1\text{H}$  dipolar coupling measured by BaBa-xy16 [18], were not found to play a significant influence on the  $^1\text{H}$  normalized build-up curves determined for the cryo-grinded materials investigated in this study. Therefore, the significant broadening of the distribution of  $[P(D_{HH})]^{BR1}_{equ NR}$  compared to  $[P(D_{HH})]^{NR}$  should be essentially interpreted in terms of a wider distribution of the cross-link density for the BR1-rich domains of NR/BR1 (30/70) than for the NR-rich ones. Nevertheless, one should also mention that the conversion of the distribution  $[P(D_{HH})]^{BR1}$  into  $[P(D_{HH})]^{BR1}_{equ NR}$ , aimed at a comparison of the network topology in the NR- and BR1-phases, relies on the constants of proportionality  $K_{NR}$  and  $K_{BR}$ . Due to the uncertainty on the determination of these later [13,22], the differences between  $[P(D_{HH})]^{NR}$  and  $[P(D_{HH})]^{BR1}_{equ NR}$  should be taken with care and interpreted more from a qualitative than from a quantitative point of view. Of course, such a limit resulting from the uncertainty on  $K_{NR}$  and  $K_{BR}$  would not be encountered if the distributions  $[P(D_{HH})]^{NR}$  or  $[P(D_{HH})]^{BR1}$ , derived using BaBa-xy16 for vulcanized NR/BR1 blends prepared under different conditions (composition, cross-linking system), were compared.

In summary, the vulcanization system and the process conditions used in this study (section 2.1) lead to a high fraction of repeat units involved in elastically-active chains, for both NR-domains ( $f_{EAC} = 95\%$ ) and BR1-domains ( $f_{EAC} = 97\%$ ). Nevertheless, the density of topological constraints (cross-links or trapped entanglements) is, on average, slightly higher and more widely distributed in the BR1 phase than in the NR one. In particular, the NMR data suggest the presence of zones within the BR1 domains that contain much more constrained chain portions than for the NR component. One may note, in particular, the occurrence of  $D_{HH}$  components in  $[P(D_{HH})]^{BR1}_{equ NR}$  that are not present in  $[P(D_{HH})]^{NR}$ , the ones above about 300 Hz (Fig. 6(a)). At least three possible reasons may be proposed to rationalize these results. First, the intrinsic difference in the cross-linking kinetics between NR and BR1 could be invoked. Indeed,  $t'_{95}$  measured for neat BR1 (about 23 min, under the conditions described in section 2.1) was found to be higher than the one determined for neat NR (about 10 min). Therefore, a lower extent of the cross-linking process within the BR1 domains of the blend could be proposed to explain the stronger heterogeneities of the density of topological constraints, compared to the ones in the NR domains. However, the percentage of repeat units contributing to the elastically-active chains is similar for both NR and BR1 phases ( $f_{EAC} = 95\%$  and  $97\%$ , respectively). For this reason, the results of Fig. 6(a) should not be explained by such a kinetic argument. Second, one may

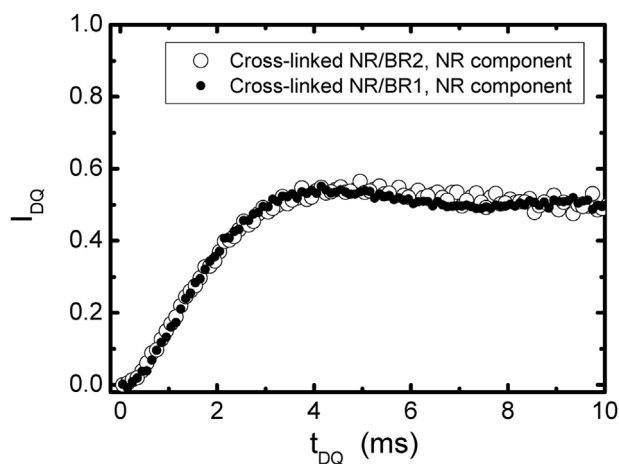
propose that the vulcanization system (sulphur and/or CBS) does not display the same local concentration within the NR- and BR1-regions of NR/BR1 (30/70): a higher concentration in the BR1-domains could account for the observed NMR results. Lastly, as the average number of repeat units between two entanglements for BR chains,  $N_e$ , depends on its microstructure [23], additional rheological measurements were carried out on the NR and BR1 elastomers considered in this work (data not shown). It turns out that  $N_e$  for BR1 is about 1.8 times lower than  $N_e$  for NR. As a result, the density of entanglements trapped during the vulcanization could lead to a higher fraction of strongly constrained chain portions in the BR1 domains, thus contributing to the extension of  $[P(D_{HH})]_{\text{equ}}^{\text{BR1}} \text{ NR}$  towards the high  $D_{HH}$  values.

### 3.3. Cross-linking in NR/BR2 blends

BR2 is composed of a significant fraction of 1,2-units (76 mol %) and as a result, this poly(butadiene) is expected to display a higher glass-transition temperature than the one of BR1. DSC measurements indeed led to a  $T_{g, \text{BR2}}$  (DSC) value equal to 248 K, using a heating ramp at  $20 \text{ K min}^{-1}$ , that is to say higher than the one determined for the neat cross-linked NR with the same heating ramp ( $T_{g, \text{NR}}$  (DSC) = 213 K). BaBa-xy16 experiments were carried out on the neat cross-linked BR2 between 323 K and 353 K and the resulting normalized  $^1\text{H}$  double-quantum build-up curve remains unchanged in this temperature range, as shown in Figure S4. As the analysis of the  $^1\text{H}$   $T_1$  relaxation signal suggests that NR and BR2 are miscible over a length scale  $\ell$  estimated about 10 nm, the glass-transition temperature of NR/BR2 (30/70) should be lower than the one from neat vulcanized BR2. Under these conditions, performing BaBa-xy16 measurements at 353 K on NR/BR2 (30/70) ensures to stand in the temperature-independent regime for  $I_{\text{DQ}}(t_{\text{DQ}})$ .

The  $I_{\text{DQ}}(t_{\text{DQ}})$ -curve deduced for NR/BR2 (30/70) at 353 K was obtained for both NR and BR2 components of the vulcanized blend. In the framework of this study, attention will be paid to the analysis of the results deduced for the NR chains only. Indeed, to the best of our knowledge,  $^1\text{H}$  DQ NMR experiments for vulcanized 1,2-poly(butadiene), performed either under static conditions or under MAS, were not reported until now in the literature. In particular, the constant of proportionality between  $D_{\text{HH}}$  and the molecular weight  $M_c$  is not known for this elastomer, thus preventing attempts to compare  $I_{\text{DQ}}(t_{\text{DQ}})$  for BR2 in NR/BR2 (30/70) with  $I_{\text{DQ}}(t_{\text{DQ}})$  derived for BR1 in NR/BR1 (30/70). In contrast, Fig. 7 shows the comparison of  $I_{\text{DQ}}(t_{\text{DQ}})$  determined for NR in NR/BR2 (30/70) to the one obtained for NR in NR/BR1 (30/70). Surprisingly, both normalized  $^1\text{H}$  DQ build-up curves are superimposed, as can be seen in Fig. 7.

Kawahara et al. reported that blends of 50 wt % of poly(isoprene) with a high content of 1,4-units and 50 wt % of poly(1,2-butadiene-co-1,4-butadiene) with 76 mol % of 1,2-units, as for BR2, were miscible between 248 K and 474 K [24]. Under these conditions, the uncured mixture NR/BR2 (30/70) would be in the single-phase state and NR chain portions should be, on average, surrounded by three BR2 chain portions, according to the lack of specific interactions between 1,4-isoprene and 1,2-butadiene units [25] and the blend composition. One may thus expect the vulcanization of the NR chains within such an environment to lead to a distribution of the cross-link density significantly differing from the one that would be obtained for NR chains surrounded by like-chains, as is the case for the immiscible blend NR/BR1 (30/70). However, such a feature was not observed experimentally. Based on the result shown in Fig. 7, one could be tempted to consider that the cross-linking of the NR chains in NR/BR2 (30/70) occurs in NR-rich domains having a characteristic size high enough to form a network topology similar as the one formed in the NR-domains of NR/BR1 (30/70). Such a hypothesis, which would allow to rationalize the result shown in Fig. 7, may imply that the uncross-linked NR/BR2 (30/70) displays a Lower Critical Solution Temperature (LCST) behavior. In this case, during the heating step of the uncured NR/BR2 up to the vulcanization temperature (433 K), an



**Fig. 7.**  $^1\text{H}$  normalized DQ build-up curve,  $I_{\text{DQ}}(t_{\text{DQ}})$ , obtained at 353 K for the NR component of the cross-linked blend NR/BR2 (30/70). The measurements derived from the NR domains of NR/BR1 (30/70) were recalled for the sake of comparison. These data were collected at  $\delta(^1\text{H}) = 5.10 \text{ ppm}$  (CH, NR), using the BaBa-xy16 pulse sequence.

onset of phase-separation would indeed lead to the formation of NR-rich domains, the growth of which being limited and even, stopped, by the cross-linking process. Their characteristic size should be lower than about 10 nm, as evidenced by the analysis of the  $^1\text{H}$   $T_1$  experiments on the cross-linked mixture NR/BR2 (30/70). Roland et al. mentioned that 1,4-units in poly(1,2-butadiene-*co*-1,4-butadiene) could result in a reduced miscibility and the occurrence of a LCST for the blends with *cis*-1,4-poly(isoprene) [25]. For fractions of 1,4-units lower than 15 mol %, the resulting mixtures were found to be miscible within the accessible temperature ranges whereas at 59 mol % of 1,4-units, phase separation was observed above around 50 °C [26]. Nevertheless, such a behavior was not detected by Kawahara et al. for fractions of 1,4-units lower than 53 mol %, as above-mentioned [24]. Along this line, the results obtained here for the vulcanized blend NR/BR2 (30/70) using the experiment BaBa-xy16 call for complementary investigations to get a better understanding of the phase diagram displayed by the uncross-linked NR/BR2 mixtures and thus, the mixture morphologies obtained after curing.

#### 4. Conclusion

Though of considerable industrial importance, vulcanized NR/BR blends are challenging materials to be characterized in several respects. Part of the difficulty stands in the close chemical structure of the corresponding repeat units, particularly between NR and BR 1,4-units. Nevertheless,  $^1\text{H}$  solid-state MAS NMR at high field provides the opportunity to differentiate the contributions of the NR protons from the ones related to the BR protons in cross-linked NR/BR blends. In this context, the  $^1\text{H}$  double-quantum MAS recoupling pulse sequence BaBa-xy16 is a powerful approach to investigate the effect of vulcanization for each component of NR/BR blends.

In the present study, blends prepared with 70 wt % of poly(butadiene) chains displaying different microstructures were considered.  $^1\text{H}$   $T_1$  relaxation measurements under static conditions were used to assess the extent of miscibility between NR and BR components within the cross-linked blends. Poly(butadiene) with a high content of *cis*-1,4 units (96 mol %) leads to a sulphur-cured NR/BR blend with a two-phase morphology composed of NR-rich and BR-rich domains, as expected. The distribution of the cross-link density in the corresponding NR-rich and BR-rich regions was then derived using the BaBa-xy16 pulse sequence. The density of topological constraints is found to be, on average, slightly higher in the BR phase than in the NR one and also, significantly more distributed. In particular, local BR regions with a higher density of cross-links/entanglements were detected in comparison to the NR phase of the same blend. As the fraction of 1,2-units is raised up to 76 mol %, NR and BR chains are found to be miscible at a length scale of about 10 nm. In this case, the BaBa-xy16 approach indicates a similar distribution of cross-links/entanglements for the NR chains as the one determined for the NR domains of the vulcanized immiscible blend, suggesting a possible onset of temperature-induced phase separation for the uncured mixture during the blending process.

For cross-linked immiscible NR/BR blends, the study of the influence of the BR microstructure, the blend composition and the process conditions on the distribution of the topological constraint density, as determined by BaBa-xy16, should lead to a deeper knowledge of the relationships between the preparation conditions of the cured blends and their mechanical behavior.

#### CRedit authorship contribution statement

**Pierre Daniel:** Investigation, Validation, Visualization, Writing – original draft. **Cristina Coelho-Diogo:** Resources, Data curation. **Valérie Gaucher:** Validation, Funding acquisition. **Grégory Stoclet:** Validation, Funding acquisition. **Clément Robin:** Conceptualization, Resources, Writing – review & editing, Funding acquisition. **Cédric Lorthioir:** Conceptualization, Validation, Writing – original draft, review & editing, Funding acquisition.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Acknowledgement

The authors acknowledge the financial support from the French National Research Agency (ANR) [grant number ANR-22-CE06-0031]. They are extremely grateful to Delphine Machin for her support in the blend preparation. They also thank Florence Lim for her assistance in some of the solid-state NMR measurements.

#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.mrl.2024.200155>.

## References

- [1] P.J. Corish, 12 - elastomer blends, in: J.E. Mark, B. Erman, F.R. Eirich (Eds.), *Sci. Technol. Rubber*, second ed., Academic Press, San Diego, 1994, pp. 545–599, <https://doi.org/10.1016/B978-0-08-051667-7.50017-2>.
- [2] B. Rodgers, A. Halasa, Compounding and processing of rubber/rubber blends, in: A.I. Isayev (Ed.), *Encycl. Polym. Blends*, first ed., Wiley, 2011, pp. 163–206, <https://doi.org/10.1002/9783527805242.ch4>.
- [3] Y. Ikeda, 4 - understanding network control by vulcanization for sulfur cross-linked natural rubber (NR), in: S. Kohjiya, Y. Ikeda (Eds.), *Chem. Manuf. Appl. Nat. Rubber*, Woodhead Publishing, 2014, pp. 119–134, <https://doi.org/10.1533/9780857096913.1.119>.
- [4] X. Liu, T. Zhou, Y. Liu, A. Zhang, C. Yuan, W. Zhang, Cross-linking process of *cis*-polybutadiene rubber with peroxides studied by two-dimensional infrared correlation spectroscopy: a detailed tracking, *RSC Adv.* 5 (2015) 10231–10242, <https://doi.org/10.1039/C4RA13502D>.
- [5] C.A. Trask, C.M. Roland, A nearly ideal mixture of high polymers, *Macromolecules* 22 (1989) 256–261, <https://doi.org/10.1021/ma00191a048>.
- [6] S. Kawahara, Natural rubber based non-polar synthetic rubber blends, in: *Nat. Rubber Mater.*, 2013, pp. 195–212, <https://doi.org/10.1039/9781849737647-00195>.
- [7] M. Bahani, F. Lauprêtre, L. Monnerie, NMR and DSC investigations of the miscibility of blends of *cis*-1,4-polyisoprene with polybutadienes of different microstructures, *J. Polym. Sci., Part B: Polym. Phys.* 33 (1995) 167–178, <https://doi.org/10.1002/polb.1995.090330202>.
- [8] P.J. Flory, J. Rehner, Statistical mechanics of cross-linked polymer networks I. Rubberlike elasticity, *J. Chem. Phys.* 11 (1943) 512–520, <https://doi.org/10.1063/1.1723791>.
- [9] P. Tanasí, M. Hernández Santana, J. Carretero-González, R. Verdejo, M.A. López-Manchado, Thermo-reversible crosslinked natural rubber: a Diels-Alder route for reuse and self-healing properties in elastomers, *Polymer* 175 (2019) 15–24, <https://doi.org/10.1016/j.polymer.2019.04.059>.
- [10] T. Ha-Anh, T. Vu-Khanh, Prediction of mechanical properties of polychloroprene during thermo-oxidative aging, *Polym. Test.* 24 (2005) 775–780, <https://doi.org/10.1016/j.polymertesting.2005.03.016>.
- [11] C. Hiranobe, G. Ribeiro, G. Barrera, E. Reis, F. Cabrera, A. Job, L. Paim, R. dos Santos, Cross-linked density determination of natural rubber compounds by different analytical techniques, *Mater. Res.* 24 (2021), <https://doi.org/10.1590/1980-5373-mr-2021-0041>.
- [12] K. Saalwächter, P. Ziegler, O. Spycykerelle, B. Haidar, A. Vidal, J.-U. Sommer, <sup>1</sup>H multiple-quantum nuclear magnetic resonance investigations of molecular order distributions in poly(dimethylsiloxane) networks: evidence for a linear mixing law in bimodal systems, *J. Chem. Phys.* 119 (2003) 3468–3482, <https://doi.org/10.1063/1.1589000>.
- [13] K. Saalwächter, Proton multiple-quantum NMR for the study of chain dynamics and structural constraints in polymeric soft materials, *Prog. Nucl. Magn. Reson. Spectrosc.* (2007) 1–35, <https://doi.org/10.1016/j.pnmrs.2007.01.001>.
- [14] A. Vieyres, R. Pérez-Aparicio, P.-A. Albouy, O. Saneau, K. Saalwächter, D.R. Long, P. Sotta, Sulfur-cured natural rubber elastomer networks: correlating cross-link density, chain orientation, and mechanical response by combined techniques, *Macromolecules* 46 (2013) 889–899, <https://doi.org/10.1021/ma302563z>.
- [15] K. Saalwächter, Multiple-quantum NMR studies of anisotropic polymer chain dynamics, in: G.A. Webb (Ed.), *Mod. Magn. Reson.*, Springer International Publishing, Cham, 2018, pp. 755–781, [https://doi.org/10.1007/978-3-319-28388-3\\_59](https://doi.org/10.1007/978-3-319-28388-3_59).
- [16] M.J. Duer, Dipolar coupling: its measurement and uses, in: *Solid-State NMR Spectrosc. Princ. Appl.*, John Wiley & Sons, Ltd, 2001, pp. 111–178, <https://doi.org/10.1002/9780470999394.ch3>.
- [17] K. Saalwächter, F. Lange, K. Matyjaszewski, C.-F. Huang, R. Graf, BaBa-xy16: robust and broadband homonuclear DQ recoupling for applications in rigid and soft solids up to the highest MAS frequencies, *J. Magn. Reson.* 212 (2011) 204–215, <https://doi.org/10.1016/j.jmr.2011.07.001>.
- [18] A. Karekar, K. Oßwald, K. Reincke, B. Langer, K. Saalwächter, NMR studies on the phase-resolved evolution of cross-link densities in thermo-oxidatively aged elastomer blends, *Macromolecules* 53 (2020) 11166–11177, <https://doi.org/10.1021/acs.macromol.0c01614>.
- [19] A. Karekar, C. Schickanz, M. Tariq, K. Oßwald, K. Reincke, V. Cepus, B. Langer, K. Saalwächter, Effects of artificial weathering in NR/SBR elastomer blends, *Polym. Degrad. Stabil.* 208 (2023) 110267, <https://doi.org/10.1016/j.polymdegradstab.2023.110267>.
- [20] R. Dejean de la Batie, F. Lauprêtre, L. Monnerie, Carbon-13 NMR investigation of local dynamics in bulk polymers at temperatures well above the glass-transition temperature. 3. *cis*-1,4-Polybutadiene and *cis*-1,4-polyisoprene, *Macromolecules* 22 (1989) 122–129, <https://doi.org/10.1021/ma00191a024>.
- [21] F. Mellinger, M. Wilhelm, H.W. Spiess, Calibration of <sup>1</sup>H NMR spin diffusion coefficients for mobile polymers through transverse relaxation measurements, *Macromolecules* 32 (1999) 4686–4691, <https://doi.org/10.1021/ma9820265>.
- [22] K. Saalwächter, B. Herrero, M.A. López-Manchado, Chain order and cross-link density of elastomers as investigated by proton multiple-quantum NMR, *Macromolecules* 38 (2005) 9650–9660, <https://doi.org/10.1021/ma051238g>.
- [23] C. Liu, J. He, E. van Ruymbeke, R. Keunings, C. Bailly, Evaluation of different methods for the determination of the plateau modulus and the entanglement molecular weight, *Polymer* 47 (2006) 4461–4479, <https://doi.org/10.1016/j.polymer.2006.04.054>.
- [24] S. Kawahara, S. Akiyama, A. Ueda, Miscibility and LCST behavior of polyisoprene/poly(*cis*-butadiene-co-1,2-vinylbutadiene) blends, *Polym. J.* 21 (1989) 221–229, <https://doi.org/10.1295/polymj.21.221>.
- [25] D.W. Tomlin, C.M. Roland, Negative excess enthalpy in a van der Waals polymer mixture, *Macromolecules* 25 (1992) 2994–2996, <https://doi.org/10.1021/ma00037a033>.
- [26] C.M. Roland, C.A. Trask, Miscible elastomer mixtures, *Rubber Chem. Technol.* 62 (1989) 896–907, <https://doi.org/10.5254/1.3536282>.



**Pierre Daniel** has graduated from the Ecole Nationale Supérieure de Chimie de Rennes, a “French Grande Ecole”, since 2021. After two fixed-term contracts as a research engineer in Cargill and Avignon University, he is currently pursuing his Ph.D degree at Sorbonne University in the framework of a collaborative work with the Center of Research and Innovation of Hutchinson (Montargis) and the University of Lille. His research interests focus on understanding the relationships between the morphology of elastomer blends and their mechanical behavior, with a particular focus on the cross-linking phenomena, mostly investigated by solid-state NMR.



**Clément Robin** received his master's degree in Polymer Material Science from Pierre and Marie Curie University in Paris and his Ph.D. in Polymer Chemistry from Paris-East University in 2016. From 2017 to 2023, he served as an R&D Project Manager at the Hutchinson Research and Innovation Center, where he specialized in rubber formulation. Since November 2023, Clément has taken on the role of Rubber Materials Specialist within Hutchinson's Fluid Management Systems business unit. His primary focus is the development of rubber compounds for applications such as fuel, air conditioning, and dielectric cooling hoses. His research is dedicated to advancing the understanding of rubber nanocomposite structures through innovative characterization methods, exploring the dynamics and rheology of both uncross-linked and cross-linked rubbers, and investigating the thermo-oxidative behavior of rubber materials.



**Cédric Lorthioir** defended his Ph.D thesis at the University of Paris-South XI (now named as "Paris-Saclay University") in 2001, under the guidance of Prof. Bertrand Deloche. After a post-doctoral stay in the research group of Prof. Juan Colmenero at the University of the Basque Country (San Sebastián), he became a CNRS researcher at the East Paris Institute of Chemistry and Materials Science, in the group of Prof. Françoise Lauprêtre, in 2003. In 2018, he joined the Laboratory of Condensed Matter Chemistry at Sorbonne University, in Paris. His research aims at investigating the polymer dynamics within bulk materials in order to get a better understanding of their macroscopic (mostly mechanical/rheological) properties. His research activities mostly rely on the use of solid-state NMR.