UNIVERSITÀ DEGLI STUDI DI MILANO BICOCCA Ph.D. COURSE IN MATERIALS SCIENCE



# Nuclear Magnetic Resonance: structural characterization of polymers and biochars

Risonanza magnetica nucleare: caratterizzazione strutturale di polimeri e biochars

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«My friend: the deeper you dig into science, the more troublesome it gets»

«No, dude: that is life»

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### ABSTRACT

Nuclear magnetic resonance (NMR) spectroscopy is a powerful tool to investigate inner properties of matter and it is used for both fundamental and applied research. If not-zero nuclear spins are embedded in a magnetic field, a detectable magnetization is formed. Its subsequent manipulation allows the study of scientifically interesting microscopic parameters: they can mostly be correlated to macroscopic properties which need to be tuned for industrial applications.

On top, polymer science and porous media research exploit NMR peculiarities a lot. Particularly, low-field (LF) time domain (TD) <sup>1</sup>H-NMR can provide valuable information about bulk, nanostructured and polymer films rapidly, accurately and cheaply. Additionally, NMR-active noble gases combine their almost null reactivity with a high sensitivity to the local environment: they are effective probes to check the presence of pores, their dimensions and degree of accessibility.

Firstly, since theories link the NMR-accessible residual dipolar coupling constants ( $D_{res}$ ) and their distribution to macroscopic crosslink density (CLD) of vulcanized elastomers, LF TD <sup>1</sup>H-NMR was used to evaluate the CLD of polyisoprene/polybutadiene (IR/BR) rubber blends at their optimum curing time. Compared to the ideal case where the two homopolymers evolve independently, small but still significant experimental differences in  $D_{res}$  values suggesting the vulcanizing agents may act differently on the two polymer phases were collected. Introducing new experimental variables (experimental temperature, different vulcanization times) we tried to enhance a single phase only and measure their CLD separately: if ever enhanced, CLD differences in the two phases were however below the technique sensitivity. Additionally, a direct evaluation of the  $D_{res}$  distributions and CLD on IR, BR single-polymer rubber vulcanized at different times in undercuring conditions was performed. The compared analysis of NMR and equilibrium swelling data allowed to propose a new model for rubber network growth with time: the crosslinks are not formed randomly in the sample, but instead islands with a precise morphology are formed and then they merge together.

LF TD <sup>1</sup>H NMR techniques were applied on polymeric nanostructured systems as well. On top, changes in measured T1 values can be correlated to the activation of different molecular motions. Mostly, we investigated the T1 change in oxygenfree divinylbenzene (DVB)-crosslinked polystyrene (PS) nanoparticles (NPs) due to temperature and different amount of crosslinker: we eventually differentiated the collective motion of the main chain from the PS and DVB phenyl rings ones. Similarly, a precise quantification of the amount of protons which are rigid  $(f_r)$  and mobile was performed on poly(n-butylacrylate)/polystyrene (PBA/PS) core-shell NPs. A  $f_r$  temperature-dependent study and its direct comparison with the synthesis conditions at temperatures far away from both PS and PBA glass transition temperatures proved the two phases of PBA/PS NPs behaved as two independent homopolymers. Again, a comparison of the experimental  $f_r$  values with the theoretical ones of two and three-components BEVA ®731-replacement mixture for cultural heritage applications helped understanding the improved adhesive properties of the three-components mixture over the two-components ones: only in this case a perfect miscibility was obtained.

Lastly, high-field <sup>129</sup>Xe NMR was applied to study the morphology of differently activated pecan and almond shells-based biochars: on top, 1D conventional and pressure-dependent spectra proved the biochars structure is porous with an average dimensions of around 10 Å. T1 and 2D exchange measurements probed the pores accessibility. It strongly depended on the activation conditions: only the pecan-based biochars cured with the higher airflow or the longer-cured, rain-washed almondbased ones showed <sup>129</sup>Xe exchange, proving them effective as filtration systems.

#### SOMMARIO

La risonanza magnetica nucleare (NMR) è una tecnica spettroscopica basata sull'induzione di una magnetizzazione macroscopica ottenuta applicando un campo magnetico: la sua manipolazione permette di studiare grandezze fisiche microscopiche in diretta correlazione con proprietà macroscopiche di interesse applicativo. L'NMR nel dominio del tempo (TD) a bassi campi (LF), in particolare, trova possibilità applicative nella scienza dei polimeri poiché permette di studiare sistemi *bulk*, nanostrutturati o a film in maniera rapida, accurata ed economica. La loro reattività quasi nulla e la loro elevata sensibilità all'ambiente circostante rendono i gas nobili NMR-attivi delle sonde efficaci per lo studio delle dimensioni e dell'accessibilità di eventuali strutture porose.

Dal momento che, a partire da misure LF TD <sup>1</sup>H-NMR delle distribuzioni delle costanti di accoppiamento dipolari residue  $(D_{res})$  è possibile calcolare la densità di reticolo (CLD) macroscopica di elastomeri reticolati, si sono analizzate miscele di poliisoprene/polibutadiene (IR/BR) vulcanizzate all'optimum curing time. Quando queste vengono paragonate con la situazione ideale (in cui le due fasi sono indipendenti l'una dall'altra), sono state misurate differenze nei valori di  $D_{res}$  che suggeriscono come gli agenti vulcanizzanti agiscano diversamente nelle due fasi. Con l'introduzione di nuove variabili sperimentali (temperatura sperimentale e tempi di vulcanizzazione), si è cercato di mettere in evidenza una sola delle due fasi e misurare la CLD della stessa: è emerso che, nel caso in cui sia presente, l'esaltazione della singola fase è inferiore alla sensibilità minima dell'NMR. Inoltre, è stato condotto uno studio analogo su campioni di IR e BR vulcanizzati in condizioni di undercuring. Un'analisi comparata dei dati NMR e di equilibrium swelling ha suggerito l'introduzione di un nuovo modello descrittivo per la formazione del reticolo polimerico: i punti di reticolazione non si formano in maniera casuale nello spazio ma si originano isole (morfologicamente uguali) che si fondono l'una con l'altra.

Oltre che ad elastomeri *bulk*, le tecniche LF TD <sup>1</sup>H-NMR sono state applicate a sistemi polimerici nanostrutturati. Poiché i cambiamenti dei tempi di rilassamento T1 sono correlabili con l'attivazione di diversi moti molecolari, abbiamo studiato come i T1 di nanoparticelle (NP) di polistirene (PS) reticolate mediante divinilbenzene (DVB), in assenza di ossigeno, subiscano variazioni in funzione della temperatura e della quantità di reticolante utilizzata: si sono potuti distinguere i moti di traslazione delle catene polimeriche da quelli di rotazione degli anelli fenilici del DVB e del PS.

Le tecniche LF TD <sup>1</sup>H-NMR hanno permesso la misura della frazione di protoni rigidi  $(f_r)$  in NP core-shell di poli(n-butilacrilato)/polistirene (PBA/PS): l'analisi dell'andamento in funzione della temperatura e una sua diretta correlazione con le condizioni di sintesi ha verificato che le due fasi polimeriche si comportano come due omopolimeri indipendenti.

Un confronto tra la  $f_r$  teorica e sperimentale di miscele bi- e trifasiche applicabili come sostituti del BEVA ®731 nell'ambito dei beni culturali ha chiarito perché la miscela trifasica manifesti migliori proprietà adesive: solo in questo caso è stata ottenuta una miscibilità perfetta tra le diverse fasi.

Da ultimo, sono state condotte analisi <sup>129</sup>Xe NMR ad alto campo per studiare la morfologia di *biochars* ottenuti da gusci di pecan e di mandorle tramite diversi sistemi di attivazione: in particolare, spettri 1D convenzionali ed in funzione della pressione di <sup>129</sup>Xe hanno verificato la loro struttura microporosa. L'analisi dei T1 ed esperimenti di scambio hanno evidenziato come la diversa accessibilità dei pori dipenda dalle condizioni di attivazione: solo quelli sottoposti a trattamenti più intensi manifestano fenomeni di scambio che li rendono funzionali a possibili applicazioni come filtri.

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#### INTRODUCTION

Nuclear magnetic resonance (NMR) spectroscopy is a powerful tool to investigate inner properties of matter and it is now extensively used for both fundamental and applied research: applications range from the chemical discrimination of functional groups of organic molecules to diffusion of gases and liquid in polymer matrices and imaging of human body organs.

NMR is based on the intrinsic quantum-mechanical property some nuclei have: the *spin*. If not-zero nuclear spins are embedded in an external magnetic field, they start preceding around it with a peculiar frequency and a macroscopic, detectable magnetization is formed. The subsequent manipulation of the induced magnetization through carefully chosen pulse sequences allows the study of scientifically interesting microscopic parameters such as the chemical shift, T1, T1 $\rho$ , T2, multiple quantum excitations, field gradient-induced diffusion effects which give insight on the physical and chemical properties of the different systems. Apart from the intrinsic scientific interest, they can mostly be correlated to macroscopic properties which need to be known for real-life applications, making NMR a helpful tool for industrial R&D and quality control as well. On top, polymer science and porous media research exploit NMR peculiarities a lot: the possibility of performing NMR experiments on different nuclei and isotopes additionally expand the range of informations which can be obtained. Particularly, solution and solid state high-field <sup>1</sup>H and <sup>13</sup>C NMR allows the determination of the polymer chemical composition, its stereochemistry and in case it can distinguish the different phases of composite systems. By eschewing Fourier Transform and its requirement of high homogeneity of the magnetic field, low-field time domain (TD) <sup>1</sup>H NMR can provide informations about polymer mobility rapidly and accurately: it is particularly suited to study the mobility of polymeric phase-separated systems at different temperatures and therefore gather information about their morphology and phase transitions. NMRactive noble gases (<sup>129</sup>Xe, <sup>83</sup>Kr, etc) combine their almost null reactivity with a high sensitivity to the local environment: they may be used as probes to check the presence of pores, their dimensions and degree of accessibility.

In this work, we applied NMR technique to study the morphology of several bulk, nanoscaled-polymeric and carbonaceous porous system. Particularly, low-field <sup>1</sup>H-TD-NMR has been used to evaluate the crosslink density of polyisoprene/polybutadi-

#### Introduction

ene rubber blends at their optimum curing time and of single-polymer polyisoprene or polybutadiene rubber in undercuring conditions. As already reported in the literature, Baum-Pines multiple quantum pulse sequence allows a precise evaluation of dipolar coupling constants and their distribution, thus a calculation of the average crosslink density for given polymers is possible. Experimental evidences suggest the vulcanizing agents may act differently on the two polymer phases: introducing new experimental variables (experimental temperature, different vulcanization times, different relative percentage in polymer blends) a possibly independent measurement of the crosslink density in the two different polymer phases would help clarifying the issue. Additionally, a direct evaluation of the rubber crosslink density on single-polymer rubber vulcanized at different times has been performed: no detailed description of the way the network structure develops as the vulcanizing process proceeds has ever been reported in the literature.

Low-field TD <sup>1</sup>H NMR techniques were applied on divinylbenzene (DVB) crosslinked polystyrene (PS) nanoparticles (NPs), poly(*n*-butyl acrylate)/polystyrene (PBA/PS) core-shell NPs and bi- and triphasic components BEVA ®731-replacement mixture for cultural heritage preservation as well. Mostly, we investigated the T1 change in oxygen-free DVB-crosslinked PS NPs due to temperature and different amount of crosslinker: T1 is sensitive to the chemical environment and its changes can be correlated to the activation of different molecular motions. Magic sandwich echo (MSE) pulse sequence allows a precise quantification of the amount of protons in a sample which are mobile and rigid. A PBA/PS NPs temperature-dependent study of the rigid fraction and a direct comparison of the synthesis conditions with the proton mobile fraction give a deep insight on the PBA/PS NPs internal morphology. Similarly, a comparison of the experimental rigid fraction values of the BEVA ®731-replacement mixtures with the theoretical ones helps understanding the miscibility of different components and thus macroscopic adhesive properties.

Lastly, we exploit <sup>129</sup>Xe NMR to study the porous structure of conveniently treated carbonaceous biochars such as pecan and almond shell-based ones. Due to their massive production worldwide and treatment easiness, biochars are getting more and more attention as possible new and renewable materials. As a noble gas, xenon is almost not reactive and its chemical shift is extremely sensitive to the local environment xenon lives in, such as pores and their surfaces. Theoretical and experimental comprehensive studies use <sup>129</sup>Xe NMR to investigate the structure and dimension of pores in zeolite and their accessibility. Here we try to verify if the same technique can be successfully applied to unconventional green materials such as biochars.

#### CHAPTER 1

## NMR spectroscopy

NMR spectroscopy is based to the intrinsic quantum property some nuclei have the *spin*. Not all the nuclei have a not-null spin number: in this case, the nuclei are not NMR-active. Since the spin is strictly correlated to the number of protons and neutron within the nuclei, isotopes of the same chemical specie may have different spin number, leading to different NMR properties and different kind of information accessible.

In the following paragraph (par 1.1) a brief description of the NMR working mechanisms for a generic nuclei will be given. Subsequently, the main kinds of relaxations (par 1.2) will be described, the important distinction between Fourier-transformed (par 1.3) and time-domain NMR for polymer science will be provided (par 1.4) and lastly a quick description of the pulse sequences used in the reported experiments (par 1.6) will be given.

#### 1.1 The nuclear magnetic resonance

If a single not-null spin nucleus is embedded in an external static magnetic field  $B_0$ , it experiences the so-called Zeeman interaction

$$\mathbf{H}_{\mathbf{Z}} = -\gamma \mathbf{I} \cdot \mathbf{B}_{\mathbf{0}},\tag{1.1}$$

which splits the nucleus ground energy level in m + 1 levels with an energy of:

$$E_m = m\hbar\gamma B_0 = m\hbar\omega_0 \tag{1.2}$$

where  $\gamma$  is the nucleus-dependent gyromagnetic ratio and  $\hbar$  the reduced Planck's constant.  $\omega_0$  is called *Larmor* frequency. An example of energy splitting is shown in figure 1.1. The quantization axis is supposed to be parallel to the external magnetic field, and m is the quantum number. The energies  $\hbar\omega_0 = \hbar\gamma B_0$  involved are in the range of the radiofrequency and strictly depend on the external field strength and the analysed nucleus: higher the external magnetic field strength  $B_0$  and higher  $\gamma$ , bigger the energy separation.

If a radiofrequency (RF) pulse of appropriate frequency  $\omega$  is applied as an oscillating magnetic field  $B_1$  perpendicularly to the static magnetic field direction, then



Figure 1.1: Energy splitting after a magnetic field is applied to a single spin whose  $I_z$  quantum number is 5.

not only the Zeeman interaction is effective for on the nucleus. During the pulsing, its additional hamiltonian needs to be considered  $\mathbf{H}_{\mathbf{rf}} = -\gamma B_1(I_x \cos(\omega t) + I_y \sin(\omega t))$  and its effect on the spin can be described as an excitation on the nucleus from the lowest energy level to higher energy one. After the pulse has been applied, only the Zeeman interaction is active again: the spin relaxes back to a lower energy level, releasing the energy as a detectable RF pulse. This energy exchange between the spin and RF pulses is called the nuclear magnetic resonance phenomenon.

Apart from very specific applications, thanks to their easiness in handling and enhanced NMR phenomenon - as suggested by equation 1.2 -, nuclei whose spin number is 1/2 and with relatively high  $\gamma$  values such as <sup>1</sup>H and <sup>13</sup>C are chosen for NMR experiments.

However, in a sample, not only a single nucleus is involved in the NMR resonance. Instead, a large number of nuclei (around the Avogadro's number) needs to be considered: once an external magnetic field is applied and thermal equilibrium with the lattice is achieved, the nuclei's spins would populate the different available energy levels accordingly to Boltzmann's equation:

$$P_m \propto e^{\frac{-E_m}{k_B T}} \tag{1.3}$$

where  $P_m$  is the number of nuclei in the *m* level,  $k_B$  is the Boltzmann's constant and *T* the absolute temperature. Clearly, the lower the energy level, the more populated. Particularly, at thermal equilibrium, different energy levels cannot have the same population. Through equations 1.2 and 1.3, the level population depends on the temperature and the external magnetic field strength: higher the magnetic field strength and lower the temperature, the more the difference in population. Figure 1.2 shows the effect of increasing the magnetic field strength on the population mismatch in a two level spin system.

Since the macroscopic magnetization **M** is defined by equation 1.4:

$$\mathbf{M} = \sum_{m} \gamma \hbar P_m, \tag{1.4}$$



Figure 1.2: Effect of increasing the external magnetic field  $B_0$  on level population of a spin system of 1/2 nuclei.

the difference in population between energy levels is the element responsible for the emergence of a macroscopic, detectable magnetization. At thermal equilibrium, it can be easily visualised as a vector parallel to the direction of the external magnetic field  $\mathbf{B}_{0}$ .

As in the case of the single nucleus, the application of carefully chosen RF pulses induce an excitation of the nuclei to higher energy levels and thus a change in the levels population. Through equation 1.4, this behaviour is reflected to the macroscopical magnetization as well: particularly, carefully choosing of the pulse length and power, the magnetization orientation can be tilted off by an arbitrary angle, most commonly 90 or 180 degrees. Particularly, 180 degree pulses flip the magnetization and 90 degree pulses can tilt the magnetization in any direction on the XY plane: the chosen direction is said pulse phase. The careful choice of the pulses phases (the so-called phase cycle) allows several advantages: first errors in the pulsing is minimised, since they are averaged out to zero; then some particular complicated excitation can be suppressed (par. 1.5.1). Figure 1.3 provides a graphical representation of the effect of RF pulses on both the level populations and corresponding macroscopical magnetization. Lastly, with time, the energy levels population relaxes back to the thermal equilibrium configuration: macroscopically, it goes back to its original direction, parallel to the external magnetic field and energy is released as RF pulses.

Intrinsically, the relaxation takes place on two different time scales: the T1 and the T2. The T1 is defined as the time that the macroscopical magnetization needs to recover 1 - 1/e of its initial value in the direction parallel to  $\mathbf{B}_0$ . It is due to an energy exchange between the spin system and the external lattice. Instead, the T2 can be thought as the time the magnetization needs to lose 1 - 1/e of its component in the plane perpendicular to  $\mathbf{B}_0$ . This coherence loss is due to interaction between spins at the same energy level: no energy is given back to the external lattice. The study of the T1 and T2 is the field of the NMR relaxometry and allows deep insight of the environment the spin system lives in.



Figure 1.3: Schematic representation of 90 and 180 degree pulses on a 1/2 spin system and the corresponding macroscopical magnetization.

The versatility of NMR spectroscopy lies in easiness to manipulate the induced magnetization through several pulse sequences and phase cycles: different manipulation ways imply the possibility to investigate different properties of the spin systems.

#### 1.2 Relaxation mechanisms

Several mechanisms are responsible for the relaxation of the spin system to the lowest energy configuration once it has been excited by appropriate pulse sequences: they assume different importance accordingly to the kind of system in analysis (solid, liquid, etc.) and the kind of information required to be acquired.

For a generic spin system, the effective hamiltonian responsible for the spin system relaxation is the sum of the always present Zeeman hamiltonian 1.1 and:

$$\mathbf{H}_{relax} = \mathbf{H}_{CS} + \mathbf{H}_{D} + \mathbf{H}_{J} + \mathbf{H}_{Q}$$
(1.5)

where  $\mathbf{H}_{\mathbf{CS}}$ ,  $\mathbf{H}_{\mathbf{D}}$ ,  $\mathbf{H}_{\mathbf{J}}$ ,  $\mathbf{H}_{\mathbf{Q}}$  are the chemical shift, dipolar, indirect spin-spin and quadrupolar interactions respectively. Particularly, only the chemical shift interaction is a single spin one: all the others kind of interaction the require two spin to be effective.

#### 1.2.1 Chemical shift interaction

The splitting of the nuclear levels due to the nuclear spin interaction with external magnetic field  $B_0$  is the core of NMR. However, the same field is experienced by the electrons in the atoms: the electrons energy levels are changed as well; particularly, the ground energy level. This small, field-proportional perturbation is responsible of an additional electron-driven magnetization which thus induce an additional magnetic field which changes the nuclear energy levels again. Clearly, it is strongly dependent on the electronic environment of the nucleus, therefore on the chemical bonds of the atoms it belongs to.

Mathematically, the hamiltonian experienced by the spin system is:

$$\mathbf{H}_{\mathbf{CS}} = \gamma \mathbf{I} \cdot \boldsymbol{\sigma} \cdot \mathbf{B}_{\mathbf{0}},\tag{1.6}$$

where  $\sigma$  is the spatially-dependent *chemical shift* (CS) tensor. In liquids, the molecular rotations are responsible for a fast variation of the chemical shift tensor: the spin system normally experiences only the time-averaged  $\sigma$ , and equation 1.6 simplifies to:

$$\mathbf{H}_{\mathbf{CS}} = \gamma \sigma \mathbf{I} \cdot \mathbf{B}_{\mathbf{0}}.$$
 (1.7)

The fact the chemical shift is sensitive to the electronic environment make NMR spectroscopy extremely suited for molecular characterization: determination of the molecular structure of single organic molecules or polymers is one the most exploited peculiarities of NMR spectroscopy.

#### 1.2.2 Dipolar interaction

The dipolar interaction is the second most important relaxation system in a spin system. As the name already suggests, it is a direct interaction between two different spins, labelled as 1 and 2. Its hamiltonian is given by:

$$\mathbf{H}_{\mathbf{D}} = \frac{\mu_{0}\gamma_{1}\gamma_{2}\hbar^{2}}{2\pi} [(\mathbf{I}_{1} \cdot \mathbf{I}_{2})r_{12}^{-3} - 3(\mathbf{I}_{1} \cdot \mathbf{r}_{12})(\mathbf{I}_{2} \cdot \mathbf{r}_{12})r_{12}^{-5}] \\ \approx \frac{\mu_{0}}{2\pi} \frac{\gamma_{1}\gamma_{2}\hbar^{2}}{r_{12}^{3}} P_{2}(\cos(\theta_{12}))[\mathbf{I}_{1} \cdot \mathbf{I}_{2} - 3I_{1,z}I_{2,z}] = \\ = D_{1,2}[\mathbf{I}_{1} \cdot \mathbf{I}_{2} - 3I_{1,z}I_{2,z}], \qquad (1.8)$$

where  $r_{12}$  and  $\theta_{12}$  are the distance and the angular separation between the two nuclei respectively,  $P_2$  the second order Legendre polynomial and

$$D_{1,2} = \frac{\mu_0}{2\pi} \frac{\gamma_1 \gamma_2 \hbar^2}{r_{12}^3} P_2(\cos(\theta_{12})) \tag{1.9}$$

the *dipolar coupling*, as reported in figure 1.4.

The second term in equation 1.8 is based on the secular approximation [1] and holds in all the reported applications.

Clearly, the distance  $r_{12}$  between the two spins, their angular separation and the

time the two nuclei spend at the same place play an important role in the dipolar interaction effectiveness: shorter the distance and longer the time, more effective the dipolar relaxation. At the limit, if the spins are moving fast and do not stay still for enough time, the dipolar relaxation is ineffective.



Figure 1.4: Parameters of the dipolar interaction.

#### 1.2.3 Indirect spin-spin interaction

This kind of interaction is similar to the electron-induced CS interaction. Its working principle is exactly the same: the perturbed electrons induce an additional magnetic field which is experienced by the the nuclei. Differently, the initial perturbation on the electron energy levels is not due by the external magnetic field  $B_0$ , but by the nuclei magnetic moments.

Mathematically, its hamiltonian is:

$$\mathbf{H}_{\mathbf{J}} = \mathbf{I}_{\mathbf{1}} \cdot \mathbf{J} \cdot \mathbf{I}_{\mathbf{2}},\tag{1.10}$$

where  $I_1$  and  $I_2$  are two different spins and J is a tensor. Analogously to the CS, in the case of liquid-state NMR, the molecular motions average out the spatial components of the tensor J and the interaction becomes isotropic.

#### 1.2.4 Quadrupolar interaction

This is a kind of interaction which takes place for nuclei whose spin number is higher than  $\frac{1}{2}$  only. In this case, the charge is not spherically distributed within the nucleus: it becomes sensitive to local electric field too. Its hamiltonian is

$$\mathbf{H}_{\mathbf{Q}} = \frac{eQ}{2I_z(2I-1)\hbar} \mathbf{I} \cdot \mathbf{V} \cdot \mathbf{I}, \qquad (1.11)$$

where e is the elementary charge, Q the nuclear quadrupole moment and  $\mathbf{V}$  the electric field gradient tensor.

#### 1.3 1D and 2D Fourier transformed NMR

Most of the NMR spectroscopy is performed in the so-called *Fourier transformed* space. After the application of a pulse sequence, the magnetization relaxes back to its equilibrium configuration: the *free induction decay* (FID) is collected as a

#### 1.3 | 1D and 2D Fourier transformed NMR

function of time. As shown in figure 1.5, it is an oscillating, decaying function. Particularly, the oscillations are related to the chemical shifts and indirect spin-spin interaction and are enhanced by the application of strong external magnetic field  $\mathbf{B}_0$ . The decay is instead due to relaxation phenomena and is not particularly sensitive to the strength of the external magnetic field. If experiments are performed on high-field ( $B_0 \ge 5 \mathrm{T}$ ) spectrometer, the FID transformation from the time domain (TD) to the frequency domain through the application of the Fourier transform allows to detect different functional groups. Different multiplets related to different chemical shifts would appear in the NMR spectrum at different frequencies: the line splitting inside them is instead due to indirect spin-spin interactions between neighbouring functional groups. The relaxation effects are evident in the line-shape of the single peaks only.



Figure 1.5: FID schematic representation: both oscillations and decay are shown.

Even more information can be acquired if two dimensional NMR experiments are performed. The general scheme of 2D experiments is shown in figure 1.6. First, during the preparation time, the spin system is excited by a pulse sequence. Then, during the evolution time  $t_1$ , it is allowed to evolve before the mixing period, which normally is another pulse sequence. Lastly, the signal is recorded in the time  $t_2$ . Particularly, the signal is acquired as a function of two variable times  $t_1$  and  $t_2$ : the time  $t_1$  is regularly increased and the pulse sequence is run and the signal acquired for a time  $t_2$  for each  $t_1$  value.

Most of the times, the data analysis is performed by a double Fourier transform in both the  $t_1$  and  $t_2$  time domain variable: the resulting spectrum is thus a 2D spectrum with two frequency domains. Clearly, the kind of information acquired depends on the exact nature of the preparation and mixing period.



Figure 1.6: General 2D and MQ experiments pulse scheme.

#### 1.4 Time domain NMR

In polymer science, apart from the structural characterization, the investigation of the dynamic of the system as a whole is sometimes equally or even more informative to elucidate the polymer system properties: a comprehensive analysis of the relaxation phenomena is thus required.

Since the relaxation properties are directly linked to the decay of the recorded FID, relaxation experiments can be performed on low-field ( $B_0 = 0.5 - 1 \,\mathrm{T}$ ) spectrometers. Additionally, low-field spectrometers present several experimental advantages: lower fields make the data acquiring much faster than high-field spectrometers, and different kind of system (solid, liquid, rubber-like, gel, etc.) can be analysed without the technical complication of high-field spectrometer. Moreover, the data analysis is directly performed on the FID: no Fourier transform is required, leading to a faster data analysis. On the contrary, since the information about the chemical shift is not available, only global information of the relaxation mechanisms is acquired while the information about the role of the single functional group is lost. However, the easiness of experiments, the direct analysis of the FID in the time-domain and the relatively wide range of information which can be acquired by low-field NMR makes it a precious tool for polymer science.

#### 1.5 Spin echoes

The concept of *spin echo* is of fundamental importance for the analysis of different NMR properties - mainly for low-field TD applications.

After the application of a pulse, the spin system relaxes back: the magnetization returns to its original configuration and the acquired energy is given back as RF pulses which are recorded by the spectrometer. However, if the magnetization relaxes before the acquisition is performed, normally there is no way to get the signal back and acquire it later. This phenomenon can be a serious issue for complex pulse sequences, the investigation of relaxation properties in systems where more than one relaxation mechanism is effective and on low-field instrumentation, since the electronic response of such spectrometers is not as fast as in high-fields.

A possible solution for such a problem may be the excitation of the so-called spin echo. The application of a carefully time-spaced 180 pulse, two 90 degree pulses in a row or even more complex pulse sequences turns the magnetization evolution around: for a certain amount of time the magnetization is evolving the other way around compared to what would have done if the echo is not excited. This leads to a signal refocusing after a time t (t depends on the pulse sequence used): it can be acquired and analyzed. Examples of spin echo pulse sequences are the *Hahn echo* and *CPMG* for T2 measurements (par. 1.6.1) and *magic sandwich echo* for dipolar interaction refocusing (par. 1.6.2).

#### 1.5.1 Multiple quantum NMR

As already mentioned in paragraph 1.2, CS interaction is a single spin interaction, while all the other ones require two spins to be effective: in the limiting case NMR

of a single nucleus is performed, only the CS interaction would be present.

However, in the case two spins interactions are active, they complicate the energy level, making room for several other NMR experiments. For example, if two 1/2 spins are interacting through the dipolar interaction, then four energy levels are formed: the ground energy level, the highest double-excited level and two additional intermediate energy level with the same energy. Figure 1.7 shows the energy splitting and the relative spin orientation in each level. If dipolar interaction between more the a spin pair is involved, then the energy splitting gets more and more complex. Transition between such newly-formed levels are said as multiple quantum (MQ) transitions.

Multiple quantum NMR can be particularly informative if this kind of interaction is exploited. Generally speaking, every times three or more pulses are applied, some MQ transitions are excited. In most of the experiments, MQ transition are unwanted: thus, they are filtered out by appropriate phase cycles. However, as in the case of the study of cross-link density in rubber, carefully chosen MQ excitation can be very informative of the dynamics of spin system. Particularly, as for the case of 2D NMR experiments (par. 1.3), all MQ experiments have a general scheme: during the preparation phase MQ transitions are excited by appropriate pulse sequences, then they evolve freely for a fixed time  $t_{ev}$ , lastly they are reconverted back into single-quantum excitation before detection (figure 1.6). In chapter 1.5.1 the Baum-Pines MQ pulse sequence will be described.



Figure 1.7: Energy levels for a two spin 1/2 systems: zero-, single- and double-quantum transitions are shown.

#### 1.6 Pulse sequences

Accordingly to the different kind of effective relaxation mechanism on the system and the kind of information required to be investigated, several pulse sequences with different peculiarities have been developed during the years. In the following, a quick overview about the main sequences used for the experiments in this thesis are reported: particularly, they are described accordingly on the main interaction involved.

#### 1.6.1 CS interaction

All the experiments described in this section deserve a special mention between NMR experiments: particularly, they are all really explicative and easy to perform - their pulse sequences are extremely simply: mostly a few 90 and 180 degree pulses. On top, chemical shift experiments on high-field spectrometer highlight the samples' molecular structure and 2D EXSY enlighten the exchange-dynamic of spin systems. Proton counting on low-field instruments allows a precise determination of the proton content and T1 and T2 experiments give the experimentalist information about the systems relaxation properties. Nutation experiments are required for the correct determination of 90 and 180 degree pulse lengths.

#### Bloch experiment

The chemical shift determination is the simplest NMR experiment which can be performed. The so-called Bloch experiment simply consists into the application of one single 90 degree pulse. Once the magnetization has been tilted in the XY plane, it relaxes back to its original configuration: the *free induction decay* (FID) is thus recorded.

Possibly, only the Zeeman and CS interactions need to be active on the system: if a the spin quantum number is equal to 1/2, then the quadrupolar interaction is not effective. The dipolar interaction is averaged out by brownian molecular motions if liquid-state NMR is performed while it is killed off by magic angle spinning (MAS) conditions in case of solid-state (SS) NMR: an analysis of equation 1.8 indicates that the sample fast rotation (up to 10 - 15 kHz) at a specific angle (54.74 degree) makes the dipolar interaction ineffective [2].

A particular mention needs to be given to the high-field SS cross-polarization (CP)-MAS experiment and nutation technique for pulse length determination. The CP-MAS technique [3] is a high-field SS experiment where both <sup>1</sup>H and <sup>13</sup>C are excited simultaneously for a contact time  $\tau$ . The <sup>1</sup>H are then decoupled during signal acquisition. A graphical representation of the pulse sequence is showed in figure 1.8.

If the Hartman-Hahn condition [4]

$$\gamma_H \omega_H = \gamma_C \omega_C \tag{1.12}$$

is matched, then the magnetization is transferred from the <sup>1</sup>H to <sup>13</sup>C, leading to an enhanced <sup>13</sup>C FID signal. If performed at MAS conditions, this kind of experiment is particularly suited to find out the chemical structure of rigid polymers, at temperature below their characteristic  $T_g$ . Particularly, shorter the contact time, the more enhanced the rigid components.



Figure 1.8: CP-MAS pulse sequence and phase table.

#### 2D EXchange SpectroscopY

This experiment (EXSY) is still based on the chemical shift relaxation interaction. Compared to the Bloch experiment, it is theoretically a bit more complicated, since it is a 2D experiment. The preparation period consist of a single 90 degree pulse, which excite the magnetization. During the evolution time  $t_2$ , the the different magnetization components are labelled the different accordingly to their different chemical shifts. Then the mixing period consist of another 90 degree pulse and a fixed mixing time ime  $t_{mix}$ : the system is allowed to exchange accordingly to the chemical shift components. Finally the signal is acquired after the last 90 degree pulse [5]. The data analysis is performed through the conventional double Fourier transform: particularly, on the diagonal, the 1D spectrum is reported. If the different magnetization components have exchanged during the mixing time, then some crosspeaks appear in the spectrum.

#### Proton counting

The proton counting technique is a low-field TD experiment which allows an exact quantification of the number of protons in a given sample [6]. It simply consists in a Bloch excitation: just after pulsing, the magnetization in the XY plane is directly proportional to the number of excited protons. Therefore, a correlation between the theoretical value and the experimental data can be performed. Table 1.1 present the initial magnetization intensity normalised over the sample mass measured at the fixed temperature of 313 K of a set of known liquid substances. Figure 1.9 shows their correlation with the proton content as calculated by the molecular structure. Particularly, they fit linearly, accordingly to:

$$\frac{I_0}{w} = 0.16612\%^1 H - 0.01906$$
(1.13)

If the relation is inverted, then the exact number of proton is easily measurable. However, equation 1.13 has a severe limitation: if the sample is rigid, most of the signal related to the rigid fraction is lost during the instrumental dead time. A simple Bloch experiment is thus not enough to measure the signal of the totality of the protons in the sample. A way to overcome this problem is to perform a Bloch experiment at a temperature the sample is mostly mobile at, measure the signal intensity at that temperature and then extrapolate the corresponding value at the temperature the calibration line has been obtained. On top, hexadecane is a simple alcane whose boiling point is closed to 560 K. At temperatures above 400 K, all polymers we concerned about in this work are above their  $T_g$ , therefore they are totally mobile. Figure 1.10 reports the change in the initial magnetization intensity of the normalized hexadecane at different temperatures, ranging from 313 K to 413 K. The data are linearly fitted by:

$$\frac{I_0}{w} = -3.28 \cdot 10^{-4} \%^1 \text{H} + 0.227.$$
(1.14)

The reduction of the initial magnetization intensity suggested by equation 1.14 is strictly related to they way NMR works and it is sample-independent: particularly, it can be ascribed to the effect the temperature has on the spin system energy levels, as reported by equation 1.3.

Substance	$^{1}{ m H}$ (%)	$I_0/{ m w}~(\%/{ m mg})$
1,2-Dichlorobenzene	2.72	0.45
Thiophene	4.75	0.75
Formamide	6.66	1.08
Toluene	8.68	1.44
Xylene	9.42	1.53
Polybutadiene	11.10	1.83
Water	11.10	1.83

Table 1.1: Theoretically proton content and experimental magnetization intensity normalized over mass. The experiments were run at 313 K and the instrument gain set at 88.



Figure 1.9: Correlation between mass-normalized signal intensity and theoretical proton counting, as reported in table 1.1.



Figure 1.10: Effect of temperature on signal intensity in hexadecane.

#### Τ1

The relaxation time T1 can be measured through a wide range of sequences. The most commonly used os the *inversion recovery* pulse sequence: a 180 pulse inverts the magnetization and the signal recovery after an increasing time  $t_{inv}$  is measured. However, due to the intrinsic difficulty into exactly flipping the magnetization of 180 degree with a single 180 pulse at low-field, instead of the inversion recovery pulse sequence, we mainly used the *saturation recovery* pulse sequence, reported in figure 1.11. It consists in a train of arbitrary pulses which destroys the induced magnetization. After an evolution time  $\tau_{exp}$ , a 90 degree pulse is applied before recording the signal. A sequence of analogous experiments with varying evolution times are performed: if  $\tau_{exp}$  is closed to zero, the magnetization has no time to recover before detection. Instead, if  $\tau_{exp}$  is long enough, the magnetization has partially or fully recovered and, in the limit of very long  $\tau_{exp}$ , it reaches a *plateau*. In low-field experiment on polymers, a MSE train is applied before acquiring the signal: as explained in section 1.6.2, the MSE pulse train allows for the recovering of both the rigid and mobile components. Particularly, the magnetization recovering can be easily fitted by equation

$$I(\tau_{exp}) = I(0)(1 - e^{-\tau_{exp}/T_1}).$$
(1.15)



Figure 1.11: Saturation recovery pulse sequence: the MSE pulse train is shown as well.

The first sequence used to measure the T2 is the *Hahn echo* pulse sequence [7]. The shown sequence is the easiest example of spin echo. As shown in figure 1.12, it simply consists of a single 90 degree pulse followed by a 180 degree pulse after a time  $\tau$ . An echo shows up a time  $2\tau$  after the 180 pulse. As for the T1 measurement, if a set of experiments with increasing  $\tau$  is performed, the value of T2 can be obtained fitting the measured magnetization intensity with the equation:

$$I(\tau) = I(0)e^{-\tau/T_2}.$$
(1.16)

Another sequence which allows the T2 measurement is the *CPMG* (Carr-Purcell-Meiboom-Gill) pulse sequence (figure 1.13) [8,9]. Technically, it works similarly to the Hahn echo: spaced by a time equal to  $2\tau$ , a train of 180 pulses is applied and a spin echo is formed a time  $\tau$  after each 180 pulse. At the echo occurrence, the signal is acquired. The data analysis is based on equation 1.16 as well. Compared to the Hahn echo, the main advantage of the CPMG sequence is a faster measurement of the T2, since one single experiment needs to be performed. However, the sensitivity of the measurements is strongly affected by the number of echoes which can be acquired, therefore on the minimum spacing  $\tau$  the spectrometer electronic is able to handle.



Figure 1.12: Hahn echo pulse sequence and phase table.



Figure 1.13: CPMG pulse sequence and phase table.

Even if not explicitly used for T2 measurements, Hahn echo and CPMG pulse sequences are particularly helpful in low-field experiments: since they help clearing up chemical shifts defocussing, they are often combined within other more specific pulse sequences, as magic sandwich echo one (par. 1.6.2).

Τ2

#### 1.6 | Pulse sequences

#### Nutation experiments

All the low-field TD NMR experiments here reported have been performed using calibrated 90 and 180 degree pulses. Figure 1.14 shows the pulse sequence used. It basically consists of a single pulse of increasing pulse length  $t_{pl}$ . Immediately after the pulse, the signal is acquired. The maximum magnetisation values are then fitted through the following equation:

$$I(t_{pl}) = A \times \sin(\pi \frac{t_{pl} - t_c}{w}).$$
 (1.17)

Since the 90 and 180 pulse lengths are defined as the pulse lengths at which the measured magnetization is maximum and null respectively, they are given by:

$$\begin{cases} \frac{w}{2} + t_c, & \text{for 90 degree pulse} \\ w + t_c, & \text{for 180 degree pulse.} \end{cases}$$
(1.18)



Figure 1.14: Nutation experiment pulse sequence.

#### 1.6.2 Dipolar interaction

Direct dipolar interaction between two nuclei is one of the most effective NMR relaxation mechanism (par. 1.2). Accordingly to the kind of information required to be acquired on the system, its role may need to be disregarded or, instead, enhanced. In the previous paragraph, it has already been mentioned that dipolar interaction would make the high-field CS analysis completely meaningless: some technical methods to average its effect out on high-field spectrometers have thus already been mentioned. Here the description of the another pulse sequence (MSE) to make this interaction ineffective on low-field instruments is reported.

Apart from refocusing the dipolar interaction, in paragraph 1.5.1 a full description of the advantages of exciting MQ NMR transition has been performed. Here we describe the commonly used Baum-Pines pulse sequence in rubber cross-link density measurement through NMR techniques.

#### Magic sandwich echo

As already mentioned in paragraph 1.6.1, if a polymeric system is particularly rigid at the experimental temperature, after a 90 degree pulse the rigid fraction component's signal is lost because it relaxes during the instrumental dead time. While mobile spin systems move around in space, their rigid counterparts cannot: as mentioned in paragraph 1.2.2, they stay still in the same place long enough to experience dipolar interaction, which normally takes place in  $15-20 \,\mu$ s. Since instrumental dead time on low-field TD spectrometer is on the same order of magnitude, most of the rigid components signal cannot be detected.

The easiest way to overcome this problem is to reduce the instrumental dead time employing spectrometers with faster electronic circuits. However, if this cannot be performed, new techniques need to be employed. One of the most effective is the application of a peculiar pulse sequence (MSE) [10, 11]: instead of one single 90 degree pulse, the magic sandwich echo pulse sequence. As shown in figure 1.15, it consists of one 90 degree pulse, followed by an echo time  $t_{echo}$  and the so-called sandwich train: two blocks of four 90 degree pulses with opposite phases. After a time  $t_{echo}$  an echo is formed. Doing all the math, the hamiltonian  $\mathbf{H}_{MSE}$  governing the pulse sequence is simply [12]:

$$\mathbf{H}_{\mathbf{MSE}} = -\frac{1}{2}\mathbf{H}_{\mathbf{D}}.$$
 (1.19)

Clearly, the application of the MSE pulse sequence partially (out of a factor 1/2) refocuses the signal lost because of the dipolar interaction. Figure 1.16 shows the effect of MSE refocusing on the NMR signal.

Normally, the MSE sequence is applied to directly quantify the amount of rigid and mobile components in a polymeric system. The acquired signal is then analysed through the following equation [13]:

$$I(t) = R e^{-(t/T_{2R})^2} + (1 - R) e^{-(t/T_{2M})^{na}}.$$
(1.20)

The first fast decaying curve is due to the relaxation of the rigid components: it can be described by a gaussian function and the rigid fraction R and its T2 relaxation time  $T_{2R}$  can be measured. Analogously, the slowing decaying curve is related to the relaxation of the mobile components: 1 - R is the mobile fraction,  $T_{2M}$  its relaxation time and the temporal dependence can be approximated by a stretched gaussian.



Figure 1.15: MSE pulse sequence and phase table.



Figure 1.16: MSE pulse sequence recovery effect: 1) Decay induced by dipolar relaxation; 2) Signal recovery 3) Signal detection.



Figure 1.17: MSE-refocussing: different components and data fitting. The vertical lines are guides for the eye. Readapted from [13].

#### Baum-Pines sequence

The excitation of MQ NMR transition can be obtained by the application of several pulse sequences. The easiest sequence both conceptually and to perform is the three pulse sequence: several echoes are excited at different times and they can selectively filtered choosing the appropriate acquisition time or by phase cycles. However, the excitation efficiency is low and the time scales involved are not effective for the applications required by this Ph.D work, particularly if applied on low-field spectrometers with long dead times. Instead, a specifically modified version of Baum-Pines pulse sequence for low-field spectrometer has a much higher efficiency and works fine on the time scale required by rubber samples.

Globally, the pulse sequence follows the general scheme for the MQ NMR experiment reported in paragraph 1.5.1. Figure 1.18 shows the pulse sequence for the excitation period only: an application of such a pulse sequence allows for a total refocussing of all interaction linear in the spin operators [1]. Particularly, the excitation of all even-order MQ transitions [14], since its governing hamiltonian is a pure averaged dipolar one. The reconversion period is exactly the same as the excitation period: the only difference lies in their phase cycle. A four steps phase cycle is commonly used: if the phases in the excitation period are labelled as  $\Phi_0$ , the ones in the reconversion period are  $\Phi_0 + \Delta \Phi$ , where  $\Delta \Phi = (0^\circ, 90^\circ, 180^\circ, 270^\circ)$ . After a last 90 degree pulse the signal is acquired: interestingly enough, transitions of different order can be selected through appropriate receiver phase cycle. Particularly, if the receiver phase cycle is exactly the same as the excitation phase cycle, then the signal from all MQ transitions of 4n + 2 order (on short time scale, mainly double quantum excitation: higher order transitions are effective on longer times and

#### 1.7 | Conclusions

not significative time scales only) is acquired. Instead, if it is kept fixed to  $(0^{\circ}, 0^{\circ}, 0^{\circ}, 0^{\circ}, 0^{\circ}, 0^{\circ})$ , the signal from transitions of order 4n and dipolar-encoded single-quantum transition is detected: therefore, in the long-times limit  $I_{DQ} = I_{ref}$ . The combined study of  $I_{\sum DQ} = I_{DQ} + I_{ref}$  leads to a comprehensive description of the full spin system.

Compared to the original Baum-Pines sequence [15], the introduction of the 180 degree pulse between the two 90 degree pulses and the definition of the time spacing  $\Delta_1 = t_c/24 - t_{pl}/2$  and  $\Delta_2 = t_c/12 - 3t_{pl}/2$  ( $t_c$  is global time for one single cycle and  $t_pl$  the 90 degree pulse length) are due to instrumental limitations. The original Baum-Pines sequence particularly suffers field inhomogeneities and pulse imperfections and in low-field instrument they may play an important role, leading to significant losses in the acquired signal. The introduced changes in the pulse sequence allows instead for an increased pulse sequence stability and a minimisation of the effects of imperfection in the field and pulses, still keeping the duty cycle at minimal [16].



Figure 1.18: Baum-Pines MQ pulse sequence.

#### 1.7 Conclusions

In this chapter, a description of the basic physical principles NMR spectroscopy is based on was provided.

Starting from the basic quantum effects the application of an external magnetic field has on a single not-null spin, a theoretical explanation of the way it induces a detectable, classically-describable magnetization on complex spin systems is then given. Many interactions (chemical shift, dipolar, quadrupolar, etc.) affect NMR properties in different ways: particularly, the magnetization manipulation through appropriate pulse sequences allows for the suppression of unwanted ones and/or the detection of important NMR parameters (chemical shift, T1, T2, etc.) which provide an insight of the system microscopic properties and eventually lead to a better

understanding of the macroscopical behaviours they are correlated to. Therefore, a detailed description of the different kinds of magnetic interactions was provided: because of their significant use in the subsequent chapters, particular attention was given to the magic sandwich echo refocusing, multiple quantum excitations, T1 and proton counting measurements as well as 2D exchange experiments.

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### CHAPTER 2

## <sup>1</sup>H-TD-NMR for rubber

Types used for automotive applications normally consist of appropriate blends of different polymers and eventually some additional components such as carbon black, silicon dioxide nanoparticles or other additives. The choice of the polymers and the additives used depends on the different properties the type needs to have, accordingly to the application. At the core of all elastic and adhesive rubber properties lies the *vulcanization* process: after the addition of vulcanizing agents (such as zinc, zinc dioxide and sulfur or peroxide, accordingly to the different methods), accelerators and an appropriate thermal and pressure treatment for a fixed time, the polymer chains are chemically linked together. Particularly, some of the double bonds still present within a single polymer chain are broken and new connections between two chains are formed. In most cases, sulfur and peroxides are used as vulcanizing agents: figure 2.1 shows two polyisoprene chains sulfur and peroxide-vulcanized respectively. In the first case, one or more sulfur atoms connect the two polymer chains; in the second one carbon-carbon crosslinks are created. Independently on the vulcanization method, the *crosslinking* between different polymer chains induces the formation of a 3D *network* within the rubber sample: the system is not plastic anymore but it has acquired some elastic behaviour.



Figure 2.1: Different vulcanizing systems. Top: sulfur-based crosslinking. Mono and poly-sulfuric crosslinking is shown as well. Bottom: peroxide-based crosslinking.

The investigation of the network structure and morphology is a fundamental

#### 2 | <sup>1</sup>H-TD-NMR for rubber

branch of rubber characterization: since the microscopic properties of the network are strictly related to the macroscopic ones [1], its knowledge is required to improve rubber performances. Among all network parameters, the *crosslink density* is a crucial one: it is defined as the inverse of the molecular weight between two crosslink points. Several measurement methods exist: on top, the most used in the industry are equilibrium swelling and equilibrium stress-strain measurements. In the first case, the rubber sample is placed in a good solvent: since it is crosslinked, rubber does not dissolve but it swells up, until an equilibrium condition between the free mixture energy which force the solvent to penetrate into the polymer network and the elastic response of the network itself is reached and the swelling is stopped. The state of the swelling can be related to the crosslink density through several models (phantom, affine, ...) [2–6]. Analogously, a measurement of the low strain modulus of rubber can lead to the determination of the crosslink density, since the elastic response to an external force is directly related to the crosslink density itself [7]. Despite being informative, both the techniques have strong limitations. Firstly, they are strongly model-dependent: many models exist and sometimes it is not perfectly clear which model should be used. Secondly, they only provide information about the average properties of the network: the crosslink densities obtained are just average values, regardless of the different components of the polymer blends and/or local peculiar properties.

Low-field MQ <sup>1</sup>H-TD-NMR measurements have been proven as an effective tool for network characterization: despite being a recently new technique, good characterization results have been obtained on specifically-made crosslinked systems [8]. Recently, its effectiveness has been demonstrated on industrial raw single-polymer rubber network too [9]: measurements are fast, precise and are in good matching with the results provided by other characterization techniques. Moreover, such a technique is more informative than the previously-mentioned ones: not just a single average crosslink density value is given, but instead a distribution is provided.

However, no comprehensive report but preliminary analysis only have been reported concerning low-field MQ <sup>1</sup>H-TD-NMR application on polymer blends. In this work, we focussed on the investigation of the network structure of two-polymers (polyisoprene/butadiene) (IR/BR) rubber blends at their optimum curing time. Particularly, we first checked the technique capabilities on rubber blends as well as on single-polymer rubber; subsequently, we tried to figurate out whenever low-field MQ <sup>1</sup>H-TD-NMR technique can be applied to gather information on the network structure of two single phases separately and therefore investigate the way the vulcanizing process is affected by the presence of two different polymers blended together.

Additionally, since the first discovery of the sulfur-based vulcanizing process, most of the academic and industrial research have been focused on the understanding of the basic chemical reactions which lead to the formation of the crosslinks in rubber: because of the system high complexity, complicated sequences of reactions occur, many of which are competitive and most of which involve equilibrium. Moreover, the rubber insolubility strongly reduces the investigation techniques available,

#### 2.1 | The linking theory between polymeric network and NMR

leading to difficulties in the study of the going-on vulcanization process. Most of the rubber properties have thus been studied under the condition the optimal vulcanization has been obtained: namely, the vulcanization process was performed for the *optimum curing time*, which strongly depends on the polymer involved, the vulcanizing agents and their relative amounts used and can easily measured by rheological experiments. However, the investigation of the network structure at shorter vulcanization times can shed light on the dynamic of the vulcanization process itself. Here we exploited the already-proven capabilities low-field MQ <sup>1</sup>H-TD-NMR techniques

we exploited the already-proven capabilities low-field MQ <sup>1</sup>H-TD-NMR techniques to investigate the network structure of sulfur-vulcanized IR and BR rubber samples in undercuring conditions: particularly, a new network-growing model is proposed as well.

In the following paragraphs, a fast description of the theory which allows the evaluation of the crosslink density through <sup>1</sup>H-TD-NMR MQ experiments will be given (par. 2.1). Later a description of the <sup>1</sup>H-TD-NMR MQ measurements performed on IR/BR blends and the obtained results will be provided (par. 2.2). Lastly, an investigation of the network structure at different vulcanizing times for single polymer rubber is provided (par. 2.3).

#### 2.1 The linking theory between polymeric network and NMR

In this section a short description of the underlying theory and equations relating the crosslink density of a polymer network and the experimental accessible NMR properties is proposed (par. 2.1.1). All the described theoretical background is largely used to evaluate the effective parameters describing the rubber systems for the investigation of morphological properties of both IR/BR rubber blends (par. 2.2) and single polymer-based systems (par. 2.3).

#### 2.1.1 The theoretical approach

The introduction of crosslinks in the polymeric matrix strongly reduce the polymer chains mobility, even temperature higher than their  $T_g$ : particularly, the motional averaging of the chains is imperfect since the chains segments within two crosslink points are allowed to fastly fluctuate, but the slower full chain motions are blocked due to the presence of the crosslink points.

If the sample is placed in an external magnetic field, the polymer dynamics is effectively described by the autocorrelation function:

$$C(|t_a - t_b|) = \langle P_2(\cos(\theta_{t_a})) \cdot P_2(\cos(\theta_{t_b})) \rangle, \qquad (2.1)$$

where  $\theta(t)$  is the angular orientation of the polymer backbone chain respect to the external magnetic field and  $P_2$  the Legendre polynomial of second order. The function C(t) practically indicates the probability of finding a chain segment, that has been observed in a particular orientation at the time  $t_a$ , again in the same orientation after the time  $t = |t_a - t_b|$  has passed.



Figure 2.2: Autocorrelation function for polymer melts (not-crosslinked) and polymer networks. A schematic view of the reptation and crosslink-blocked motions is provided.

Figure 2.2 is a schematic representation of the autocorrelation function for polymer melts (not-crosslinked) and polymer networks. Particularly, the first decrease at a very short time scale (ns- $\mu$ s) is due to fast segmental motions: they destroy almost all the correlation (part A in figure 2.2). At longer time scale (ms-s), the autocorrelation curve is instead related to slower cooperative motions (part B in figure 2.2) of the full polymer chain. Not-crosslinked polymers show a decrease of the autocorrelation function, down to zero: accordingly to *Rouse* theory [10], the polymer chains are free to reptate in the allowed free volume, the only limitation being the presence of other polymer chains. Instead, crosslinked polymers show a plateau: the introduction of crosslinks does not allow further motions to the polymer chains. Particularly, the height of the plateau is the square of the so-called *backbone order parameter* S<sub>b</sub> given by [11, 12]:

$$S_b^2 = \frac{3}{5} \frac{r^2}{N},\tag{2.2}$$

where N is the number of statistical vectors between the constrains and  $r^2 = \mathbf{r}^2/\mathbf{r_0}^2$ , being **r** the end-to-end vector between crosslinks,  $\mathbf{r}_0$  the end-to-end vector for chains in the unperturbed state. Once the number N is know, the crosslink density (CLD) can be easily calculated applying the conventional models for semi-flexible chains [13]. Particularly, CLD is defined as the inverse of the molecular weight between two crosslinks, which is

$$M_c = \frac{NC_{\infty}}{4c^2} M_0 \tag{2.3}$$

where  $M_0$  is the molar mass of the monomer unit,  $c = l_p/l$  is the ratio of the projection length  $l_p$  of the bond onto the backbone at its maximum extension over the total bond length square root and  $C_{\infty}$  the Flory's characteristic ratio [14]. Mostly, c and  $C_{\infty}$  are simulated or experimental values are available for the calculations [14–17].

Clearly, the backbone order parameter needs to be accessible through experimental techniques to make all the previous considerations consistent. Since the plateau
Polymer	$D_{stat}/k$ (Hz)
IR	$2\pi \times 6300$
BR	$2\pi \times 8100$

Table 2.1: Calculated  $D_{stat}/k$  values for polyisoprene and polybutadiene.

of the autocorrelation function is due to the local motions blocked by the crosslinks, then the dipolar interaction between protons at the crosslinks is not totally averaged out, leading to a NMR semi-local anisotropy. Hence, a direct connection between NMR and the backbone order parameter can be proposed.

Particularly,  $S_b$  can be measured through low-field MQ <sup>1</sup>H-TD-NMR experiments:

$$S_b = k \frac{D_{res}}{D_{stat}},\tag{2.4}$$

where k accounts for the time-averaging due to fast intra-segmental motions and  $D_{stat}$  is the static limit dipolar coupling when no motion is supposed to take place. The ratio  $D_{stat}/k$  is polymer-dependent: particularly, it has been simulated [13] and the values for IR and BR are reported in table 2.1.

 $D_{res}$  is the residual dipolar coupling and results as a time-average over the fluctuations of the dipolar tensor covering the time until the plateau region is reached and is an experimentally accessible, model free parameter. Since equations 2.2 and 2.4 hold,  $D_{res}$  can be considered as the key network descriptor: particularly, lower the  $D_{res}$  value, higher the  $M_c$ , thus looser the network and viceversa. Additionally, if the simulated, polymer-dependent conversion factor  $D_{stat}/k$  is known, then the network crosslink density can be easily calculated starting from the <sup>1</sup>H-TD-NMR data, making such an NMR approach directly comparable with other experimental techniques.

#### 2.1.2 Data analysis

The residual dipolar coupling  $D_{res}$  can be easily measured on low-field spectrometers by MQ <sup>1</sup>H-TD-NMR experiments, such as the application of the Baum-Pines MQ pulse sequence.

Particularly, the excited MQ transitions are directly related to interactions between two crosslinking points, since interactions between protons on the polymer chain are averaged out by the fast molecular motions. As reported in paragraph 1.6.2, all 0-order and odd-order excitations can be filtered out by an appropriate phase-cycle and stored in  $I_{ref}$ . Higher even-order excitation are normally ineffective, since they take place at longer time-scales: normally, just double-quantum (DQ) excitation are thus considered and stored into  $I_{DQ}$ . Particularly, since both  $I_{DQ}$  and  $I_{ref}$  relax the same way, the relaxation contributions can be removed through a point-to-point normalisation:  $I_{DQ}/I_{\sum DQ}$ . However, within the  $I_{ref}$  signal, contributions from longitudinal relaxation of isotropically highly mobile components not-related to the network such as dangling chains and sols are still present and need to be removed.

#### 2.1 | The linking theory between polymeric network and NMR

Therefore, the considered normalised build-up function would be:

$$I_{nDQ} = \frac{I_{DQ}}{I_{DQ} + I_{ref} - A \exp(-2t_{DQ}/T_{2A})},$$
(2.5)

where the exponential term in the denominator is the correction imposed by the presence of imperfection within the polymeric network. The parameters A and  $T_{2A}$  are obtained by a single exponential fitting of the long-time components ( $\geq 20 \text{ ms}$ ) of  $I_{DQ} - I_{ref}$ : imperfections in the network imply that the relation  $I_{DQ} = I_{ref}$  in the long-time limit does not hold anymore.

After the normalised intensity  $I_{nDQ}$  is obtained, the  $D_{res}$  average value can be obtained by fitting the data through an appropriate function. Assuming a gaussian distribution of the crosslinking points, if the second-momentum approximation [18] is applied then the solution of the Fredholm integral equation governing the fitting [19,20] leads to equation

$$I_{nDQ}(D_{res},\sigma) = \frac{1}{2} \left( 1 - \frac{\exp(-\frac{\frac{2}{5}D_{res}^2}{1 + \frac{4}{5}\sigma^2 t_{DQ}^2})}{\sqrt{1 + \frac{4}{5}\sigma^2 t_{DQ}^2}} \right)$$
(2.6)

which can be used as a fitting function of the acquired data. However, the fitting of the data through equation 2.6 gives good results only if the distributions are monomodal and narrow. If the system is bimodal, the distributions are particularly large or the network is inhomogeneous, then a superposition of gaussian-distributed functions as equation 2.6 is required. In the literature, the most used technique is to apply a numerical inversion procedure to calculate the  $D_{res}$  distribution. Particularly, an improved version of the conventional fast Tikhonov regularization [19,21,22] has been used: the Abragabriam-like kernel function

$$I_{nDQ}(t_{DQ}, D_{res}) = \frac{1}{2} \bigg[ 1 - \exp(-0.378D_{res}t_{DQ})^{1.5} \times \cos(0.583D_{res}t_{DQ}) \bigg]$$
(2.7)

has proven itself as one of the most reliable way to fit the experimental data, despite the introduction of a smoothing parameter is required since such an inversion is an intrinsically ill-posed problem [19].

The fitting of the experimental data through the Tikhonov regularization process provides not only an average  $D_{res}$  value, but its distribution as well. Such an information is extremely significant for the investigation of the rubber network morphology: chemically speaking, the molecular weight between two crosslink points is not fixed, but it shows a distribution. Up to our knowledge, low-field MQ <sup>1</sup>H-TD-NMR experiments are the only way to access such kind of information: the equilibrium swelling and torque measurement provide average CLD values only.

Technically, all low-field MQ <sup>1</sup>H-TD-NMR experiments needs to be performed at a specific experimental temperature. The experimental temperature choice depends on two main consideration; firstly, it needs to be significantly lower than the vulcanization temperature. In fact, temperatures close to it for long times might induce additional vulcanization, permanently modifying the network structure: the crosslink points would be thermally removed or added, whenever the rubber had been vulcanized for the optimum curing time or shorter. Secondly, the experimental temperature needs to be around 140 K higher than the polymers  $T_g$ , in order to avoid to measure effects due to the reduced mobility induced by the glass transition phenomenon [12]. In blends, it needs the be 140 K higher than the higher  $T_g$  of the polymer used in the blends.



Figure 2.3:  $D_{res}$  changes at different temperatures. Readapted from [12].

## 2.2 IR/BR rubber blends

In this section, attention is focused on the the possibility to perform low-field MQ <sup>1</sup>H-TD-NMR experiments to gather information on the morphological structure of different phases in IR/BR rubber blends at their optimum curing time. Polyiso-prene an polybutadiene were chosen because of their significant importance in tyre industry and their relatively processability easiness.

Since no detailed analysis of the technique capabilities on rubber blends has been reported in the literature, firstly MQ <sup>1</sup>H-TD-NMR experiments on IR/BR blends are described and the technique sensitivity for blends as well is proven. Then, experiments trying to separate the two different phases and obtain information on the network structure of the two phases by themselves are described. Particularly, comprehensive studies regarding the effect of the experimental temperature and the different vulcanization times are reported.

## 2.2.1 Technique capabilities and $D_{res}$ distribution in blends

Figure 2.4 and table 2.2 show the  $D_{res}$  distributions and average values for the set 1 of pristine IR/BR blends respectively (MIX30, MIX50, MIX70) and the vulcanized pure components (IR, BR). Details on the samples formulation, operative NMR parameters and additional thermal and rheological characterizations are reported in appendix A.1.2. Since polyisoprene and polybutadiene T<sub>g</sub> are around 213 K and 171 K respectively, all experiments were performed at a temperature of 353 K: the experimental temperature is a good trade-off between both the polymers T<sub>g</sub> and vulcanization temperature.

Particularly, pure IR sample shows the lowest  $D_{res}$  average value while pure BR the highest. At the same time, pure IR has a peaked and symmetrical  $D_{res}$ distribution, whereas pure BR instead shows a much broader one, with a tail for highest  $D_{res}$  values. Accordingly to paragraph 2.1, pure IR has therefore a much looser network than the BR. Moreover, the high symmetry in the IR  $D_{res}$  distribution suggests the molecular weight between two crosslinks points differs from the average value in an equal way in both directions:the distribution is therefore much homogeneous. On the contrary, BR presents a tighter network on average, but the molecular weight between crosslink points is not equally distributed: the network is thus much less homogeneous, with an increased change in the molecular weight mainly towards higher values.

Surprisingly, all the blends present a monomodal distribution: the shape of the  $D_{res}$  distribution closely resembles the one pure IR and BR have; separate contributions from the two crosslinked polymers cannot be detected on the  $D_{res}$  distribution. However, despite being on the same order of magnitude, a slight change in the measured average  $D_{res}$  (<0.100 kHz) is detected, resembling the different ratio of IR and BR in the sample. On top, the blends average  $D_{res}$  lie in the middle of the two pure components' ones: particularly, their average  $D_{res}$  values increase with the amount of BR present in the samples. Similarly, their distributions change shape as well: they shift from an IR-like distribution to one closer to the BR.

The error on each measurement (calculated as reported in appendix A.2.3) additionally proves the technique sensitivity on rubber blends. Despite the average  $D_{res}$  differences being just a few hertz, it is still bigger than the experimental error, estimated as 0.002 kHz: the technique is therefore able to distinguish different IR/BR polymer blends. The creation of a blends  $D_{res}$  database would allow for the discrimination of unknown components in polymer blends and quality control.



Figure 2.4:  $D_{res}/2\pi$  distributions for polymer blends and pure components.

Rubber sample	$D_{res}/2\pi~({ m kHz})$
BR	0.293
MIX30	0.250
MIX50	0.240
MIX70	0.226
IR	0.188

Table 2.2:  $D_{res}/2\pi$  values for pristine IR/BR polymer blends and pure components. The error is 0.002 kHz.

## 2.2.2 Network structure in the different phases and dynamics of the vulcanizing process

The easiest way the vulcanization process may evolve in a rubber blend is that it is unaffected by the presence of two different polymers. Hence, the vulcanization process evolves independently in the two polymer phases leading to a network structure which resemble the one the single polymer alone would have if vulcanized with the same vulcanizing agents and accelerators in the same operative conditions.

If such hypothesis holds, the blend average  $D_{res}$  is simply given by the linear combination of the pure components  $D_{res}$  weighted by the mass relative concentration, accordingly to the formula:

$$D_{res,calc} = c_{IR} D_{res,IR} + c_{BR} D_{res,BR}$$

$$(2.8)$$

where  $D_{res,IR}$ ,  $D_{res,BR}$  and  $c_{IR}$ ,  $c_{BR}$  are the pure IR and BR  $D_{res}$  and relative mass concentration in the blends, respectively.

On the contrary, if the linear combination 2.8 does not match the experimental  $D_{res,exp}$  within the experimental error, some other phenomena take place during the vulcanization process.

Table 2.3 reports the linear combination calculated by equation 2.8 and the discrepancy

$$\Delta D_{res} = D_{res,exp} - D_{res,calc} \tag{2.9}$$

between the experimental and calculated  $D_{res}$  the for the three previouslyinvestigated rubber blends MIX30, MIX50, MIX70 whose experimental  $D_{res,exp}$ are reported in table 2.2. Errors have been propagated accordingly to conventional error propagation theory.

Apart for the sample MIX50, all other blends show a slight discrepancy between the calculated and experimental  $D_{res}$ , higher than the experimental error. To our opinion, this behaviour can be related to two different reasons. Firstly, the MQ <sup>1</sup>H-TD-NMR measurements are able to detect some interphase crosslinking points: chemically, the vulcanizing agents induce a network in the two different phases singularly and between the two phases as well. Figure 2.5 schematically shows the three different kinds of crosslinking points in a two-polymers rubber blend. Secondly,

Sample	$D_{res,calc}/2\pi$ (kHz)	$\Delta D_{res}/2\pi$ (kHz)
MIX30	0.262	-0.011
MIX50	0.241	0.000
MIX70	0.219	0.006

Table 2.3: Calculated and discrepancy  $D_{res}$  values for pristine IR/BR polymer blends. The error is 0.003 kHz for  $D_{res,calc}/2\pi$  and 0.0035 kHz for  $\Delta D_{res}/2\pi$ .

a different network structure into the two phases is truly induced: the mixing of two polymers, vulcanizing agents and accelerators together is responsible for a vulcanization process which is different from the one the single polymer alone would have, leading to different network in the two phases.



Figure 2.5: Schematic representation of different kind of crosslinking points.

#### Interphase crosslinking: rubber blends microscopies

In order to verify the first hypothesis, transmission electron microscopies (TEM) were performed on MIX30, MIX50, MIX70. NMR is intrinsically a massive technique: in order to get a measurable signal, a reasonable amount of nuclei responsible for that specific signal needs to be present within the sample. Therefore, we performed some microscopies to check the size of IR and BR phases within the sample: specifically, we need to verify whether the surface-to-volume ratio is high enough to have a signal from interphase crosslinking points.

Figure 2.6, 2.7, 2.8 shows the TEM microscopies for the MIX30, MIX50, MIX70 rubber blends. The experimental procedure is reported in appendix A.2.4. Particularly, MIX30 shows an island structure: since IR is the minor component, IR islands are dispersed in the BR matrix; analogously, MIX70 shows BR islands in a IR matrix. MIX50 instead shows a semicocontinous structure: neither IR or BR is a minor component in the blend. In MIX30 and MIX70, the islands are cylindrically-shaped and their average dimension is in the order of micrometers. Similarly, MIX50 shows even larger domains, because of its semicocontinous structure. In conclusion, the surface-to-volume ratio is too big for MQ <sup>1</sup>H-TD-NMR experiments to detect the presence of some crosslinking points, thus invalidating the first hypothesis.



Figure 2.6: MIX30 TEM. BR domains are black.



Figure 2.7: MIX50 TEM. BR domains are black.



Figure 2.8: MIX70 TEM. BR domains are black.

Effect of the experimental temperature and different vulcanizing times

In order to verify if the vulcanization process evolves differently in the two phases of the polymer blends, two strategies were developed.

Firstly, the temperature the experiments were performed at was changed: the underlying idea is to exploit the different  $T_g$  the polyisoprene and the polybutadiene have to enhance one single phase only. Secondly, an investigation of undercured samples

was performed: hopefully, at short vulcanization times only the fastest vulcanizing component would show some network structure.

As mentioned in paragraph 2.1.2, MQ <sup>1</sup>H-TD-NMR experiments on rubber samples needs to be performed at temperatures around 140 K higher than the polymer  $T_g$ : in this way  $D_{res}$  values are only related to the crosslinking and not to changes in the mobility due to the  $T_g$ . As a way to highlight one phase only, we performed MQ <sup>1</sup>H-TD-NMR experiments at different temperatures as well: if the two polymer phases vulcanize differently, a change in the  $\Delta D_{res}$  values at different temperatures should be detected. On top, since BR  $T_g$  is lower than IR one, the role of IR should be slightly enhanced. However, the temperature is always kept sufficiently far away from both the vulcanizing temperature and the polymer  $T_g$ , in order not to compromise the measurement validity.

Figures 2.9, 2.10, 2.11 and tables 2.4, 2.5 show the results for blends at different temperatures, ranging from 313 K to 363 K. Moreover, the same measurements were repeated on the same samples after 5 months: all the samples were naturally aged at room temperature. The  $D_{res}$  values for the pure components at different temperatures and ageing are reported in table A.2 and A.3. Experimental  $D_{res}$  distributions are reported in appendix A.1.2: no significant change in the distribution shapes is verified.

At most temperatures, a difference higher than the experimental error between measured and linearly combined  $D_{res}$  values can be detected: again, such measurements demonstrate that the network structures in the two phases are probably different. However, no temperature trend can be distinguished neither in the pristine or aged samples: thus, all the reported data do not help clarifying the physics behind the vulcanization process in blends. Particularly, concerning both pristine and aged samples, MIX30 has negative  $\Delta D_{res}$  values, while MIX50 and MIX70 have instead positive values at all the investigated temperatures. But mainly, as the temperature is increased no change in the  $\Delta D_{res}$  is measured in most cases: for samples MIX50 and MIX70 all the data points lie within the error bars; only the aged MIX30 sample shows a difference between high (353 K, 363 K) and low (313 K, 333 K) experimental temperatures. The comparison between pristine and aged samples is not significant neither: MIX30 has an increase in  $\Delta D_{res}$  values at temperature 353 K, MIX70 at 313 K and MIX50 no shift at all.

Change in the experimental temperature is therefore a not effective way to separate the vulcanization effects in the two polymer phases through MQ <sup>1</sup>H-TD-NMR experiments: no information about the network structure within the two phases separately can be gathered.



Figure 2.9:  $\Delta D_{res}/2\pi$  at different temperatures for sample MIX30. Red points refer to measurements performed on pristine samples, black ones on 5-months samples.



Figure 2.10:  $\Delta D_{res}/2\pi$  at different temperatures for sample MIX50. Red points refer to measurements performed on pristine samples, black ones on 5-months samples.



Figure 2.11:  $\Delta D_{res}/2\pi$  at different temperatures for sample MIX70. Red points refer to measurements performed on pristine samples, black ones on 5-months samples.

Sample	Temperature (K)	$D_{res,exp}/2\pi$ (kHz)	$D_{res,calc}/2\pi$ (kHz)	$\begin{array}{c c} \Delta D_{res}/2\pi \\ (\text{kHz}) \end{array}$
	313	0.261	0.269	-0.008
MIX30	353	0.250	0.262	-0.011
MINEO	313	0.257	0.247	0.011
MIA00	353	0.240	0.241	0.000
MIX70	313	0.229	0.225	0.004
MIXIO	353	0.226	0.219	0.006

Table 2.4: Experimental, calculated and discrepancy  $D_{res}$  values for pristine IR/BR polymer blends at different temperatures. The error is 0.002 kHz for  $D_{res,exp}/2\pi$ , 0.003 kHz for  $D_{res,calc}/2\pi$ , 0.0035 kHz for  $\Delta D_{res}/2\pi$ .

Sample	Temperature	$D_{res,exp}/2\pi$	$D_{res,calc}/2\pi$	$\Delta D_{res}/2\pi$
Sample	(K)	(kHz)	(kHz)	(kHz)
	313	0.263	0.270	-0.012
MIX30	333	0.257	0.268	-0.011
MIA30	353	0.259	0.257	0.002
	363	0.253	0.257	-0.004
	313	0.251	0.243	0.007
MIX50	333	0.245	0.244	0.001
MIAJO	353	0.243	0.236	0.006
	363	0.240	0.234	0.006
	313	0.229	0.217	0.012
MIX70	333	0.227	0.220	0.007
	353	0.225	0.215	0.009
	363	0.220	0.212	0.008

Table 2.5: Experimental, calculated and discrepancy  $D_{res}$  values for 5-months aged IR/BR polymer blends at different temperatures. The error is 0.002 kHz for  $D_{res,exp}/2\pi$ , 0.003 kHz for  $D_{res,calc}/2\pi$ , 0.0035 kHz for  $\Delta D_{res}/2\pi$ .

The second way we exploited to enhance single polymer phases and investigate the two single phases network structure is changing the rubber vulcanization time (set 2). Vulcanization times and operative NMR parameters are reported in appendix A.1.2. Particularly, for the IR/BR blends, only undercured samples have been investigated: the curing optimum time was determined through torque measurements, as reported in appendix A.1.2.

Figures 2.12, 2.13, 2.14 and table 2.6 report the data regarding the MIX30, MIX50 and MIX70 rubber blends vulcanized at the t30, t95 and tMH respectively: for linear combinations, the BR and IR  $D_{res}$  measured on samples vulcanized for the corresponding absolute time were used. Particularly, in sample MIX30 all the  $\Delta D_{res}$  are overlapping, MIX50 have t30 and tMH data overlapping while MIX70 present the same behaviour for t30 and t95. Similarly to the experimental temperature, the vulcanizing time is thus a not effective way either to gather separate informations on the network structure and the underlying vulcanization process of the different phases of rubber blends: if present, such differences are below the technique sensitivity.



Figure 2.12:  $\Delta D_{res}/2\pi$  for different vulcanizing times for sample MIX30.



Figure 2.13:  $\Delta D_{res}/2\pi$  for different vulcanizing times for sample MIX50.



Figure 2.14:  $\Delta D_{res}/2\pi$  for different vulcanizing times for sample MIX70.

#### 2.3 | Different vulcanizing times for single polymer-based rubber

Sample	Vulcanizing time	$D_{res,exp}/2\pi$	$D_{res,calc}/2\pi$	$\Delta D_{res}/2\pi$
Sampro	(min)	(kHz)	(kHz)	(kHz)
	4.01	0.279	0.284	-0.005
MIX30	6.03	0.289	0.294	-0.005
	10.94	0.273	0.281	-0.008
	3.36	0.250	0.255	-0.005
MIX50	5.00	0.274	0.269	0.005
	9.57	0.260	0.268	-0.008
	3.36	0.231	0.284	-0.008
MIX70	5.00	0.252	0.294	-0.005
	9.57	0.264	0.281	0.011

Table 2.6: Experimental, calculated and discrepancy  $D_{res}$  values for IR/BR polymer blends vulcanized at different times. The error is 0.002 kHz for  $D_{res,exp}/2\pi$ , 0.003 kHz for  $D_{res,calc}/2\pi$ , 0.0035 kHz for  $\Delta D_{res}/2\pi$ .

## 2.3 Different vulcanizing times for single polymer-based rubber

In this section, attention is focused on the the possibility to perform low-field MQ <sup>1</sup>H-TD-NMR experiments to gather information on the network structure of pure IR and BR rubber have if vulcanized for different times. A comparison with swelling measurements additionally validates the obtained NMR data. Implicitly, a description of the network provides information on how the vulcanization process evolves in time: a validation of the conventional random-based network growing-up model (figure 2.18) or the formulation of new model can be done.

Three sets of rubber samples (set 3) have been considered for the study. The samples formulation details and additional characterizations are reported in appendix A.1.2. Particularly, one set of BR and two sets of IR samples were analyzed: the IR processability is much more higher than the BR, but instead the BR allows for a wider torque curve and thus a better discrimination of the vulcanizing times. For all samples, t30, t60, tMH are investigated: the vulcanizing times are provided by the torque measurements (figure A.14 and table A.7).

Figure 2.15, 2.16 and 2.17 and table 2.7 show the obtained  $D_{res}$  distributions and average values for the three different sample sets considered in this study.

Vulcanizing time	$D_{res}/2\pi$ (kHz)		
	BR	IR123	IR323
tMH	0.284	0.222	0.2845
t90	0.280	0.227	0.295
t60	0.290	0.209	0.282
t30	0.303	0.107	0.222

Table 2.7: Measured  $D_{res}/2\pi$  for the BR, IR123 and IR323 samples sets. The error is 0.002 kHz.



Figure 2.15: BR  $D_{res}/2\pi$  distributions for different vulcanizing times.



Figure 2.16: IR123  $D_{res}/2\pi$  distributions for different vulcanizing times.



Figure 2.17: IR323 $D_{res}/2\pi$  distributions for different vulcanizing times.

Interestingly enough, the three sample sets have a peculiar behaviour. Particularly, all BR samples show almost the same  $D_{res}$  distributions and very similar average  $D_{res}$  values: they differ from each other only slightly, the mismatch being not

#### 2.3 | Different vulcanizing times for single polymer-based rubber

comparable to the difference in the torque values measured by rheometry. Samples sets IR123 and IR323, instead, act similarly to BR for the three longest-vulcanized samples only; samples t30 show much lower average  $D_{res}$  and more peaked distributions. Similar considerations on the torque measurements hold. Apparently, in the BR the network structure does not particularly change when the vulcanization time is increased from t30 to t60, suggesting the network formation takes place during the early stage of the vulcanization process, for times shorter than t30. Both IR sample sets behave similarly: in these cases, however, samples t30 present much looser crosslink distributions than samples t60. For longer times, the distributions and the average  $D_{res}$  do not evolve significantly if the time is still increased: at a time between t30 and t60, the IR network structure is formed and it is only slightly evolving during the subsequent vulcanizing time.

To validate the NMR data, equilibrium swelling experiments have been performed on samples set BR and IR323, as reported in table 2.8. CLD NMR-calculated starting from  $D_{res}$  values are reported as well; the evident mismatch in the absolute values are due to the dependence of equilibrium swelling data analysis on the assumed underlying model: as reported in the literature [2–6], a change in the model and in parameter used leads to significantly different CLD values. In these cases, the Mooney-Rivlin model was used. Despite such considerations, sample set BR shows almost constant total swelling-based CDL, apart for sample t60: due to the large value difference compared to all other sample, we suppose there was a mistake in the measurement. Sample set IR323 shows a progressive increase in the CDL: however, samples t90 and tMH show the same CLD. In conclusion, a good agreement between the NMR and equilibrium swelling trend is achieved in both samples sets.

Vulcanizing	BR		IR3	23
time	Swelling total CLD $(X \ 10^{-5} \text{ mol/g})$	NMR total CLD (X $10^{-4}$ mol/g)	Swelling total CLD $(X \ 10^{-5} \text{ mol/g})$	NMR total CLD (X $10^{-4}$ mol/g)
tMH	3.955	4.33	3.09	4.61
t90	4.00	4.27	3.02	4.78
t60	1.72	4.42	2.41	4.57
t30	3.955	4.62	1.96	3.60

Table 2.8: Total swelling and NMR CLD for the BR, IR123 and IR323 samples set.

In conclusion, both <sup>1</sup>H-TD-NMR and equilibrium swelling measurements suggest the existence of a cut-off time after which it is not evolving anymore. However, such considerations apparently disagree with rheometry measurements: by definition, change in the shear modulus is up to 30, 60 and 90 percent in sample t30, t60, t90 respectively.

In the literature, the conventional network growing-up model [23] supposes that the crosslink points randomly form in space, accordingly to increased presence of vulcanizing agents. Despite coherently explaining torque measurements, it does not with <sup>1</sup>H-TD-NMR and equilibrium swelling ones. A possible interpretation for all the reported data could be provided by the introduction of an alternative network

#### 2.4 | Conclusions

growing-up model: the vulcanization process starts in specific points, such as closed to an increased concentration of zinc-complexes [24] but subsequently islands of vulcanized rubber with a specific morphology are formed; the evolution of their internal network structure is evident for short vulcanizing times. Later, new islands with the same structure are formed and their number progressively increases: lastly, they merge together. The mass of vulcanized rubber thus increases, but the network structure is only slightly or not-evolving. A schematic view of such an island-based growing up is shown in figure 2.19.



Figure 2.18: Conventional random model for vulcanized rubber growth: A) Unvulcanized rubber; B) Crosslink points in random position; C) Full-formed network.



Figure 2.19: Proposed island model for vulcanized rubber growth: A) Unvulcanized rubber; B) Islands of vulcanized rubber with the same network structure; C) Full-formed network.

## 2.4 Conclusions

In this chapter, low-field <sup>1</sup>H-TD-NMR has been applied to investigate rubber systems. Particularly, two families of rubber systems were considered: two-polymers (IR/BR) rubber blends vulcanized for the optimum curing time and single-polymer rubber in undercuring conditions.

Concerning rubber blends, first the technique capabilities have been checked: low-field <sup>1</sup>H-TD-NMR MQ measurements have proven to be experimentally reliable and informative on rubber blends as well as on single polymer systems. On top, due to its high sensitivity, it may be introduced as complementary technique for rubber blend miscibility quality control. Moreover, a comparison between the measured  $D_{res}$  values and the ones obtained by linear combination of the corresponding pure components using their relative amounts as weighting factors suggests the vulcanization process is acting differently on rubber blends as it would in single-polymer systems, leading to different network structure in the two phases. Such conclusions have been validated by TEM microscopies, which prove the measured discrepancy

#### 2.5 | Bibliography

cannot be ascribed to crosslinks between the two different phases. Lastly, several experimental techniques (such as changes in the experimental temperatures or different vulcanizing time) have been proposed to enhance one single phase of the polymer blend and thus obtain measurable information about the corresponding network structure: however, the introduced differences were too small and below the technique sensitivity.

Concerning single-polymer systems, a combined NMR and equilibrium swellingbased analysis of undercured IR and BR samples was performed. Both the techniques suggest the existence of a cut-off time the CLD is only slightly evolving after. If rheological measurements are considered as well, the obtained data allows to propose a still preliminary new model for the vulcanization process: first some islands of vulcanized rubber with a peculiar morphology are formed, later they merge together increasing the total mass of vulcanized rubber, while only limited or none changes in the network structure is induced.

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## CHAPTER 3

# <sup>1</sup>H-TD-NMR for polymer nanoparticles and films

Since the first experimental reports, nanotechnology has proven itself as one of the most successful tool for several applications: different kinds of nanoparticles (NPs) with multiple properties are nowadays available on the market. Defined as materials which can be shaped at dimensions of the order of a few hundreds nanometers or less, NPs may have properties totally different from their corresponding bulk materials, widening the possible range of materials applications.

Recently, nanoparticles have been extensively used for very different aims and purposes: inorganic NPs have found application in solar concentrators [1–3] and in batteries as energy-storage systems [4, 5]; biocompatible NPs are used as active drug-delivery agents [6, 7], or as contrast agents in imaging NMR [8]; thanks to their multiple properties such as light absorption, high resistance to oxidation, high thermal conductivity, high local magnetic susceptibility, antibacterial activity and more, NPs have been extensively incorporated into diverse materials of everyday use such as cosmetics [9, 10] or clothes (i.e. to effectively change the cosmetic colour), optical devices (as internal scatters, up-conversion devices) [11], catalytic [12], bactericidal [13], electronic [14], sensor technology [15], biological labelling [16] and contrast agents in medicine.

Among different materials classes, polymers are surely one of the most successful and still promising: many polymers (i.e. polystyrene, poly(*n*-butylacrylate), polymethilmethacrilate, polyethylene glycol, etc.) with totally different properties can be shaped into nanoparticles through various advanced synthetic techniques with relative easiness. On top, the dimension, shape and inner morphology of nanoparticles can be controlled at the same time: numerous protocols which allow for a fine-tuning of such characteristics have already been proposed, successfully tested in research laboratories and eventually widely applied in the industries. Moreover, if the properties of different polymers are tailored together, then multicomponent systems become available down at the nanoscale, eventually leading to the creation of innovative materials with antagonistic, contrasted properties (elastomeric/plastic, hydrophilic/hydrophobic, etc. components). Lastly, the effective combinations of polymers and inorganic nanoparticles (i.e. silver, gold, titanium dioxide, etc.) implies an enhancement of the inorganic NPs properties and the possibility to easily

#### 3.1 | DVB-crosslinked PS nanoparticles

transport the NPs in green, eco-friendly solvents.

As already mentioned in the chapter about rubber blends, low-field NMR is an incredible informative tool for polymer characterization. Here we present several NMR applications on different nanostructured systems and polymeric films. On top, in paragraph 3.1, we describe the molecular properties of monophasic polystyrene (PS) NPs, differently crosslinked through various amounts of divinyl-benzene (DVB). Fundamental polymer properties are changed if PS is shaped at the nanoscaled and crosslinked: aside with a comprehensive description of the NPs shape, dimensions and thermal properties the description of the thermally-activated molecular motions is provided. Through a T1 comprehensive analysis, the tight relationship between activation energies, temperature and amount of crosslinker in the nanoparticles is investigated.

In paragraph 3.2, attention is focused on two-phase core-shell poly(n-butyl-acrylate)/polystyrene (PBA/PS) NPs: here the properties of an elastomeric and thermoplastic polymer are merged together. Particularly, the combined use of high-field SS-NMR and low-field rigid fraction measurements has experimentally demonstrated how the two different polymeric phases behave within the single nanoparticle, fuelling potential NPs applications as impact modifier and glue.

Lastly, in paragraph 3.3 an analysis of a BEVA ®731-replacement two- and three components mixture for cultural heritage is provided. Due to commercial reasons, the original BEVA ®731 has been dismissed and an alternative version, BEVA ®731b was introduced to the market. However, the proposed new material does not match the original properties: it does not stick the same way and it is not colorless anymore. Here a full <sup>1</sup>H-TD-NMR is proposed: since the mixture stickyness is strictly related to miscibility between the different components, rigid fraction measurements were performed on mixture films: a comparison between experimental values and theoretically calculated ones allows for a detailed investigation of the miscibility degree and the role of interphases between the three different components.

## 3.1 DVB-crosslinked PS nanoparticles

Polystyrene-based nanoparticles have been extensively studied in the literature: PS is an extremely easy-to-manipulate polymer both in bulk and, throughout appropriate synthetic protocols, down at the nanoscale. The easiness in the production and the significant structural stability of such systems make PS-based polymer systems very informative case-studies to investigate how polymer fundamental properties change at the nanoscale and model-systems for several industrial applications. In this section, attention is focused on the investigation of the way fundamental polymer properties are modified if nanostructured systems instead of bulk polystyrene is considered. Particularly, since T1 relaxation time is sensitive to the chemical environment and is affected by molecular motions, a description of DVB-crosslinked PS NPs relaxation properties is reported: mostly, a comprehensive study of the effect of oxygen on relaxation properties and the T1 temperature-dependence for PS NPs crosslinked by different amount of DVB are given in paragraph 3.1.2 and 3.1.3 respectively.

Details about the synthetic protocol, the shape and dimension characterization by DLS and SEM, the thermal properties (DSC) and evidence of their porous structure can be found in appendix B.

#### 3.1.1 T1 as an effective parameter for the study of molecular motions

Several molecular motions can take place within bulk polymers and polymeric nanoparticles: vibrational, translational and rotational ones are the most prominent. All of them have peculiar activation energies: they can be activated by simply changing the applied temperature. The longitudinal relaxation time is a proven effective parameter to monitor the activation of such molecular motions: it is widely known it is particularly sensitive to both the chemical environment and the molecular motions [17].

Accordingly to conventional NMR theory, the measured T1 has a minimum when the motion correlation time  $t_c$  fulfils the relation:

$$\omega_0 t_c \sim 1 \tag{3.1}$$

where  $\omega_0$  is the Larmor angular frequency and the motion correlation time  $t_c$ is implicitly defined as the time a single spin experiences a determined magnetic field for: after  $t_c$ , molecular motions make the spin experience a different magnetic field. Since motions activation depends on the energy the molecules have, a direct relation between  $t_c$  and the applied temperature can be introduced. A study of the T1 temperature-dependence can thus help identifying the different molecular motions: if at a given temperature a specific motion has a characteristic correlation time which matches the inverse of the Larmor angular frequency then a minimum in the T1 appears in the T1 temperature-dependence plot (see figure 3.1).



Figure 3.1: T1 behaviour with correlation time.

#### 3.1 | DVB-crosslinked PS nanoparticles

Mostly, T1 experiments are performed at high-field on solution or MAS SS-NMR spectrometers: the chemical shift can be resolved and a T1 measurement for each functional group can be performed. However, at high-field the T1 are normally longer than at low-field, as shown in figure 3.1. The side effect of such an approach is the requirement of longer recycle delays and thus longer experimental times if a good S/N is required.

In the following, T1 measurements on DVB-crosslinked NPs are performed at lowfield and the chemical shift resolution is lost: in most cases, only one single T1 value is measured. However, the measured T1 is not the averaged T1 of all contributions coming from all the functional groups experiences different molecular motions. Instead, it is the T1 of the fast relaxing motion, still validating the idea of using T1 to monitor molecular motions. Due to the small dimension of the NPs, the *spin diffusion* phenomenon is taking place within the NPs: as soon as the Larmor angular frequency matches the resonating frequency of a proton undergoing a particular motion then the magnetization is trasferred to all others.

#### 3.1.2 Effect of oxygen on T1

Being paramagnetic, the O<sub>2</sub> molecule is known to be a relaxation agent in NMR experiments. Studies regarding its relaxation effects on bulk polystyrene at high-field have already been reported in the literature [18, 19]. Particularly, low-temperature (200 K), high-field T1 experiments performed on syndiotactic polystyrene proved T1 has two different components: a really fast one ( $T_{1,f} < 100 \text{ ms}$ ) and a slow one ( $T_{1,s} \sim 1 \text{ s}$ ). The emergence of these two components is due to the oxygen being selectively absorbed by the protons on the phenyl rings or on the main chain: wherever absorbed, their relative relaxation times are remarkably shortened. As proved by additional T1 measurements performed on main chain-deuterated samples, oxygen is mainly absorbed by protons on the phenyl rings.

Here we tested out the oxygen role as relaxation agent in the DVB-crosslinked NPs at low-field. Particularly, three different sets of samples have been considered: untreated commercial PS in chips, treated commercial PS and not-crosslinked PS NPs. The description of the samples preparation is reported in appendix B.1.3. Figure 3.2 shows the T1 temperature-dependence. The investigated temperatures are always below the PS T<sub>g</sub> in order to preserve the morphology. Particularly, at relatively high temperatures no differences in T1 values have been measured: high temperature-activated molecular motions are unaffected by the oxygen relaxation effect. Instead, low temperature-activated ones are: significant changes have been reported for temperatures <330 K. The reasons explaining such a behaviour lies in the different morphology untreated, treated commercial PS and PS NPs have and thus the efficiency of the oxygen extraction process: on top, oxygen in PS chips cannot easily diffuse out of the chips themselves. Improved extraction has been obtained in treated commercial PS: the molecular packing is obviously reduced, leading to an easier oxygen removal. Lastly, PS NPs have a porous morphology and therefore the oxygen removal is simplified.



Figure 3.2: Oxygen effect on T1 for differently treated PS-based samples.

#### 3.1.3 T1 temperature-dependance: the excitation of different motions

Figure 3.3 shows the T1 temperature-dependence for the differently DVB-crosslinked PS NPs. Mostly, sample PS-DVB0% and PS-DVB5% present a monotonic T1 increase as the temperature is decreased. Instead, sample PS-DVB7.5% and PS-DVB30% firstly present a T1 increase, then a maximum and lastly T1 starts decreasing again as temperature reaches low values. As for the  $O_2$  T1 measurements, the temperature never exceeded the PS  $T_g$  in order to preserve the NPs morphology. Despite the accessible temperature range could not allow for a direct observation of minima in the T1 curve, the change in T1 is eventually ascribed to the progressive activation of different motions within the PS NPs. Particularly, at high temperatures (>340 K) the T1 shows relative short values (<600 ms). Collective reptating motions of the PS main chains are temperature-activated: the protons easily exchange energy with the external environment and the T1 is short. Moreover, no dependence on the amount of DVB in the samples is observed: within the experimental error, the T1 has the same values; such an observation additionally strengthens the proposed hypotesis.

As the temperature is decreased, the reptating motions start slowing down: the energy exchange between the protons on the main chains and the external environment is less effective and the T1 thus becomes longer. However, in samples PS-DVB7.5% and PS-DVB30% the T1 values firstly reach a maximum, then start decreasing again. Such an unexpected behaviour is a consequence of the DVB crosslinking itself: the slowing down of the main chains reptating motions makes the activation of rotational motions of the phenyl rings of the DVB molecules much easier till eventually being the predominant motion. The phenyl ring protons thus start exchanging energy with the external environment thus leading to another reduction in the T1. If even lower temperatures were experimental accessible, minima at lower temperatures would be expected for crosslinked samples PS-DVB5%, PS-DVB7.5% and PS-DVB30% whereas a monotonic increase would be expected for the the not-crosslinked NPs (PS-DVB0%).



Figure 3.3: T1 temperature-dependence for differently DVB crosslinked NPs.

The temperatures at which the T1 shows a maximum are reported in table 3.1. Interestingly enough, the temperature and the increase in the amount of crosslinker work cooperatively: higher the DVB amount, higher the temperature the T1 maximum occurs at. As already described by SEM micrographs and DLS measurements, an increased amount of the crosslinker leads to a reduction of the NPs average dimensions: the polymer mesh becomes tighter and tighter. This reduction of the free volume in the NPs makes the translational motions easier to be blocked: higher temperatures are enough to inhibit them. The rotational motions of the DVB phenyl rings are instead unaffected, being them extremely small in dimensions.

Sample	T1 maximum: temperature value (K)
PS-DVB0%	ND
PS-DVB5%	ND
PS-DVB7.5%	$243 \pm 5$
PS-DVB30%	$303 \pm 5$

Table 3.1: Temperatures at which the T1 shows a maximum for differently DVB crosslinked PS NPs.

## 3.2 PBA/PS nanoparticles

The synthesis of multicomponent NPs with well-defined internal structures is one of the front-edge topic in polymer science [20–22]. Concerning the main physical properties, different polymers present contrasted properties, sometimes opposite and often not compatible with each other in bulk conditions. At the nanoscale, however, an accurate tailoring of the structure and morphology of the nanoparticles is possible [23–25]: a tuning of the desired properties and eventually the realisation of devices where opposite characteristic properties are merged together can be done [26–28].

#### 3.2 | PBA/PS nanoparticles

Multicomponent NPs normally show complex morphologies: if biphasic, the easiest one is the ideal core-shell structure, which implies a complete phase separation between the two chemically distinct components. However, this is not the case for most real systems: they present an interphase sometimes strengthening the connection between the core and the shell [29–31], or modifying the NPs peculiar properties.

In the following, we investigated the properties of poly(*n*-butylacrylate)/polystyrene (PBA/PS) core-shell NPs synthesised through a new miniemulsion polymerization protocol (see section B.2.1): the highly-adhesive PBA is confined within an external PS shell, which instead guarantees the structural stability of the NPs at low cost per unit weight of PS. Nevertheless, the actual morphology and the extent of a possible interphase in PBA/PS NPs obtained by different synthetic protocols are still under vivid debate in the scientific community: examples of phase inversion, occluded and not-ideal structures are reported in literature for PBA/PS NPs [32–34]. Here we exploited low-field NMR characterizing tools to investigate the inner structure of PBA/PS NPs: if the characteristic properties of the two polymers are not affected by each other but instead preserved, they can possibly find applications as impact modifier or glue-delivery devices.

As for the DVB-crosslinked NPs, sections 3.2.1 and 3.2.2 report the NMR characterization of the NPs only: the dimension, shape thermal properties analysis are reported in appendix B.2. Lastly, section 3.2.2 describes a simplified two-phase model to calculate the relative dimensions of the inner PBA core and external PS shell.

## 3.2.1 Solid State <sup>13</sup>C-MAS NMR

SS  $^{13}$ C-MAS experiments give clear evidence of a good phases separation of the two different polymer phases and thus of coexistence in the same particle of a fully embedded soft core within a hard shell.

Figures 3.4 and 3.5 show CP and SPE  ${}^{13}$ C-MAS spectra performed at room temperature (298 K) respectively. The pulse sequence descriptions are provided in section 1.6.1 and the NMR operative details are reported in appendix B.4.6.

Particularly, in the CP-MAS experiments a short contact time of 1.5 ms was used: such a choice allows for a specified selection of the rigid components of the NPs only: indeed only the characteristic PS peaks (40, 42, 47, 130, and 147 ppm) are observed in the spectrum. Instead, SPE <sup>13</sup>C-MAS NMR spectrum was acquired with 2s recycle delay: it selects the mobile components endowed with fast <sup>13</sup>C relaxation times only. In this case, the characteristic PBA peaks (16, 21, 30, 33, 40, 66, and 176 ppm) appear in addition to the PS peaks.

The comparison of the two spectra provides the picture of a phase-separated system: PBA shows a higher mobility compared to PS. This view is additionally confirmed by the different linewidth (LW) of PBA and PS resonances: ranging from 130 to 60 Hz, PBA resonances are much narrower than the PS values of over 300 Hz. Theoretically, such a behaviour can be easily explained: at room temperature, PBA is above its characteristic glass transition temperature (see appendix B.2.2 for thermal characterization of the two phases). <sup>13</sup>C resonances of amorphous polymers well above their characteristic glass transition temperature present quite narrow LW due to high frequency of local motions, which almost approach the extreme narrowing regime. Instead, at room temperature PS is below its  $T_g$ : in glassy polymers, the molecular motions do not increase the polymer mobility; strong proton-carbon dipolar couplings lead thus to wide resonances.



Figure 3.4: <sup>13</sup>CP-MAS spectrum of PBA/PS NPs and peak assegnation. (\*) refers to spinning sidebands.



Figure 3.5: <sup>13</sup>SPE-MAS spectrum of PBA/PS NPs and peak assegnation.

#### 3.2.2 Rigid fraction measurements

An additional proof of a good phase separation between the PBA core and the PS external shell is provided by low-field rigid fraction measurements.

In PBA/PS NPs powder, a fraction  $(f_r)$  of protons with very restricted mobility was isolated: its temperature-dependence is shown in 3.6. Particularly, when the temperature is below PBA T<sub>g</sub> (<220 K) it approaches unity: the protons relaxation

#### 3.2 | PBA/PS nanoparticles

of all components is indicative of polymer chains without significant mobility in the NMR timescale; no motion is temperature-activated. Conversely,  $f_r$  decreases to zero well over the PS T<sub>g</sub> (> 380 K): all the system is mobilized and the polymer chains are eventually reptating. In correspondence of DSC measured glass transitions (see appendix B.2.2 for thermal characterization), the  $f_r$  value may present a complex evolution. However, if pristine NPs are measured at temperature far away from both PBA and PS T<sub>g</sub>, such as in the temperature range close to room temperature (see inset in figure 3.6) the  $f_r$  measured value is quantitatively dependent on the proton weighted fraction of the two polymers. The observed value corresponds to the theoretical  $(73 \pm 2)\%$  value for ideal core-shell NPs expected by the synthesis conditions used (see appendix B.2.1 for the synthetic protocol), indicating full phase separation and very weak interphase contribution.



Figure 3.6: temperature-dependence of PBA/PS core-shell NPs rigid fraction: the line is a guide to the eye. Error bars are smaller than the point size. The inset shows the region close to room temperature: the line represents the expected composition for ideal core-shell structure, as derived from synthesis feed conditions.

Ideal core-shell NPs: theoretical model

If we suppose the NPs are perfectly spherical and ideal core-shell conditions are met then a simplified theoretical model based on mass conservation can be introduced. A schematic view of the model proposed is shown in figure (3.7).



Figure 3.7: Schematic view of a NP with no interface

Particularly, if we define the fraction masses

$$f'_{PBA} = \frac{m'_{PBA}}{m_{tot}} \qquad f'_{PS} = \frac{m'_{PS}}{m_{tot}}$$
(3.2)

where  $m'_{PBA}$ ,  $m'_{PS}$  are the mass of the PBA sphere and PS spherical shell respectively and  $m_{tot}$  the total mass, the following relations hold:

$$\frac{4}{3}\pi R_1^3 \rho_{PBA} = \frac{4}{3}\pi R_T^3 \rho_{tot} f'_{PBA}$$

$$\frac{4}{3}\pi (R_T^3 - R_1^3) \rho_{PS} = \frac{4}{3}\pi R_T^3 \rho_{tot} f'_{PS}.$$
(3.3)

 $R_1$ ,  $R_T$  are the PS sphere and the total radius respectively,  $\rho_{PBA}$ ,  $\rho_{PS}$  the PBA and PS densities and  $\rho_{tot}$  an homogeneous global density of the NP.

Therefore, the radius  $R_1$  of the PBA core and the thickness  $R_2$  of the PS spherical shell are:

$$R_{1} = R_{T} \left( \frac{\rho_{PS}}{\rho_{PS} + \rho_{PBA}/f_{PBA}' - \rho_{PBA}} \right)^{1/3}$$

$$R_{2} = R_{T} - R_{1}.$$
(3.4)

If low-field rigid fraction experiments are performed at a temperature where all the PBA is mobile and all PS is rigid, then  $f'_{PBA}$  is the mobile proton fraction. Since  $\rho_{PBA} = 0.898 \,\mathrm{g/cm^3}$ ,  $\rho_{PS} = 1.05 \,\mathrm{g/cm^3}$  and  $f'_{PBA} = 0.25$  (average value for the room temperature range) and  $R_T = 92 \,\mathrm{nm}$  as measured by DLS then the PBA core diameter is  $120 \pm 11 \,\mathrm{nm}$  (the error is dominated by the  $R_T$  one). The good matching between theoretical and measured values additionally strengthens the hypothesis that the synthesised NPs have an almost ideal structure.

## 3.3 BEVA ®731-replacement for cultural heritage

The preservation and restoration of historic paintings is a another scientific topic where polymer science can play a big role.

As schematically shown in figure 3.8 (left), a painting is made of many different layers, each accomplishing a specific function. At the really bottom lies the textile structure over which a substrate and a primer layers are placed: all of them provide structural stability and background support. Finally, the painting and protective layers are placed on the top. In order to maintain the colours with their original brightness for years, all the layers need to be kept perfectly preserved, with no degradation. However, due to the ageing of the painting itself and/or bad preservation procedures, cracks often open up in the different layers, eventually leading to a complete removal of painting fragments, as shown in figure 3.8 (right).



Figure 3.8: Structure of a well preserved (left) and cracked (right) painting.

Hot-melt adhesives play a big role for cracks restoration. Based on thermoplastic materials, they are solvent-free systems which are solid at the working temperature but molten at the (usually higher) applying temperature: their reduced viscosity allows the adhesives to get into the crack easily and wet the substrate. Lastly, when they are cooled down, they return solid and develop tack properties and bond strength, without involving any chemical reaction which might alter the painting colours. Additionally, this process is reversible and repeatable just by re-heating and re-cooling the system.

Mixture of several components in different proportions have been commercially proposed as hot-adhesive melts for cultural heritage preservation. The main component is usually a thermoplastic polymer, which mainly provides structural stability, strength and fracture energy [35]. Nevertheless, thermoplastic polymers do not provide tack and wettability on their own, therefore different products are added to impart such properties. Tackifiers can be used as secondary raw components in order to enhance the wettability and adhesive strength and lower the viscosity (which during the application is a fundamental characteristic) [36]. If the rigidity or the flexibility needs to be modulated, fillers and plasticizers are added, respectively. Lastly wax, microcrysta@731-replacementlline wax and paraffin wax act as diluents at the application temperature: they lower the viscosity, improve the wettability of the adhesive and promote a rapid development of the setting [35, 37, 38], but they can also be exploited as anti-bleaching agents.

Improved properties are obtained if all the components are perfectly mixed together: the presence of separate phases with prominent interface effects strongly decrease the adhesive properties of the system.

Among commercial hot adhesive for cultural heritage application, great attention was obtained by BEVA ®731. In late 2010, however, a new product (BEVA ®731b) was introduced as its replacement, because the main tackifier became commercially unavailable. However, according to conservators' opinion, the introduced new product does not stick as well as the original: it is not colourless anymore and it degrades pretty quickly [39].

In this section, a comprehensive NMR study of bi - and triphasic mixtures for BEVA ®731-replacement as proposed by researchers at Turin State University (Turin, Italy) is reported. Particularly, low-field NMR techniques have proven themselves as an effective tools to investigate the proper mixing of the different component and related interphase effects in a fast, non-invasive and cheap way. Informations about samples labels, formulations and operative parameters are re-

#### 3.3.1 Single component

Preliminary informations were acquired by investigating the temperature dependance of the pure components by themselves. On top, figures 3.9, 3.10, 3.11 refer to the EBA, wax and UA later used in the mixtures.

All the three components show the following general behaviour; at relatively high temperatures, the rigid fraction  $(f_r)$  approaches a null value: motions are thermally activated, leading to all the protons being highly mobile. Instead, at low temperatures,  $f_r$  is closed to unity: no significant mobility is measured, since no motion is thermally activated. Instead, the way the rigid fraction decreases in value as the temperature is increased strictly depends on the analyzed material.

Particularly, the EBA shows a smooth decrease associated to the material  $T_g$ : however, despite the EBA being a copolymer of polyethylene/poly(*n*-butylacrylate), the measured NMR-associated  $T_g$  is around 227±5 K. Such a value is closed to the bulk poly(*n*-butylacrylate)  $T_g$ , while an intermediate value between polyethylene and poly(*n*-butylacrylate)  $T_g$  was expected, as suggested by Flory's equation [40]. Similarly, the rigid fraction is negligible starting from 320 K, a temperature lower than the DSC melting point of 338 K. This discrepancy can be ascribed to fact that NMR and DSC determination of melting points are based on the measurement of physical different processes, which can take place at slightly different temperatures. The measured low rigidity at temperatures >320 K explains why the copolymer proved effective in hot-melt adhesives: at the hot-melt application temperature (around 333 K) the high mobility provides hot tacking.

Instead, wax does not show any smooth decrease in the rigid fraction, but the  $f_r$  drops down to zero in a really short temperature range (around 15 K, between 325-340 K): because the chains are too short, a crystalline structure is induced; such a behaviour can thus be ascribed to a melting phenomenon. Interestingly, a step shows up at 325  $\pm 1$  K; it is probably due to a solid-to-solid transition: a chain rearrangement is taking place just before melting. Lastly, the paraffin shows a progressive softening of the material as the temperature is increased, leading to a negligible rigid fraction only at temperature above 400 K. For both the tackifier and the wax, the fast change in mobility at high temperatures is responsible for the fast development of the setting required by hot-melt adhesives at around application temperature. Lastly, note that no temperature hysteresis is observed.



Figure 3.9: EBA rigid fraction temperature-dependence. Error is 2%: it is smaller than the dot size. The dotted line is a guide to the eye.



Figure 3.10: Wax rigid fraction temperature-dependence. Error is 2%: it is smaller than the dot size. The dotted line is a guide to the eye.



Figure 3.11: UA rigid fraction temperature-dependence. Error is 2%: it is smaller than the dot size. The dotted line is a guide to the eye.

#### 3.3.2 Mixtures

In this section, the rigid fracture temperature-dependences of bi- and triphasic mixtures are reported. Additionally to experimental data, the expected theoretical behaviour is plotted as well: discrepancy between theoretical and experimental data would help clarifying the miscibility between phases and the emergence of interphase effects.

For each temperature, the theoretical data were punctually calculated accordingly to the formula:

$$f_{r,mixture}(T) = \sum_{i} f_{r,i}(T) \cdot \%^{1} H_{i}$$
(3.5)

where the sum is performed over all the *i* components in the mixture;  $f_{r,i}$  is the rigid fraction at temperature T as measured for each component whereas  $\%^1 H_i$  is the corresponding number of protons. Since not all the single components' chemical structure is known,  $\%^1 H_i$  were measured by proton counting experiments: particularly, due to the not-negligible rigid fraction at 303 K, all proton counting experiments were performed at temperatures high enough for the rigid fraction to be neglectable and then extrapolated back to the temperature required by the proton counting calibration line. Details about proton counting technique and operative procedures are reported in section 1.6.1.

Figures 3.12, 3.13, 3.14 show the rigid fraction measurements for binary EW, EU and UW mixtures.

Mostly, EW and EU mixtures rigid fraction behaviours are dominated by the copolymer, being EBA the dominant component in both mixtures. On top, the addition of wax makes the mixture more rigid at temperatures above polymer  $T_g$ , till around 335 K. A similar behaviour is typical of EU mixture too: in this case,  $f_r$  is still detectable up to 390 K. Note that in both the polymer-based mixtures no clear wax or tackifier-related melting transition is detectable through NMR: the rigid fraction does not decrease sharply over a narrow temperature range as melting phenomena suggest, but instead drops down over a wider one, suggesting at least a partial miscibility between phases.

The theoretical  $f_r$  curves give additional insight on the microscopic structure of the mixtures themselves: the experimental data show the same behaviours as the theoretical curves, generally validating the calculation model. Concerning EW mixture, the calculated values lie slightly below for temperature <263 K while slightly above for temperature >263 K. Similarly, they lie always below the measured ones for EU mixture. Such a comparison proves the obtained miscibility is not perfect in either mixtures, leading to significant interface effects which may affect adhesive properties.

Similar conclusions hold for UW mixture: in this case the urea-aldehyde effect is particularly notable at high temperatures -  $f_r$  is still not negligible till almost 400 K. Since the wax is the minority component in the mixture, the structural chain rearrangement detected at 325 K is not present anymore: a partial miscibility between phases is achieved. However, the measured data do not match with the theoretical ones for temperature below 303 K: still a significant, unexpected mobile fraction is detectable at low temperatures, suggesting interphase effects are anyway present.



Figure 3.12: EW rigid fraction temperature-dependence. Error is 2%: it is smaller than the dot size. The dotted line is a guide to the eye.



Figure 3.13: EU rigid fraction temperature-dependence. Error is 2%: it is smaller than the dot size. The dotted line is a guide to the eye.



Figure 3.14: UW rigid fraction temperature-dependence. Error is 2%: it is smaller than the dot size. The dotted line is a guide to the eye.

#### 3.4 | Conclusions

Lastly, figure 3.15 shows the rigid fraction experimental and theoretical data for the ternary EUW mixture. Again, being EBA the main component, the general trend resembles the EBA one. However, the effect of the paraffin and urea-aldehyde addition in the mixture is significant: particularly, two *plateau* associated to wax and tackifier were measured. On top, the rigid fraction is strongly reduced at the application temperature: the polymer hot tacking properties are thus preserved. Meanwhile, if temperature is reduced, the rigid fraction rapidly increases, allowing for a fast development of the setting. Additionally, the expected theoretical behaviour is perfectly followed by the experimental data at all the investigated temperatures: good miscibility among phases was obtained and no interphase effects which could affect the mixture properties take place. Lastly, no hysteresis phenomena were observed, suggesting the adhesive mixture can undergo several thermal treatments without change in its microscopic structure.



Figure 3.15: EUW rigid fraction temperature-dependence. Error is 2%: it is smaller than the dot size. The dotted line is a guide to the eye.

## 3.4 Conclusions

In this section, combined to imaging and thermal analysis, low-field <sup>1</sup>H-TD-NMR and high-field <sup>13</sup>C-MAS NMR techniques have been successfully applied to characterize several polymeric systems. Particularly, great attention was focused on morphological investigation of nanostructured and film polymeric materials: a detailed knowledge of their inner morphology allows for both an improvement of the final, required applications the polymeric systems have been designed for and a better understanding of the way fundamental polymer properties change down at nanoscale.

Firstly, the activation of motions at different temperatures within porous, oxygenfree PS NPs crosslinked by different amount of DVB has been investigated: longitudinal relaxation time is proven to be an effective parameter to monitor motions activation. Mostly, T1 temperature-dependent analysis clearly indicates that at high temperatures collective motions of the full PS chains are taking place: as soon as the temperature is decreased, they progressively slow down till eventually rotational motions of the DVB phenyl rings start being predominant. Increase of the crosslinking works cooperatively with the temperature: in fact, the reduction of the free volume

#### 3.5 | Bibliography

is responsible for an easier arrest of the reptating motions, thus the activation of rotational motions can take place at higher temperatures.

Secondly, an analysis of the morphology of biphasic PBA/PS core-shell NPs obtained through a new synthetic protocol has been performed. Conversely to other NPs reported in the literature, high-field SS-<sup>13</sup>C-MAS experiments proved the internal PBA core and the external PS shell have two distinct mobilities, suggesting the NPs morphology may be that of an ideal core-shell with no interphases. Similarly, low-field rigid fraction measurements performed at temperatures far away from both PBA and PS T<sub>g</sub> additionally verified the hypothesis: PS and PBA behave as two independent homopolymers, thus preserving their peculiar properties and functionality.

Lastly, the miscibility properties of bi- and triphasic mixtures proposed as BEVA ®731-replacement for cultural heritage preservation have been tested out. Particularly, a comparison between experimental low-field temperature-dependent rigid fraction measurements and the corresponding theoretical values demonstrated that binary mixtures are affected by interphases phenomena due to partial miscibility between phases. Instead, the ternary mixture presents a good agreement between experimental and theoretical data. Therefore, the obtained miscibility is good enough not to introduce interphase effects which might affect the desired adhesive properties: additionally, an effective reduction of the mobility at the presumptive BEVA ®731-replacement applying temperature and fast setting development as soon as the temperature is changed have been verified as well.

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## CHAPTER 4

# <sup>129</sup>Xe NMR for biochars

In recent years, agri-based materials are getting more and more interest from both the academy and industry. On top, materials obtained from nuts shell have received huge attention: the main reason being the great availability of such bio-material due to the high request of nuts human consumption and their extremely low price: in 2012, 137 000 t of Pecan shells were produced in southern United States only, as reported by official papers by the US Department of Agriculture [1].

Nuts shells are made up of biopolymers such as cellulose, hemicellulose, pectin, and lignin [2]: in most cases, they are simply incinerated for energy production. More recently, industry has started selling them as landscaping materials or animal feed. However, the chemical and physical characteristics of the shell structure provide opportunities for alternative uses. Among all, some additional uses of almond shells include the production of furfural [3], xylan antioxidants [2] and substrates in sweet pepper production [4].

One of the most significant application is the production of biochar, through different thermal and chemical treatments. Particularly, they can be obtained through pyronlyzation process [5–9], or high temperature treatement without oxygen [5,6], low temperature treatments in the presence of ammonium chloride [10], or a twostep process first involving heating at a fixed temperature in controlled gaseous nitrogen atmosphere and then curing in presence of  $CO_2$  at a different temperature [7,8]. Accordingly to the different process used, the complex structure due to the phytotomy of the shells can be preserved or strongly modified. On top, biochars have an induced micro- and mesoporous structure which can be effectively exploit in catalysis, purification, water treatment, soil conditioning, and even reversal of climate change [11–13] or as composite fillers and nanodevices.

Thermal <sup>129</sup>Xe NMR has proven itself as an effective tool to investigate porous structures: in the literature, several theoretical and experimental papers proving the technique effectiveness for the evaluation of pores dimensions and accessibility of organic, inorganic and mixed organic/inorganic porous structures such as zeolites and MOFs have been reported. Here we applied <sup>129</sup>Xe NMR for Pecan and almond shell-based biochars characterization. In the raw conditions, both the agri-materials have an high production volume and commercial low value: however if their porous structure is preserved or enhanced through appropriate processes, the value of the obtained biochars can be extremely increased since they may be considered for use in removal of impurities and toxic organic compounds from water and industrial streams [7] (Klasson et al, 2013), and mercury removal in flue gas [6].

In the following paragraphs, an overview over <sup>129</sup>Xe NMR as a successful tool for pores investigation will be provided (par. 4.1). Later, a description of the obtained results concerning pecan (par. 4.2) and almond shell-based biochars (par. 4.3) will be given.

## 4.1 <sup>129</sup>Xe NMR as a tool for pores investigation

Being in the eighteen group of the periodic table,  $^{129}$ Xe is a mostly inert element: it has a Van der Waals diameter of 4.3-4.5 Å and a boiling point of 165 K at 1 bar. It is therefore a non-interactive, relatively small atom which remains in the gaseous state in most experimental conditions. Moreover, it has a spin of one-half, its gyromagnetic ratio is  $-73.997 \cdot 10^{6}$  rad s<sup>-1</sup> T<sup>-1</sup> and its natural abundance among all isotopes is 26.4%. All these properties make  $^{129}$ Xe an atom particularly suited for high-field NMR experiments. Additionally, if  $^{129}$ Xe atoms are allowed to diffuse within pores, then its NMR observable characteristics are sensitive to the chemical and physical environments:  $^{129}$ Xe is thus a effective probe to space voids and pores [14].

On of the more important kind of information which can be acquired by <sup>129</sup>Xe NMR is a measurements of pore size. In the literature, several theories and models relate the <sup>129</sup>Xe chemical shift at zero pressure to the pore size. Despite being based on some geometrical assumptions (i.e. the pores being spheres or cylinders), they were proven effective for several systems such as zeolites, silicate materials [14, 15] and more complex systems like layered clays [16, 17] or even ill-defined stones with large local inhomogeneities in terms of composition and pore size. Particularly, the zero pressure <sup>129</sup>Xe chemical shift  $\delta_S$  can be linked to the travelled mean free path  $\Gamma$  by the <sup>129</sup>Xe atoms through:

$$\delta_S = 243 \frac{2.054}{2.054 + \Gamma}.\tag{4.1}$$

The calculation of the pores dimensions starting from the mean free path  $\Gamma$  changes accordingly to the geometrical description of the pores assumed to be valid for the system under investigation.

At the base of all the theories, however, the correct calculation of the zero pressure  $^{129}$ Xe chemical shift lies. In most cases, Fraissard's and Demarquay's equation [14]

$$\delta = \delta_0 + \delta_S + \delta_E + \delta_{Xe-Xe}\rho_{Xe} \tag{4.2}$$

is supposed to be valid. Particularly, the equation takes into account several factors which are strictly sample-dependent:  $\delta$  is the measured pore chemical shift at a given xenon pressure  $\rho_{Xe}$ ,  $\delta_0$  is an internal reference - normally the signal arising from the free <sup>129</sup>Xe gas within the sample;  $\delta_E$  is the chemical shift induced by

electric fields within the sample and  $\delta_{Xe-Xe}$  is the chemical shift contribution due to interaction between Xe atoms themselves. Lastly,  $\delta_S$  is the chemical shift due to the interaction between the xenon atoms and the pore surfaces. The strong hypothesis  $\delta_{Xe-Xe}$  is pressure-independent has been made [18]. Cases where equation 4.2 is not valid over a wide pressure range have already been reported in the literature and one is going to be described in paragraph 4.3: the generalized application of this shift-pore size relationship to every kind of materials has been questioned because some carbonaceous solids have been found not to follow this relationship. However, equation 4.2 has the big advantage of being self-consistent: its validity can be easily proved simply performing several experiments at different xenon pressures.

## 4.2 Pecan shell-based biochars

Pecan shell-based biochar (PSC) production and pores size control have been performed by a controlled oxidation of the pecan shells at different oxygen-based airflow rates. Details are reported in appendix C.1. Structural characterization through  $N_2$ BET and SS-<sup>13</sup>C-NMR providing a full description of the biochars morphologies and properties has already been performed and reported in the literature. In the following, the characterisation of the pores structure and accessibility through <sup>129</sup>Xe NMR is reported.

#### 4.2.1 Pore size

Figure 4.1 and table 4.1 report the <sup>129</sup>Xe NMR spectra and chemical shift values for the differently oxidised samples, at 5 bar. Except for the untreated sample which shows one peak only - all others samples present two different peaks. The upfield peak at around 5-10 ppm is related to a not-adsorbed (non-ads) xenon: it represents a fast-exchanging equilibrium between free xenon gas and xenon atoms bound on the surfaces of biochar particles [19]. It is really sharp and the error on the chemical shift determination was estimated in  $\pm 0.1$  ppm. Since not-adsorbed <sup>129</sup>Xe chemical shift has a linear temperature-dependence and is limited in its dependence on density  $(0.548 \pm 0.004 \text{ ppm/amagat up to } 100 \text{ amagats})$ , its signal can be used as internal reference [20]. The downfield peak between 100-150 ppm, instead, can be related to the xenon adsorbed (ads) in the biochars pores [19, 21]. Due to the bigger linewidth (LW) of the peak, the apex peak can be determined with an error of  $\pm 1$  ppm. If pores are in the 5-1000 Å range, the precise chemical shift position of the adsorbed <sup>129</sup>Xe peak is a function of pore size: smaller shifts correspond to larger pore sizes. In treated samples, the longer the oxidation process, the more the peak apex shifts to smaller chemical shift, suggesting micropores of bigger dimensions are on average formed during the process. The peak linewidth is a measure of the heterogeneity of pore sizes; as in all these samples, broader linewidths suggest a more heterogeneous distribution of pore sizes.

The peak intensity is theoretically related to the material adsorptivity, but uncertainty in the determination of inaccessible void spaces and inability to detect all the xenon signal (some xenon atoms are outside the instrument coil) make a quantitative comparison of the two peaks not reliable. However, the high intensity of the adsorbed xenon peak underlines the importance of adsorption within pores in all samples.



Figure 4.1: 1D <sup>129</sup>Xe NMR for the differently oxidised samples, at 5 bar.

Sample	Nominal pressure (bar)	Non-ads <sup>129</sup> Xe chemical shift (ppm)	Ads <sup>129</sup> Xe chemical shift (ppm)
PSC-100	5.11	10.5	136.5
PSC-400	5.11	10.1	135
PSC-1200	5.11	9.9	129
PSC-2000	5.13	8.6	128

Table 4.1: <sup>129</sup>Xe chemical shift of the non-adsorbed and adsorbed <sup>129</sup>Xe in all biochars.

A precise measurement of pores size can be performed if variable-pressure 1D spectra are collected. If a linear pressure-dependance is verified, then equations 4.2 and 4.1 can be applied. Figure 4.2 and table 4.2 show the data regarding sample PSC-2000 at around 1, 3, 5, 7 bar. Looking at the peaks lineshapes, at all xenon pressures the shape is preserved suggesting the hypothesis that  $\delta_{Xe-Xe}$  is pressure independent is valid. Moreover, the non-adsorbed xenon peak intensity lowers if xenon pressure is decreased and eventually disappears for the 1 bar sample, proving a high affinity between xenon and biochar. The application of equations 4.2, 4.1 and a cylindrical pore model provides a pore average diameter of  $8.4 \pm 0.1$  Å.

Table 4.3 sums up the data for all the different biochars, supposing the pressuredependance is the same as sample PSC-2000. The calculated pore sizes (cylindrical pores assumed) are in good agreement with the DFT calculations based on nitrogen adsorption data [22].



Figure 4.2: PSC-2000 <sup>129</sup>Xe 1D NMR spectra at different pressures.

Nominal pressure (bar)	Non-ads <sup>129</sup> Xe chemical shift (ppm)	Ads <sup>129</sup> Xe chemical shift (ppm)	Shift difference (ppm)
1.08	$5.0^{\mathrm{a}}$	93	88
3.04	6.5	110	104
5.13	8.6	128	119
7.14	9.1	142	133

Table 4.2: <sup>129</sup>Xe NMR chemical shift of the micropore <sup>129</sup>Xe signal for sample PSC-2000 as a function of pressure. <sup>a</sup>Back extrapolation of the values at 3, 5, and 7 bar pressure; actual peak not observed

Sample	Shift difference (ppm)	Shift difference at 0 bar (ppm)	Cylindrical pore diameter (Å)
PSC-100	126	89	7.9
PSC-400	125	88	8.0
PSC-1200	119	82	8.4
PSC-2000	119	82	8.4

Table 4.3: <sup>129</sup>Xe chemical shift and estimated pore size through back extrapolation for all biocharsamples. The pressure-dependance is supposed to be the same for all samples.

## 4.2.2 Pore accessibility

The pore accessibility was studied by T1 and 2D EXSY experiments: a combined analysis allows to gather information about system dynamics at different time scales. Particularly, table 4.4 shows the T1 results for both non-adsorbed and adsorbed xenon in all biochar samples. On top, the untreated sample presents an extremely long non-adsorbed <sup>129</sup>Xe T1, closed to free xenon value. As the oxidising process gets longer, the non-adsorbed <sup>129</sup>Xe T1 gets shorter: the equilibrium shifts from the free xenon more towards the xenon bound on the biochar surfaces. Regarding the adsorbed <sup>129</sup>Xe T1, it slightly increases from PSC-100 to PSC-2000: xenon stays more time within the pores. This result is consistent with an increase in pore dimensions due to carbonization as deduced from the <sup>129</sup>Xe chemical shift data: bigger the pores, longer the xenon remains into them. However, it may additionally suggest that xenon atoms may interact differently with the external environment within the micropores.

Sample	Non-ads $^{129}$ Xe T1 (ms)	$\begin{array}{c} \text{Ads} \ ^{129}\text{Xe T1} \\ \text{(ms)} \end{array}$
PSC-0	60,000	-
PSC-100	5,560	275
PSC-400	570	315
PSC-1200	479	300
PSC-2000	546	428

Table 4.4:  $^{129}\mathrm{Xe}$  T1 of the non-adsorbed and adsorbed  $^{129}\mathrm{Xe}$  in all biochars.

2D EXSY experiments allow a direct investigation of xenon exchange between the pores and the surrounding environment. Particularly, when the NMR exchange time is comparable to the xenon exchange time inside and outside the micropores (i.e., the adsorbed and not-adsorbed <sup>129</sup>Xe signals at approximately 100-150 ppm and 0 ppm, respectively), crosspeaks between the two signals in the 2D plot should emerge. Several exchange times have been tested on various samples. In figure 4.3, 2D EXSY plots of sample PSC-2000 at an exchange time of 100 and 200 ms are reported. Crosspeaks are relatively low in intensity: the 200 ms one is little bit more noisy, because of relaxation effects taking place. Interestingly enough, the crosspeaks are not centred on the most intense region of the 1D peak: they seem to correspond to the rightmost part of the adsorbed xenon peak, corresponding to the largest pores. The largest pores are thus more subject to this exchange phenomenon. This result further indicates that the leftmost part of the peak corresponds to small pores with higher xenon residence time and less interactions with the not-adsorbed xenon.



Figure 4.3: PSC-2000 <sup>129</sup>Xe 2D EXSY spectra with exchange times of 100 and 200 ms.

## 4.3 Almond shell-based biochars

Almond shell-based biochar (ASC) production and pores size control have been performed by thermal treatments of the almond shells for different times in an inert atmosphere and, in case, rain water washing. Details on the preparation process and labelling are reported in appendix C.1. Structural characterization at the micro- (ESEM) and nanoscale (N<sub>2</sub> BET, <sup>129</sup>Xe NMR) has been performed as well, providing a full description of the biochars morphologies. In the following, the characterization of the pores structure and accessibility through <sup>129</sup>Xe NMR only is reported whereas mentions of the additional characterization are available in appendix C.1.2. A conclusion describing the overall considerations concerning almond shell biochars is reported in paragraph 4.3.2.

## 4.3.1 Pore size and accessibility

Figure 4.4 and table 4.5 report the <sup>129</sup>Xe NMR spectra and measured NMR important parameters for the differently treated samples, at 5 bar. On the leftmost column, unwashed samples spectra are reported. Sample **60** shows the peak related to non-adsorbed xenon only, in fast exchange between the free gas and the gas closed to the surface: the peak is extremely narrow - linewidth (LW) of 278 Hz, around 2 ppm - and an error of  $\pm 0.1$  ppm is estimated. As for the pecan case, since the chemical shift of xenon is known to have a pressure-dependence that is linear up to 100 amagats and peaks with similar chemical shift and LW appear in all the <sup>129</sup>Xe NMR spectra of ASC, it can be used as internal reference. Additionally, the measured T1 is closed to 10 s, a typical value for free xenon gas confined in a NMR tube. All these considerations suggest the system is characterized by a negligible or inaccessible porosity.

As the thermal treatment length increases, a downfield peak appears at around 166 ppm in sample **120** which moves upfield to 154 ppm for sample **240**. They show a relatively large linewidth: it increases with the thermal treatment as well (in both cases more than 20 ppm) and the error is estimated in  $\pm 1$  ppm. Since chemical shift is strictly related with pore size, these spectra are evidence of porosity with a relatively wide size distribution. Additionally, while the ratio between the integrated areas of the two peaks in sample **120** and **240** is not completely quantitative due to incomplete relaxation and the difficulty in defining actual free volume for the coarse powder, the accessible volume appears to be similar and quite stable.

The impact of washing with water is shown by comparison with the three spectra on the rightmost column in figure 4.4. Compared to the unwashed samples, the water wash has a small effect on the chemical shift: the difference relative to their pristine counterparts is limited to 2 - 3 ppm, which is reasonable considering their LW. Instead, the signal intensity increases notably: since the peak intensity and integrated area can be correlated to porosity, the water wash clears up more pores which thus become <sup>129</sup>Xe accessible. Additionally, the linewidth also increases with longer heating, suggesting the occurrence of a broader distribution of pore sizes. Evidence of complex pores structure and emergence of internal exchange phenomena in washed samples are given by **120-RW** and **240-RW** lineshapes: they are broad and asymmetric and a satisfactory line fitting can only be achieved supposing two separate peaks in chemical shift pores region (figures 4.5).

Information about pore accessibility is also provided by the reported T1 data. In sample **60-W**, the two peaks display starkly different relaxation times: closed to 5 s for the peak associated to non-adsorbed xenon and 2 s for the adsorbed gas. Notably, as thermal treatment time is increased as in sample **240-RW** the two values tend to converge, indicating an external exchange between the two environments. Particularly, for sample **120-RW** and **240-RW**, the intensity of the adsorbed xenon signal becomes similar to the non-adsorbed one. Such a behaviour is additionally validated by samples **60** and **60-RW**: no signal ascribed to pores appears in sample **60**, while it does in sample **60-RW**. Lastly, note that the spectrum of sample **60-RW** also displays a signal downfield (183 ppm) associated to the pores: that was completely absent in the unwashed counterpart and suggests that the pores are relatively smaller in size compared those in the other samples.

Figure 4.6 shows the pore chemical shift pressure dependance of samples 240 and 240-RW. Contrary to the pecan case, after an initial increase for very low pressures ( $\leq 2$  bar) <sup>129</sup>Xe chemical shift levels off: the increase is not linear but instead sublinear, expecially at high pressures. Intuitively, linearity is due to <sup>129</sup>Xe-<sup>129</sup>Xe interaction and is thus typical of system where an increase of pressure corresponds to a linear increase of xenon density within the pores, as in zeolites. Previously Oschatz et al. [23] performed pressure-dependent <sup>129</sup>Xe NMR experiments on several micro- and mesoporous carbon materials at high pressure and also observed such non-linear behaviour for some of the materials: after an initial increase, <sup>129</sup>Xe chemical shift levels off and reaches a plateau. In accordance with Oschatz, the curve can be interpreted as due to xenon being in a dynamic isothermal adsorption/desorption state: the system reaches a dynamic equilibrium where the increased gas density can

#### 4.3 | Almond shell-based biochars

be accommodated only partially on the limited pore surface whereas in higher proportion as free gas.

Nevertheless, in the ultra-low pressure limit ( $\leq 2$  bar), xenon is mostly adsorbed on the surface: the chemical shift pressure-dependence is almost linear and thus Fraissard's and Demarquay's equations 4.2 and 4.1 can be used for 0 bar chemical shift extrapolation and pore size calculation with a cylindrical model. The values obtained directly from the 0.5 bar sample chemical shift were instead used as lower bounds. The results are presented in table 4.6 and together they provide an estimate of the uncertainty in pore size measured by <sup>129</sup>Xe NMR.



Figure 4.4: Almond shell biochars 1D  $^{129}\mathrm{Xe}$  NMR spectra.



Figure 4.5: 1D spectra for sample **240-RW**. On the left, the fitting with one single peak in the pore region is reported, on the right two pores families in internal exchange are supposed to be present.

Sample	Pressure (bar)	Ads <sup>129</sup> Xe chemical shift (ppm)	NMR LW (ppm)	NMR area	T1 gas (s)	T1 pores (s)
60	5.02	-	-	-	9.2	-
120	5.02	166	20.5	1.87	-	-
240	5.07	154	26.1	2.44	-	-
60-RW	5.04	183	18.0	1.15	5.1	1.9
120-RW	4.90	163	18.0	5.11	4.0	2.3
240-RW	5.01	158	22.9	6.08	2.8	2.6

Table 4.5: Almond shell biochar 1D  $^{129}\mathrm{Xe}$  NMR measured parameters.



Figure 4.6: Chemical shift pressure-dependence for sample **240** and **240-RW**. The lines are a guide for the eyes.

### 4.3.2 Almond shell biochars global structure

Considering ESEM, <sup>129</sup>Xe NMR and N<sub>2</sub> BET data, a picture emerges of what possibly happens during thermal treatment and rain water wash. The thermal treatment is responsible for the formation of mesopores in the tenth of microns range, as shown by ESEM micrographs. Such mesopores are additionally decorated by a second level of submicrometric pores whose surface was investigated by <sup>129</sup>Xe NMR and N<sub>2</sub> BET. After heating at 1073 K for 60 minutes (sample **60**), degradation occurs in the almond shell but pores are either not well-formed or filled with soot and salt, not detected by either <sup>129</sup>Xe NMR and N<sub>2</sub> BET. The rain water wash (sample **60-RW**) allows for the soot and salts removal, opening up pores with relatively small sizes, as indicated by the NMR data. After longer thermal treatment for 120 minutes (sample **120-RW**), total pore volume increases: however, the average pore size stays the same; thus, rain water wash clears up new pores, no increased in the pores dimension is measured. Additionally longer thermal treatment from 120 to 240 minutes produces a sample (sample **240**) with slightly smaller chemical shifts

Sample	Pressure (bar)	Ads <sup>129</sup> Xe chemical shift (ppm)	Shift at 0 pressure (ppm)	$\begin{array}{c} {\rm Mean} \\ {\rm free \ path} \\ ({\rm \AA}) \end{array}$	Calculated average pore size (Å)
240	$\begin{array}{c} 0.40 \\ 1.01 \\ 2.03 \\ 3.02 \\ 5.07 \\ 7.02 \\ 10.14 \end{array}$	$93 \\ 112 \\ 131 \\ 145 \\ 154 \\ 169 \\ 181.5$	86	3.31 - 3.74	7.7 - 8.1
240-RW	$\begin{array}{c} 0.49 \\ 1.02 \\ 2.03 \\ 3.02 \\ 5.07 \\ 7.01 \\ 10.11 \end{array}$	$87 \\ 102 \\ 121 \\ 134 \\ 158 \\ 171.5 \\ 180$	78	3.68 - 4.34	8.1 - 8.7

Table 4.6: Chemical shifts pressure-dependence and calculated pore sizes (cylindrical model). Concerning the reported mean free path and calculated average pore size two values are reported: the first ones refers to the lower values based on the 0.5 bar-samples chemical shifts only; the second ones are instead based on the linear extrapolation of 0 bar chemical shift through Fraissard's and Demarquay's equation.

but increased peak area and broader linewidth; thus, the pore volume increases, but new smaller pores are formed and existing pores get larger, probably due to the breakdown or thinning of the interpore walls. Similarly, rain water wash (sample **240-RW**) further increases the pores volume but the average pore size stays the same. If one compares the data for samples **120** and **240**, the average pore size for samples **240** is slightly larger according to NMR chemical shift but slightly smaller according to nitrogen absorption data. The same trend in pore average dimensions as calculated by N<sub>2</sub> BET and Fraissard's and Demarquay's equations-based <sup>129</sup>Xe NMR is observed on samples **240** and **240-RW** as well, perhaps reflecting the different sensitivities of <sup>129</sup>Xe NMR and N<sub>2</sub> BET to the broader pore size distribution and <sup>129</sup>Xe adsorption/desorption behaviour in almond shell biochars.

#### 4.3.3 Pore accessibility

Since both the variable pressure chemical shift measurements on samples 240 and 240-RW and the chemical shift lineshape highlighted the emergence of exchange phenomena within the pores themselves and between the pores and the external environment, we directly investigated them directly through EXSY experiments.

Obviously, no exchange experiment can be performed on sample **60**, since only the peak due to non-adsorbed  $^{129}$ Xe is present. The corresponding rain water-washed sample presents instead two separate signals: several experiments with different exchange times (20, 400, 1000 ms) were performed, but no crosspeaks emerged in any experiment. Longer exchange times could not be efficiently probed, due to the

#### 4.3 | Almond shell-based biochars

intrinsic limitation of T1 relaxation that reduces S/N ratio: as reported in table 4.5, relaxation time for xenon associated to the pore systems is around 2 second. Still, the accessible experimental times allow demonstrating that there is no significant xenon exchange between adsorbed and non-adsorbed peaks on this sample up to the half second range. If we consider the samples with longer thermal treatment, sample 120 also has no crosspeaks either, similar to the 60 ones. Instead, sample 120-RW is the first washed sample which shows xenon exchange, as depicted in figure 4.7. Particularly, at 20 ms exchange time all intensities are found on the diagonal. At 400 and 1000 ms exchange times, non-diagonal peaks appear, indicating exchange between the adsorbed and the non-adsorbed peaks. Additionally, the diagonal peaks are relatively broad: note that the peak centred at 150 ppm covers a range of shifts (130 - 175 ppm), indicating exchange between different pore systems in the material. It is also broad, suggesting internal xenon exchange between different pore systems in the material. Notice only the regions at lower chemical shift exchange with the non-adsorbed gas: probably this indicates that larger pores are also more easily connected with the external environment.

Because 400 ms exchange time appears to be a good compromise between high exchange rate and sufficient S/N ratio considering the longitudinal relaxation, further experiments at 400 ms exchange time were carried out on samples 120, 240 and their rain water-washed counterparts, as shown in figure 4.8. For both samples 120 and 240, only diagonal peaks were found. However, with samples 120-RW and 240-RW, some non-diagonal elements are clearly evident, indicating xenon exchange between the adsorbed and non-adsorbed xenon. The diagonal peaks are large and show up more like a cluster, suggesting internal xenon exchange among pores is taking place as well. The water wash treatment has a significant role in increasing the accessible pores volumes and allowing the xenon to exchange.



Figure 4.7: 2D EXSY plots for sample **120-RW**. From left to right, the exchange times used are: 20-400-1000 ms. On the traces, projections are shown.



Figure 4.8: 2D EXSY plots performed at 400 ms. Clockwise, the samples are: **120**, **120-RW**, **240-RW**, **240-RW**, **240**. On the traces, projections are shown.

## 4.4 Conclusions

In this chapter, thermal  $^{129}$ Xe NMR has been performed on two different kind of biochars, in order to investigate the porous structure and the pores accessibility. In both pecan and almond shell-based biochars, two families of xenon atoms have been detected: the first one refers to xenon confined in the pores, the second one to xenon free in the material or bound to the pores surfaces. The porous structure and dimensions in the submicrometric range in both pecan and almond shell-based biochars strongly depends on the processing conditions: pecan shells pores size depends on the different oxygen airflow rate, whereas the duration of the thermal treatment at 1073 K is the key parameter in almond shell-based biochars. In both cases, the pore size order of magnitude is tens of angstrom, as calculated by 0 bar chemical

shift extrapolation and the application of Fraissard's and Demarquay's equations. Additionally, a rain water washing of the almonds shell-based biochars increases the total pore volume: the number of accessible pores rise, suggesting the rain water washing cleans up the obstructed pores from the residual salt and soot. Lastly, pore accessibility has been monitored by T1 and 2D exchange experiments on different time scales. Concerning pecan shell-based biochars, they show exchange between the two xenon families starting from 100 ms: only the bigger pores are involved; xenon confined in the smaller pores do not exchange with the external environmental. Instead, almond shell-based biochars exchange properties strictly depend on the specific treatment; particularly, it only takes place in longer thermal treated, rain water washed samples (**120-RW** and **240-RW**): only the biggest pores are again involved in the exchange with the external environment, but internal exchange between pores of different dimensions takes place as well.

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## CONCLUSIONS

Since its first introduction, nuclear magnetic resonance (NMR) has demonstrated itself as a formidable characterization tool in different fields. Its applications ranging from chemistry, physics till materials science, NMR allows for a deep investigation of fundamental properties of materials which can subsequently be correlated to macroscopic properties, possibly leading to an optimization of the required performances of real-life industrial devices.

In this Ph.D. thesis, NMR was widely applied for the characterization of biochars and polymeric systems at both the industrial and research stage: among all NMR branches, low-field time domain (TD) <sup>1</sup>H-NMR was used for the characterization of multiple polymeric systems whereas <sup>129</sup>Xe NMR found applications to verify the porous structure of carbonaceous biomaterials.

After a brief description of NMR basis in chapter 1, chapter 2 is focused on low-field <sup>1</sup>H-TD-NMR for the characterization of single-polymer and two-polymer industrial rubber blends. Due to its easiness to handle and low prices compared to other techniques, <sup>1</sup>H-TD-NMR may be widely applied in the industry for both R&D applications and quality control. On top, its capabilities were tested out trying to measure the local crosslink density of the different polymer phases by themselves in fully vulcanized industrial rubber blends: despite being capable to detect differences in their network structure which can be ascribed to different vulcanization within the single phases, such differences were below technique's sensitivity to be quantified and no modification in the experimental conditions proved effective in the enhancement of one single phase alone. On the other side, valuable informations concerning the vulcanization time evolution were acquired; particularly, experiments performed on single-polymer rubber in undercuring conditions suggest the introduction of a new developing model: islands of vulcanized rubber with a specified network structure are independently formed as the vulcanization process proceeds, lastly merging together.

As reported in chapter 3, combined with high-field solid state <sup>13</sup>C-MAS NMR techniques, electron microscopy and thermal analysis, <sup>1</sup>H-TD-NMR provided deep insights on the inner morphology of purposely-made film or nanostructured polymeric systems such as differently DVB-crosslinked polystyrene nanoparticles (NPs),

#### Conclusions

poly(n-butylacrylate)/polystyrene core-shell NPs and bi- and triphasic mixtures proposed as BEVA @731 replacement for cultural heritage preservation.

Mostly, the activation of collective chains motions and rotational ones at high and low temperatures respectively within porous DVB-crosslinked PS NPs was verified by motion-sensitive T1 measurements. The role played by different amount of crosslinker on motions activation investigated as well. Similarly, <sup>13</sup>C-MAS NMR experiments proved the PBA and PS within PBA/PS core-shell NPs have significantly different mobilities at room temperature: the PBA is totally mobile whereas the PS is rigid, as their corresponding homopolymers in bulk conditions do. The quantification of the amount of rigid protons in the NPs through rigid fraction measurements and its direct comparison with synthetic conditions additionally validates the hypothesis that the two polymers behave independently from each other with no interphase effects, still preserving their characteristic properties which can therefore be exploited in devices.

Lastly, the same characterizing experiments have been successfully applied to BEVA ®731 replacements mixtures: a comparison between experimental and theoretical values proves that binary mixtures present only a partial miscibility between phases; interphase effects thus emerge. Instead, the ternary mixture shows a perfect miscibility: the negligible interphase effects do not affect the hot tacking and fast development properties the mixture needs to have for successful applications.

Finally, chapter 4 is focused on the application of <sup>129</sup>Xe NMR for the investigation of biochars structure. Particularly, pecan shell and almond shell-based biochars activated respectively by thermal treatment in air at different airflows or cured for different times in inert atmosphere and eventually rain-washed were investigated. In most cases, the activation treatment is intense enough to induce of formation of micropores within the biochars: their dimensions were estimated as a few angstrom by pressure-dependent chemical shift experiments. Additionally, the pores accessibility degree to xenon was tested by T1 and 2D exchange experiments: in the case of pecan biochars, only the bigger pores are involved in the xenon exchange phenomenon. Concerning almond-based biochars, only the rain-washed ones show xenon exchange, suggesting the importance of the washing processing to clear up the pores from residual salts which, occluding the pores themselves, may strongly reduce the biochar possible application as filters.

## APPENDIX A

## Rubber

In this appendix, firstly general considerations about the preparation and additional rheological, thermal and NMR characterizations are provided (paragraph A.1). Secondly, a description of the instruments used, operative parameters and, if needed, details on the data analysis procedures are reported (paragraph A.2).

## A.1 Sample details

## A.1.1 Sample preparation

All rubber samples were kindly provided by Pirelli Tyres S.p.a. The label polyisoprene (IR) indicates high cis-polyisoprene (cis-1,4 content 97% min) low viscosity (Mooney viscosity (ML (1+4) 273 K) 70  $\pm$  5 MU) obtained by solution polymerization with Ziegler/Natta catalyst. The label polybutadiene (BR) refers to high cis-polybutadiene (cis-1,4 content 97% min) low viscosity (Mooney viscosity (ML (1+4) 273 K) 43  $\pm$  3 MU) polymerized by Neodymium catalysts. Samples were prepared in an open two-roll mill using standard mixing procedures. The vulcanization process was performed in a pneumatic double plate press at a temperature of 424 K for sample sets 1 and 2, 444 K for sample set 3. The cooling down process was performed using cold water.

## A.1.2 Sample set formulation and characterization

## Set 1

Sample	Polybutadiene(phr)	Polyisoprene (phr)	Sulfur (phr)
BR	100.00	0.00	1.35
MIX30	70.00	30.00	1.35
MIX50	50.00	50.00	1.35
MIX70	30.00	70.00	1.35
IR	0.00	100.00	1.35

Table A.1: Sample formulation. The vulcanizing and accelerating agents are: Zinc Ottoate: 4.00phr; DPG 80: 3.13 phr; TBBS 80: 2.50 phr.

A.1 | Sample details



Figure A.1: BR, MIX30, MIX50, MIX70, IR torque measurements. Measurements performed at  $424\,{\rm K}.$ 



Figure A.2: BR, MIX30, MIX50, MIX70, IR DSC thermographs. Exo up.

Sample	Temperature (K)	$D_{res}/2\pi~({ m kHz})$
BD	313	0.302
BR	353	0.293
ID	313	0.192
	353	0.188

Table A.2: Experimental  $D_{res}/2\pi$  values for pristine IR and BR samples at different temperatures. The error is 0.002 kHz.



Figure A.7: Pristine MIX70:  $D_{res}/2\pi$  distributions.

Sample	Temperature	$D_{res}/2\pi$
Sample	(K)	(kHz)
	313	0.309
PD	333	0.304
DR	353	0.289
	363	0.290
	313	0.177
IR	333	0.185
	353	0.184
	363	0.178

Table A.3: Experimental  $D_{res}/2\pi$  values for 5-months aged IR and BR samples at different temperatures. The error is  $0.002 \,\text{kHz}$ .



Figure A.8: 5-months aged BR  $D_{res}/2\pi$  distributions.

Figure A.9: 5-months aged IR  $D_{res}/2\pi$  distributions.





Figure A.10: 5-months aged MIX30  $D_{res}/2\pi$  distributions.

Figure A.11: 5-months aged MIX50  $D_{res}/2\pi$  distributions.

A.1 | Sample details



Figure A.12: 5-months aged MIX70  $D_{res}/2\pi$  distributions.



Sample	Polybutadiene(phr)	Polyisoprene (phr)	Sulfur (phr)
BR	100.00	0.00	1.35
MIX30	70.00	30.00	1.35
MIX50	50.00	50.00	1.35
MIX70	30.00	70.00	1.35
IR	0.00	100.00	1.35

Table A.4: Sample formulation. The vulcanizing and accelerating agents are: Zinc Ottoate: 4.00phr; DPG 80: 3.13 phr; TBBS 80: 2.50 phr.



Figure A.13: BR, MIX30, MIX50, MIX70, IR torque measurements. Measurements performed at  $424\,{\rm K}.$ 

## A.1 | Sample details

Sample	Vulcanizing time	Vulcanizing time	$D_{res}/2\pi$
Sample	(label)	$(\min)$	(kHz)
	t05	3.36	0.295
	t30	4.10	0.299
PD	t60	5.00	0.301
DR	t90	6.03	0.310
	t95	9.57	0.308
	t100	10.94	0.304
	t05	3.36	0.215
	t30	4.10	0.247
IR	t60	5.00	0.237
	t90	6.03	0.256
	t95	9.57	0.229
	t100	10.94	0.228

Table A.5: Experimental  $D_{res}/2\pi$  values for IR and BR samples vulcanized for different times. The error is 0.002 kHz.

## Set 3

Sample	Polybutadiene(phr)	Polyisoprene (phr)	Sulfur (phr)
BR	100.00	0.00	1.35
IR123	0.00	100.00	1.35
IR323	0.00	100.00	3.00

Table A.6: Sample formulation. The vulcanizing and accelerating agents are: Zinc Ottoate: 4.00 phr; DPG 80: 3.13 phr; TBBS 80: 2.50 phr.



Figure A.14: BR, IR123, IR323 torque measurements. Measurements performed at 443 K.

Vulcanizing time (label)	Vulcanizing time (min)		
	BR	IR123	IR323
tMH	8.60	2.60	1.70
t90	4.70	1.66	1.22
t60	3.30	1.30	0.95
t30	2.90	1.00	0.77

Table A.7: Vulcanizing times for the BR, IR123 and IR323 samples sets.

## A.2 Instruments and operative conditions

#### A.2.1 Rheological measurements

Rheological experiments were performed through a Monsanto Rheometer MDR (Moving Die Rheometer) 2000E in Pirelli S.p.A. laboratories at 423 K. Around 6 g of samples were used.

## A.2.2 Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) thermogram were performed on a Mettler Toledo DSC 1 Star<sup>e</sup> System.

Samples of  $20 \pm 5 \text{ mg}$  were characterized by the following method: 1) 298 K to 123 K @ -20 K/min; 2) 5 min isotherm 123 K; 3) 123 K to 473 K @ 20 K/min; 4)5 min isotherm 473 K; 5) 473 K to 123 K @ -20 K/min 6) 5 min isotherm 123 K; 7) 123 K to 423 K @ 20 K/min. All segments were driven under 80 ml/min N<sub>2</sub> flux. In the following only the bulk, thermal history-free segment 6) is reported.

## A.2.3 <sup>1</sup>H-TD-NMR

#### Instrument and operative procedure

All low-field NMR experiments have been performed on a 0.5 T Bruker Minispec mq20. It is a low resolution NMR spectrometer with a proton Larmor frequency of 19.65 MHz, equipped with a static probe and a BVT3000 temperature control unit working with nitrogen gas. The temperature was calibrated using an external thermometer with an accuracy of 1 K. The precision is 0.1 K and in these conditions the temperature is stable within that range during the measurements.

The spectrometer was set at the required operative temperature at least 8 h before starting any experiment in order to let the magnetic and gradient units and the sample' surroundings properly thermalize. The instrumental dead time was set at  $14 \,\mu$ s and the number of scans at 128, in order to allow a good signal-to-noise ratio.

All the MQ NMR experiments on rubber samples have been performed using the following operative procedure. The values of 90, 180 degree pulse lengths have been determined by nutation experiments for each sample as reported in paragraph 1.14. Analogously, the recycle delay was set as five times the T1: the T1s were measured through saturation recovery experiments (par. 1.6.1) at 353 K, if not otherwise mentioned.

## Sample preparation and operative NMR parameters

The rubber samples were sliced into two/three 3 mm thick, 7 mm diameter circular discs and then placed into a conventional NMR glass tube (OD: 10 mm, ID: 7 mm). The single discs were sampled from different positions of the original vulcanization rubber sample, in order to minimise the random errors due to the mixing procedure. Before running the measurement, each sample was thermalised for 30 min at the required experimental temperature. For MQ experiments, 128 scans were acquired.

Sample	90° $t_{pl}$ (µs)	$180^{\circ} t_{pl} \ (\mu s)$	T1 (ms)
BR	2.17	4.22	397
MIX30	2.10	4.13	271
MIX50	2.12	4.16	137
MIX70	2.11	4.15	173
IR	2.14	4.20	137

Table A.8: Set 1: NMR operative parameters.

Sample	Vulcanizing time (min)	90° $t_{pl}$ (µs)	180° $t_{pl}~(\mu {\rm s})$	T1 (ms)
	3.36	2.12	4.16	437
	4.10	2.10	4.09	441
DD	5.00	2.10	4.10	396
DR	6.03	2.07	4.07	407
	9.57	2.07	4.07	396
	10.94	2.10	4.12	401
	4.01	2.08	4.07	314
MIX30	6.03	2.19	4.27	
	10.94	2.08	4.06	287
	3.36	2.07	4.07	255
MIX50	5.07	2.08	4.16	230
	9.57	2.07	4.05	232
	3.36	2.09	4.10	202
MIX70	5.00	2.12	4.20	182
	9.58	2.08	4.06	186
	3.36	2.14	4.17	155
	4.10	2.12	4.14	154
ID	5.00	2.09	3.99	146
IN	6.03	2.08	4.06	142
	9.57	2.11	4.13	140
	10.94	2.11	4.14	140

Table A.9: Set 2: NMR operative parameters.

## A.2 | Instruments and operative conditions

Sample	Vulcanizing time	$90^{\circ} + 1(\mu_{\rm S})$	$180^{\circ} + 100^{\circ}$	T1 (ms)
Sample	v dicamizing time	$50 \ v_{pl} \ (\mu s)$	$100 \ v_{pl} \ (\mu s)$	<b>11</b> (III3)
	tMH	2.13	4.16	125
DD	t90	2.16	4.21	125
DR	t60	2.16	4.21	136
	t30	2.12	4.14	144
	tMH	2.16	4.19	141
IR123	t90	2.14	4.16	143
	t60	2.13	4.14	152
	t30	2.13	4.14	157
	tMH	2.07	4.07	255
IR323	t90	2.08	4.16	230
	t60	2.10	4.10	396
	t30	2.07	4.05	232

Table A.10: Set 3: NMR operative parameters.

#### Error determination

In order to estimate the error on the  $D_{res}$  values for each NMR MQ measurements, the NMR measurements were repeated four times on the 5-months aged sample IR reported in table A.4 at an experimental temperature of 353 K. All the  $D_{res}$  values are reported in table A.2: out of the four measurements, its standard deviation is 0.0014 kHz. Therefore, in all MQ NMR measurements an error of 0.002 kHz is assumed on  $D_{res}$  values. Figure A.15 shows the  $D_{res}$  distribution: all the distributions match really well. For the linear combinations, conventional error propagation theory was applied.

Measurement	$D_{res}$ (kHz)
1	0.184
2	0.183
3	0.184
4	0.186

Table A.11:  $D_{res}$  values of repeated measurements on the 5-months aged IR sample reported in table A.4.



Figure A.15:  $D_{res}$  distributions for IR sample repeated five times.

## A.2.4 Transmission electron microscopy

Transmission electron microscopies were performed by Lucia Conzatti, Ph.D. at Consiglio Nazionale delle Ricerche (CNR) and Istituto per lo Studio delle Macromolecole in Genova, Italy. The samples were frozen at a temperature of 128 K for 2 h and ultramicrotomed with a glass blade kept at 113 K in order to avoid the freezing of the DMSO/H<sub>2</sub>O solution the slices were floating on. Lastly, the sample slices were treated with  $OsO_4$  vapors in order to highlight the BR, which turns black in the TEM microscopies.

## APPENDIX B

## Polymer nanoparticles and films

In this appendix, details on the synthetic protocol, samples labels, NMR sample preparation and a comprehensive not-NMR characterization of the DVB-crosslinked PS NPs, PBA/PS core-shell NPs and BEVA ®731-replacement film mixtures are provided. Lastly, the instrumentation and used methods are described.

## B.1 DVB-crosslinked PS nanoparticles

## B.1.1 Synthetic protocols and sample labels

Styrene (STY, >99% ReagentPlus®4-tert-butylcatechol as stabilizer) monomer was purified through distillation on aluminum oxide (activated, basic, Brockmann I) column. 2,2'-Azobis(2-methylpropionitrile) (AIBN, purum>98%) was recrystallized twice before usage. Sodium dodecyl sulfat (SDS, purum>99%), Chromasolv Water and Divinylbenzene (DVB, technical grade 80% containing 1000 ppm p-tertbutylcatechol as inhibitor) were used as received without further purification. All reactants were purchased from Sigma-Aldrich S.r.l (Milan, Italy).

The synthetic process follows a one-step miniemulsion polymerization protocol. 40 ml of Chromasolv Water and  $0.1387\pm0.0003$  mmol of SDS were put in a two necks flask and degassed with freeze, pump and thaw (FPT). The water solution is transferred to a bottom flask and additionally degassed with bubbling N<sub>2</sub> at 308 K, under mechanical stirring (350 rpm, ALC quiet-SL 35 rotor-stator). Meanwhile, in a second flask, 3 ml of STY were added to  $0.0609\pm0.0006$  mmol of AIBN and the required amount of DVB: degassed via FPT, it is dripped into the water solution with a flux of 4.5 ml/h by means of a syringe pump. The emulsion was homogenized under mechanical stirring (1500 rpm) at 308 K for 1 h. Lastly, the reaction was allowed to proceed for 11 h at 353 K, then cooled to room temperature.

The analyzed samples were named as PS-DVB followed by a percentage, which indicates the relative amount of SVB in the sample expressed as the volume fraction over the styrene (i.e.: PS-DVB-2.5%: sample with a relative amount of DVB of 2.5% (%w/V)).

The samples were provided by S. Bonetti, Ph.D and M. Mauri, M. Sc. (State University Milan Bicocca, Milan, Italy).

## B.1.2 Not-NMR characterization

## DLS and SEM analysis

The shape and dimensions of the obtained DVB-crosslinked PS NPs were analyzed by Dynamic Light Scattering (DLS) and scanning electron micrographs (SEM). DLS measurements have been performed on the freshly collected emulsion and the average solvodynamic diameters are reported in table B.1.

Sample	Average DLS diameter (nm)	PDI
PS-DVB0%	121.7	0.061
PS-DVB5%	91.0	0.149
<b>PS-DVB7.5</b> %	75.8	0.124
PS-DVB30%	45.5	0.215

Table B.1: DLS average diameters and corresponding PDI for differently DVB-crosslinked PS NPs.

Clearly enough, DLS data show that an increase of the DVB amount in the NPs leads to a dimension shrinking, up to 63% for sample PS-DVB30%. This result suggests that the polymer mesh becomes tighter and the available free volume is reduced. SEM micrographs (figures B.1.2, B.1.2, table B.2) prove the NPs have a spherical shape and eventually tend to agglomerate. Additionally, the same shrinking behaviour is observed: the overall smaller dimensions are due to the strong capillary forces acting on the NPs during the SEM sample preparation.





Figure B.1: SEM micrographs for sample PS-DVB0% at different magnifications. Clockwise: 50kx and 140kx.



Figure B.2: SEM micrographs for sample PS-DVB7.5% at different magnifications. Clockwise:  $50\mathrm{kx}$  and  $140\mathrm{kx}.$ 

Sample	Average SEM diameter (nm)
PS-DVB0%	112.8±8
PS-DVB5%	_
PS-DVB7.5%	$72.1 \pm 11$
PS-DVB30%	-

Table B.2: SEM average diameters for differently DVB-crosslinked PS NPs. Error is calculated out of 10 NPs.

#### Thermal analysis

DSC thermal analysis were performed on powder, obtained precipitating the fresh emulsion in methanol (Sigma-Aldrich, Milan, Italy). Figure B.3 shows the first scan thermogram, which allows for an investigation of the structure-related thermal properties. Particularly, an exothermic peak shows up at temperatures just above the PS  $T_g$ : it clearly indicates the NPs are porous structures [1], which collapse as soon as  $T_g$  is reached. Such a peak is particularly evident in not-crosslinked NPs, whereas it is reduced in intensity as the amount of DVB in the sample is increased: the polymer mesh gets tighter with an increase of the crosslinking points. Interestingly enough, the emergence of a porous structure within the NPs can lead to potential applications for up-conversion devices: the porous structure can easily host photoactive up-converter molecules.

Figure B.4, instead, shows the second scan DVB-crosslinked NPs DSC thermograms, proving information concerning the thermally-stabilized properties of the systems [2]. Interestingly enough, the PS  $T_g$  value change accordingly to the amount of crosslinker in the sample. Particularly, they increase from values closed to PS bulk one up to values even 45 K higher (sample PS-DVB7.5%). Lastly, sample PS-DVB30%  $T_g$  is not-detectable, suggesting the system is now in the hypercrosslinked regime. All data are summed up in table B.3.



Figure B.3: DSC thermograph for differently DVB-crosslinked PS NPs: first scan. The exothermic peak just after the  $T_g$  proves the NPs porous structure. Exo up.

Sample	DSC $T_g$ (K)
PS-DVB0%	$375 \pm 5$
PS-DVB5%	$400 \pm 5$
PS-DVB7.5%	$420 \pm 5$
PS-DVB30%	ND

Table B.3: DSC  $\rm T_g$  for differently DVB-crosslinked PS NPs. Sample PS-DVB30% has a not-detectable (ND)  $\rm T_g.$  Exo up.

## B.1.3 NMR sample preparation

For the study of the oxygen effects on relaxation properties, the commercial PS in chips was provided by Sigma-Aldrich S.r.l. and used as received. The treated commercial PS was obtained as follows: PS chips were dissolved in dichloromethane, precipitated in methanol, filtered and dried in air. Both the described samples and all the DVB-crosslinked PS NPs samples used for T1 temperature-dependent study were degassed by firstly loosely packing a few tens of milligrams of sample powder in a heavy-walled 10 mm NMR tube (with a 7 mm inner diameter) in the sensitive volume of the NMR coil and then removing atmospheric gases by applying a dynamic vacuum ( $<10^{-1}$  mbar) on the NMR tube for 24 h at 278 K with a rotary mechanical pump equipped by a nitrogen trap. All tubes were lastly flame-sealed. Powder was obtained precipitating the emulsion in methanol (Sigma-Aldrich, Milan, Italy).

#### B.1.4 NMR operative parameters

Firstly, preliminary sample characterization (see table B.5) was performed at 313 K: 90 and 180 degree pulse lengths are reported in the following table.



Figure B.4: DSC thermograph for differently DVB-crosslinked PS NPs: second scan. The  $T_g$  values shift to higher ones if DVB is increased. Exo up.

Sample label	90° $t_{pl}$ (µs)	$180^{\circ} t_{pl} \; (\mu s)$
PS-DVB0%	2.25	4.21
PS-DVB5%	2.30	4.43
PS-DVB7.5%	2.24	4.18
PS-DVB30%	2.21	4.22

Table B.4: DVB-crosslinked PS NPs: NMR operative parameters.

For all rigid fraction measurements, 128 scans were acquired, the receiver dead time was set to  $12.7 \,\mu$ s, and phase switching time to  $2.2 \,\mu$ s.

## B.2 PBA/PS core-shell nanoparticles

## B.2.1 Synthetic protocol and sample labels

*n*-butylacrilate (BA, >99% containing 10-60 ppm monomethyl ether hydroquinone as inhibitor) and styrene (STY, >99% ReagentPlus®4-tert-butylcatechol as stabilizer) monomers were purified through distillation on aluminum oxide (activated, basic, Brockmann I) column. 2,2'-Azobis(2-methylpropionitrile) (AIBN, purum>98%) was recrystallized twice before usage. Dioctylsulfosuccinate sodium salt (AOT, purum>98%), Chromasolv Water and Divinylbenzene (DVB, technical grade 80% containing 1000 ppm p-tert-butylcatechol as inhibitor) were used as received without further purification. All reactants were purchased from Sigma-Aldrich S.r.l (Milan, Italy).

The synthetic process follows a two-step miniemulsion polymerization protocol. Firstly, the PBA core is emulsified: 160 ml of Chromasolv water were put in a four necks flask and degassed with bubbling N<sub>2</sub> at 308 K for 1 h, under mechanical stirring (350 rpm, ALC quiet-SL 35 rotor-stator). Meanwhile, in a second flask, 21 mmol of BA were added to AOT ( $0.1240\pm0.002$  mmol) and AIBN ( $0.042\pm0.0061$  mmol). The feeding solution was degassed with freeze, pump and thaw (FPT) and added to

the water with a flux of 3 ml/h by means of a syringe pump. Temperature was set at 343 K for 3 h. Secondly, the PS crosslinked shell is grown. During the polymerization of BA, a third flask was prepared with a solution of 78 mmol of STY and AIBN  $(0.179 \pm 0.0061 \text{ mmol})$ , AOT  $(0.0546 \pm 0.002 \text{ mmol})$ , DVB  $(0.695 \pm 0.002 \text{ mmol})$ . The solution was degassed via FPT and dripped into the pristine O/W emulsion. The reaction was allowed to proceed for 8 h at 343 K, then cooled to room temperature and homogenized (i.e. without turning the stirring off) for the next 8 h.

Th samples were provided by S. Bonetti, Ph.D (State University Milan Bicocca, Milan, Italy).

#### B.2.2 Not-NMR characterization

#### DLS, SEM and AFM analysis

The shape and dimensions of the synthesised PBA/PS NPs were analyzed by Dynamic Light Scattering (DLS), scanning electron microscopy (SEM) and atomic force microscopy in intermittent mode.

DLS measurements were performed on the freshly collected emulsion. The average hydrodynamic diameter of the core and the global core-shell NPs are 115 nm (PDI=0.04) and 184 nm (PDI=0.01) respectively. The corresponding distributions are reported in figure B.5.

The shape and height of nanoparticles extracted from the AFM image (see figure B.6) indicate monodisperse spheres with an average diameter of  $164\pm11$  nm (measured out of 100 NPs). This result is in good agreement with the SEM image (figure B.7) recorded without thermal treatment performed on the freshly prepared emulsion: the average diameter is  $168\pm11$  nm measured out of 100 NPs. Additionally, the nanoparticles show a remarkable shape persistence: in order to obtain the AFM and SEM micrographs, strong capillary and surface forces associated to drying and adsorption to the mica surface were applied to the NPs; such forces justify the slightly shrinked dimensions measured measured by AFM and SEM compared to DLS ones. Moreover, all micrographs clearly suggest that the external shell is made of purely PS, a polymer that can be shaped at the nanoscale into highly stable forms: if the PBA was outside, then a film would be observed, being room temperature above PBA T<sub>g</sub>.


Figure B.5: DLS hydrodynamic diameter distributions for core-shell NPs and core only.



Figure B.6: AFM image of PBA/PS NPs (4  $\mu \rm{m}~X~4\,\mu \rm{m}~X~200\,\rm{nm}).$ 



Figure B.7: SEM micrograph of PBA/PS NPs.

#### Thermal analysis

The DSC thermal characterization was performed after the NPs emulsion was precipitated in methanol (Sigma-Aldrich, Milan, Italy). The thermogram clearly reveals the presence of two distinct glass transitions  $(T_g)$  at temperatures expected for bulk PBA and PS, respectively (220 and 380 K), suggesting the two polymers evolution proceed as in two independent homopolymers. A direct observation of the different proportions of PBA and PS in the NPs is given by the different absolute value of the change in heat flow values at the glass transition temperatures.



Figure B.8: DSC thermograph for PBA/PS NPs: the PBA and PS bulk  $\rm T_g$  are clearly evident. Exo up.

#### B.2.3 NMR operative parameters

Firstly, preliminary sample characterization (see table B.5) was performed at 313 K: 90 and 180 degree pulse lengths were determined by nutation experiments, whereas T1 was determined by saturation recovery ones. The obtained parameters are: 90°  $t_{pl}=2.10 \,\mu\text{s}$ , 180°  $t_{pl}=4.10 \,\mu\text{s}$ , T1=308 ms.

For temperature-dependent analysis, temperature was first decreased and then increased, in order to preserve the inner structure. Particularly, 128 scans were acquired, the receiver dead time was set to  $12.7 \,\mu$ s, and phase switching time to  $2.2 \,\mu$ s.

## B.3 BEVA ®731-replacement for cultural heritage

#### B.3.1 Mixture formulations and labels

In all the bi- and triphasic mixtures, the following raw materials have been used. Particularly, an polyethylene-poly(*n*-butyl acrylate) (EBA, Lotryl®35BA320 supplied by Arkema S.r.l., Milan, Italy) was chosen as base-copolymer, whereas a ureaaldehyde low molecular weight resin took the role of tackifier (UA, Laropal®A81, by BASF, Ludwigshafen, Germany). A paraffin wax with a melting temperature of 338 K was finally added (Paraffin 411663 sold by Sigma-Aldrich S.r.l., Milan, Italy). The three basic components were analyzed in chips, as given by the producer.

In order to obtain the required mixture, after being weighed, the components were put in a vial and mixed together with xylene under agitation at 223 K for 1 h, being sure that none of the components undergo temperature-related chemical degradation at this temperature or below. The mixture were analyzed as films: the residual xylene was removed by evaporation at room temperature for 1 month.

Commis lobal	EBA percentage	UA percentage	Wax percentage
Sample label	(%)	(%)	(%)
EU	71.4	28.6	0.0
EW	90.0	0.0	10.0
UW	0.0	75.0	25.0
EUW	60.0	30.0	10.0

Table B.5: Mixture formulation.

The samples were provided by D. Cimino, Ph.D. (Turin State University, Turin, Italy).

#### B.3.2 NMR operative parameters

Firstly, preliminary sample characterization (see table B.6) was performed at 313 K. In order to study hysteresis phenomena still preserving the mixture film-induced properties, temperature was first decreased from 313 K down to the lowest accessible temperature, the risen up until a negligible temperature is measured and then dropped back again to 313 K.

Sample label	90° $t_{pl}$ (µs)	$180^{\circ} t_{pl} \; (\mu s)$	T1 $(ms)$
EBA	2.03	4.04	-
UA	2.08	4.07	-
Wax	2.11	4.14	-
EU	2.11	4.08	85
EW	2.16	4.17	62
UW	2.25	4.14	138
EUW	2.14	4.11	85

Table B.6: BEVA ®731-replacements: NMR operative parameters.

For all rigid fraction measurements, 128 scans were acquired, the receiver dead time was set to  $12.7 \,\mu$ s, and phase switching time to  $2.2 \,\mu$ s.

## B.4 Instruments and data analysis

#### B.4.1 Dynamic Light Scattering

Dynamic Light Scattering (DLS) measurements were performed at 25  $\check{r}$ C by a Malvern Instruments Nano Series Zetasizer optical unit (Continuos Wave 4 mW He-Ne class 1 internal laser operating at 632.8 nm, measurement angles at 13° and 175° and Avalanche photodiode detector with Q.E.>50% at 633 nm).

The solvodynamic diameters are fitted with a log-normal distribution: a continuous probability distribution of a random variable whose logarithm is normally distributed. It can be expressed as:

$$f(D, \langle D \rangle, \sigma) = \frac{1}{\sqrt{2\pi}D\sigma} e^{\left[\frac{\log(D) - \log(\langle D \rangle)}{\sigma}\right]^2}$$
(B.1)

where  $\langle D \rangle$  is the mean value of the variable and  $\sigma$  is its standard deviation (i.e. in this case is the solvodynamic diameter). PDI is the polydispersity index, which measures the width of the particle size distribution. The formula for polydispersity is:

$$PDI = \left(\frac{\sigma}{\langle D \rangle}\right)^2 \tag{B.2}$$

where  $\sigma$  is the standard deviation and  $\langle D \rangle$  is the mean value of the variable D.

#### B.4.2 Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) measurements were performed on a Mettler Toledo DSC 1 Stare System, on powder.

PS DVB-crosslinked NPs samples of  $6 \pm 1 \text{ mg}$  were characterized with the following method: 1) 273 K to 473 K @ 20 K/min; 2) 5 min isotherm at 473 K; 3) 473 K to 273 K @ -20 K/min; 4) 5 min isotherm at 273 K; 5) 273 K to 473 K @ 20 K/min. All segments were driven under 80 ml/min N<sub>2</sub> flux.

PBA/PS NPs samples of  $20 \pm 5$  mg were characterized with the following method: 1) 30 min isotherm at 123 K; 2) 123 K to 423 K @ 20 K/min; 3) 5 min isotherm at 423 K; 4) 423 K to 123 K @ -20 K/min; 5) 5 min isotherm at 123 K; 6) 123 K to 473 K @ 20 K/min. All segments were driven under 80 ml/min N<sub>2</sub> flux.

#### B.4.3 Scanning Electron Microscopy

SEM imaging was performed with a Tescan VEGA TS 5136 XM in high vacuum conditions ( $<10^{-3}$  Pa), at a voltage level of 20 kV. The spot size was 20.9 nm. All samples were first gold-coated using an Edwards Sputter Coater S150B.

#### B.4.4 Atomic Force Microscopy

AFM imaging was carried out with a JPK NanoWizard (JPK Instruments, Berlin, Germany) with closed loop scanner using silicon cantilevers with a resonance frequency of 70 kHz and a nominal spring constant of 2 N/m (OMCL-AC240TS, Olympus, Tokyo, Japan). Spring constants of cantilevers were determined using the thermal noise method. The AFM image was collected at ambient condition in intermittent contact mode on a sample deposited on freshly cleaved mica and dried in a vacuum oven at 75 K for 16 h before thermalization at room temperature

Micrographs are a courtesy of S. Bonetti, Ph.D (State University Milan Bicocca, Milan, Italy) and M. Kappl, Ph.D (Max-Planck Institut for Polymer Research, Mainz, Germany).

## B.4.5 Solid State <sup>13</sup>C-MAS-NMR

Solid state CP-MAS and SPE NMR experiments were performed on a solid state magic angle spinning Bruker Avanche 300 spectrometer (Bruker BioSpin AG, Fällanden, Switzerland) at 298 K. Sample was heavily packed in a 4 mm ZrO<sub>2</sub> rotor. Spinning rate was set to 9000 Hz for both experiments. SPE was recorded with 4096 scans using a recycle delay of 2 s. For CP-MAS, 1024 scans were acquired and a contact time of 1.5 ms and a recycle delay of 4 s were used. Experiments were performed at Instituto Ronzoni (Milan, Italy) and the data analysis by MestreC 4.9.9.9 software.

## B.4.6 <sup>1</sup>H-TD-NMR

All low-field NMR experiments have been performed on a 0.5 T Bruker Minispec mq20. It is a low resolution NMR spectrometer with a proton Larmor frequency of 19.65 MHz, equipped with a static probe and a BVT3000 temperature control unit working with nitrogen gas. The temperature was calibrated using an external thermometer with an accuracy of 1 K. The precision is 0.1 K and in these conditions the temperature is stable within that range during the measurements.

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## APPENDIX C

# Biochars

In this section, a description of the processes used for biochars activations from raw materials and non-NMR characterization is reported (par. C.1). Additionally, the instruments used and data analysis procedures are eventually described (par. C.3).

## C.1 Biochars activation and not-NMR characterization

## C.1.1 Pecan shell biochars

#### Biochars activation and sample labels

Pecan shell were acquired by USDA Southern Regional Research Center, (New Orleans, LA, USA) from H.J. Bergeron Pecan Shelling (Boyce, LA, USA). The samples were all milled and sifted. To make the biochar, pecan shells were mixed with 100 g 30% phosphoric acid overnight, and then heated at 723 K for 4 h at varying airflow rates (100, 400, 1200, and 2000 mL/min) in a furnace. After heating, the samples were permitted to cool down overnight while being bathed in a constant airflow, and then washed in water at 363 K. Sifting was done, and only particles larger than 0.25 mm were retained. All samples are named as PSC followed by a number: it makes reference to the different airflow rates (i.e. PSC-0: untreated sample, PSC-100: sample oxidised at a rate of 100 mL/min, etc.).

The samples were provided by H.N. Cheng, Ph.D. and K.T. Klasson, Ph.D (USDA Southern Regional Research Center, New Orleans, LA, USA).

#### C.1.2 Almond shell biochars

#### Biochars activation and sample labels

Almond shell biochar were prepared by treating almond shell (acquired by USDA Southern Regional Research Center, New Orleans, LA, USA) in an inert atmosphere at 1073 K for different amounts of time (60, 120, 240 min). Some aliquot of each sample was also washed with synthetic rain water at room temperature for 20 h in a tumbler. The synthetic rain water was made by adding a mixture of sulfuric and nitric acids (60:40 wt%) to distilled water until the pH was  $4.2\pm0.05$  [1]. After this treatment, each sample was then sieved to remove the water through a 400-mesh (37  $\mu$ m) screen. It was possible that some fine soot might have been lost during

#### C.1 | Biochars activation and not-NMR characterization

sifting. The sample was then dried overnight in an oven at 373 K. This treatment step, not performed on the unwashed samples, is very mild in comparison with the charring process but also with the preparation of  $^{129}$ Xe NMR tubes and we assume it will not affect sample morphology. Samples used in this work were labeled according to the duration of the thermal treatment and whether the samples were washed with rain water (i.e. sample **120**: biochar exposed to a 120 min thermal treatment; sample **240-RW**: biochar exposed to a 240 min thermal treatment and washed).

The samples were provided by H.N. Cheng, Ph.D. and K.T. Klasson, Ph.D (USDA Southern Regional Research Center, New Orleans, LA, USA).

#### Environmental Electron Scanning Microscopy

Environmental scanning electron microscopy (ESEM) was used to visualize the morphology of the biochar samples up to the microscale.

Figure C.1 shows the ESEM microscopies of sample **240** and **240-RW** at two different magnification (500x and 5000x). Particularly, at the lower magnification, samples show a mesoporous structure with pores in the micrometer range. Increased magnification shows that walls are patterned with submicrometric pores. In the unwashed sample (top pictures) part of the mesopores are obstructed by dust or ash, and even in the regions where the walls can be observed directly the image appears opaque, as if overlaid by a thin layer. Washing treatment with rain water removes the dust, fully revealing the pores of the behive-like structure (bottom pictures) with a wide range of sizes. At higher magnification, the micropores appear deeper and better defined.



Figure C.1: ESEM micrographs of almond shell chars prepared with 240 min thermal treatment at two different magnifications (500x and 5000x). Top: sample **240**. Bottom: sample **240-RW** washed with rain water. Dust removal due to washing is evident.

#### N<sub>2</sub> BET porometry and comparison with <sup>129</sup> Xe NMR

The  $N_2$  specific surface area data and the corresponding calculated average cylindrical pore diameters are reported in table C.1.

Sample	BET N <sub>2</sub> specific surface area $(m^2/g)$	$N_2$ pore diameter (Å)
60	$2\pm 2$	-
120	$81\pm0.5$	$10.1\pm0.4$
240	$201 \pm 9$	$9.3\pm0.2$
60-RW	$2\pm 2$	-
120-RW	$311 \pm 30$	$9.5\pm0.5$
240-RW	$439 \pm 40$	$9.1\pm0.2$

Table C.1: N<sub>2</sub> BET specific surface areas and pore diameter for almond shell biochars.

No  $N_2$  BET specific surface area is measured for samples **60** and **60-RW**: the thermal treatment is no long enough to induce the formation of porous structure at the nanoscale. On the other side, not null  $N_2$  BET specific surface area are detected for all other samples: a porous structure is induced. Additionally, an increase of almost two order of magnitude in the BET specific surface areas is measured after the rain water washing is performed. The calculated pore diameter shows a slight reduction in size as long as the thermal treatment length is increased and the sample is rain-washed.

Interestingly enough, <sup>129</sup>Xe NMR shows a peak related to the presence of pores even in sample **60-RW**, not detected by  $N_2$  BET data. Apparently, <sup>129</sup>Xe NMR is qualitatively sensitive to porosity below the minimum sensitivity of the BET technique.

## C.2 NMR characterization: sample preparation and 1D linefitting

#### C.2.1 NMR sample preparation

For <sup>129</sup>Xe NMR studies, about 250 mg of pecan shell-based biochar particles were loosely packed in a heavy-walled 10 mm NMR tube (with a 7 mm inner diameter) in the sensitive volume of the NMR coil. Atmospheric gases were removed by applying a dynamic vacuum ( $<10^{-1}$  mbar) on the NMR tube overnight at 453 K, using a rotary mechanical pump with a nitrogen trap. The xenon gas was transferred quantitatively from a reservoir of known volume (28.3 mL) into the sample tube via a Schlenk manifold by freezing the bottom of the sample tube with liquid nitrogen. The tube with xenon and the sample was hermetically sealed with a flame. The gas employed (Xenon 5.0, Sapio S.r.l., Monza, Italy) had a content of 26.44% (natural abundance) of the NMR-sensitive <sup>129</sup>Xe isotope. Analogous treatment have been performed on almond shell biochars.

## C.2.2 <sup>129</sup>Xe NMR 1D spectra: linefitting

The 1D spectra and linefitting for sample 120, 240, 120-RW are reported. As already mentioned in chapter 4.3.1, samples 120, 240 do not show any internal

xenon exchange: the fitting is good if one family of pores is supposed. Instead, in order to obtain good fitting for sample **120-RW**, two different populations of pores internally exchanging with each other needs to be supposed.



Figure C.2: Sample **120** 1D spectrum and linefitting: one single pore family is supposed.

Figure C.3: Sample **240** 1D spectrum and linefitting: one single pore family is supposed.



Figure C.4: Sample **120** 1D spectrum and linefitting. On the left one pore family is supposed whereas two are on the right.

## C.3 Instruments and data analysis

#### C.3.1 Environmental Scanning Electron microscopy

The instrument used for acquiring ESEM micrographs was a XL-30 environmental scanning electron microscope (FEI, Hillsboro, OR, USA). The biochars were mounted on aluminum specimen stubs with two-sided adhesive tabs (Electron Microscopy Sciences, Hatfield, PA, USA) and sputter coated with 60:40 gold:palladium to a thickness of 10 - 15 nm. Standard operating procedures were followed in obtaining the electron photomicrographs (10.0 kV voltage).

ESEM micrographs have been acquired by H.N. Cheng, Ph.D and K.T. Klasson, Ph.D at USDA Southern Regional Research Center in New Orleans, LA, USA.

#### C.3.2 N<sub>2</sub> BET porometry

The instrument used to acquire  $N_2$  Brunauer-Emmet-Teller specific surface area was measured using a NOVA 2200e nitrogen adsorption system (Quantachrome Instruments, Boynton Beach, FL, USA). In order to calculate the average pore diameter, the total pore volume was supposed to be fully occupied by liquid nitrogen at atmospheric pressure and 77 K.

N<sub>2</sub> BET measurements are a courtesy of H.N. Cheng, Ph.D and K.T. Klasson, Ph.D (USDA Southern Regional Research Center in New Orleans, LA, USA).

## C.3.3 <sup>129</sup>Xe NMR

All <sup>129</sup>Xe NMR experiments were performed at 308 K, using a Bruker Avance 500 spectrometer (Bruker BioSpin AG, Fällanden, Switzerland) equipped with a broadband 10 mm probe where <sup>129</sup>Xe resonance occurred at 138.45 MHz. If not otherwise specified, all samples have a xenon pressure of around 5 bar. Each 1D spectrum was acquired after single pulse excitation with  $32 \,\mu s \,\pi/2$  pulse length, using 800 scans and a recycle delay of 4 s. The 2D exchange experiments were run with a recycle delay of several seconds and a spectral width of 300 ppm in both t1 (128 t1 increments) and t2 dimensions. 2D data were collected in the TPPI mode. Exchange times were varied from 20 to 1000 ms. A conventional saturation recovery sequence was used for T1 experiments (par. 1.6.1; no MSE pulse train has been applied). Chemical shifts and linewidth data from the 1D spectra and 2D EXSY experiments were obtained with the use of MestreC 4.9.9.9 while T1 measurements were analyzed by MestReNova 10.0.1 software.

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