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Study of interfaces in multicomponent materials by solid-state NMR techniques

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Introduction

Nowadays, in many fields the research of materials with new and improved properties is mostly based on suitably combining different existing materials, rather than synthesizing new ones. Indeed, it is quite clear that “mixing” systems with different properties at a micrometric or (better) nanometric level can result in an interesting combination of the properties of the single components, and therefore in an improved material suitable for a wider range of applications. The single materials that are combined have a different chemical structure, and often materials with organic and inorganic nature are mixed, to which I will refer in this thesis as OIMMs (Organic-Inorganic Multicomponent Materials). This allows to simultaneously exploit the best properties of the inorganic (e.g. rigidity, barrier towards gases or fire, etc.) and the organic components (e.g. flexibility, reactivity, adhesivity, etc.). Obviously, many variables can affect the final properties of these materials, such as the number of components and the chemical and physical nature of the single components, their relative amount, etc. Actually, many classes of OIMMs exist differing for these variables, some of which are sketched in the Fig. 1, that has been divided on the basis of organic or inorganic nature of the matrix. Just taking into account the relative amount of organic and inorganic components they range from materials having an organic matrix with some inorganic components dispersed within (e.g. polymers filled with silica or clays), to materials having an inorganic matrix modified by some organic systems (e.g. organically-modified clays or zeolite-organic guest systems), to materials where organic and inorganic components are present in a similar amount (such as in many hybrid materials obtained by sol-gel processes). All this considered, the final materials could show just a combination of the properties of the single components: actually, often a suitable interface between organic and inorganic domains is able to confer to the final materials new and improved properties respect to the single components. All the aspects concerning the interfaces in composite materials are therefore of crucial importance for trying to understand the “microscopic” (here intended in general as referred to the molecular or supra-molecular level, and not to the micrometric one) origin of the macroscopic and applicative properties of a material. These aspects
Figure 1: Examples of classes of materials belonging to the general category of OIMM, divided on the basis of the organic or inorganic nature of the matrix.

are often very difficult to be investigated, and they include intrinsic properties of the interface, such as its physical and chemical nature, as well as other properties that are somewhat correlated to it, such as the degree of mixing between the different components (i.e. their average domain dimensions), or the change in the molecular dynamic behavior in passing from the pure components to the final material. The study of the interfaces and of the related properties in OIMMs is indeed the main task of this thesis.

The technique I have used to study these interfacial properties in composite materials is Solid-State NMR (SSNMR), which is actually rather an ensemble of a variety of techniques, all of them exploiting the NMR phenomenon in the solid state. Indeed, SSNMR recently revealed as a very powerful technique to investigating these materials, and in particular their interfaces, for a series of reasons, some of which are: the possibility of studying basically all kinds of materials (independently of their chemical nature or their physical state); the possibility of investigating structural and dynamic properties over very broad spatial (0.1-100 nm) and time (10^{-12} - 100 s) ranges, respectively; the ability of giving often very detailed information. This mainly arises from the huge number of experiments which is possible to devise, based on the different type of nucleus observed (the most common are ^1H, ^13C, ^29Si, ^31P, ^15N but basically each chemical element has at least a NMR-observable nucleus) and the different nuclear property measured (isotropic and anisotropic chemical shift, homo- and hetero-nuclear dipolar coupling and J-coupling,
the different kinds of relaxation times, like $T_1$, $T_2$, $T_{1\rho}$, and many others). Although there are important drawbacks in the use of SSNMR, mainly related to the cost of the instrumentation and the know-how required to run and interpret the experiments, this technique is emerging as a leading technique both in basic and industrial research of materials.

Of course SSNMR results have to be combined and integrated with those of complementary techniques, like other spectroscopies, calorimetries, microscopies, etc. Indeed, in this thesis, I have often combined and compared the results I have obtained by SSNMR with those obtained by collaborators with other techniques.

The materials here investigated range from polymer-based composite materials, where inorganic fillers (silicas or clays) are dispersed into polymeric matrices (polyethylenes or polyisoprenes), to silicas organically-modified on their surface, either encapsulated in a thin polymeric layer or impregnated with organometallic complexes.

The thesis consists of: a first chapter where the basics of NMR and, in particular, SSNMR are given; a second chapter where the main features of OIMMs are briefly described and the experimental SSNMR approach to their investigation is tackled with particular reference to the studies reported in this thesis; four more chapters reporting studies performed on four different sets of materials, going from encapsulated particles of silica with PMMA (chapter 3) to mesoporous silica nanoparticles impregnated with Yttrium complexes (chapter 4), and from polyisoprene rubbers filled with silica particles formed by sol-gel process (chapter 5) to polyethylenes filled with natural clay platelets (chapter 6).
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Chapter 1

Basics of solid-state NMR

1.1 Introduction

Magnetic Resonance [1] is a phenomenon found in magnetic systems that possess both magnetic moments and angular momentum. The term resonance implies that the radio frequency (for nuclear spins) or microwave frequency (for electron spins) applied is in tune with the frequency of gyroscopic precession of the magnetic moment in an external static magnetic field.

Nuclear Magnetic Resonance spectroscopy (NMR) relies on the interaction of the nuclei of certain atomic isotopes with the external static magnetic field. Like electric charge and mass, every elementary particle has spin. The spin is a form of angular momentum which is explained with the quantum mechanics models and it is an intrinsic property of the particle itself [2].

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The NMR phenomenon arises from the behaviour of the total nuclear spin angular momentum in the presence of external magnetic fields. The following sections will deal with the two different approaches commonly used to describe the NMR phenomenon, which make use of a vectorial and quantum - mechanical model of the spins under the effect of both static and time - dependent magnetic fields [2–6]. Though the vectorial picture has its own limitations since it applies only to uncoupled spins, it gives the understanding towards the effect of rf pulses and relaxation methods. It is interesting that this model has direct counterparts in the quantum mechanical treatment, and this common ground between these approaches helps in understanding the more complex quantum mechanical approach [3].
1.2 NMR phenomenon: a classical treatment

1.2.1 Nuclei in a static magnetic field

Similar to the classical angular momentum, the nuclear spin angular momentum or, more simply, the nuclear spin is a vector quantity, whose direction defines the spin polarization axis of the nucleus. In general, the spin polarization axis of a nucleus can point in any direction. The nuclear spin is identified by the spin quantum number $I$, which can be 0 (a nucleus with an even number of both protons and neutrons, hence the nucleus does not have a spin angular moment), an half-integer (if the total number of protons plus neutrons is odd) or an integer number different from zero (if the number of protons and number of neutrons are both odd).

Every nucleus with a non zero spin possesses a corresponding magnetic moment, which is responsible for the interaction with external magnetic fields. In terms of quantum mechanical operators\(^1\), the nuclear magnetic moment, $\hat{\mu}$, is related to the nuclear spin $\hat{I}$ by the following equation:

$$\hat{\mu} = \gamma \hbar \hat{I} \quad (1.1)$$

where each operator represents the corresponding classical three dimensional vectorial quantity and $\gamma$ is the magnetogyric (or gyromagnetic) ratio, (generally expressed in $[\text{rad s}^{-1} \text{T}^{-1} 10^7]$), is a fundamental property of the nucleus in question, determining whether the magnetic moment of a nucleus is parallel or antiparallel to the direction of the spin polarization as represented in Fig. 1.1.

\[\text{Figure 1.1: The magnetogyr}ic \text{ ratio } \gamma.\]

Therefore, the spin angular momentum of a nucleus is directly related with its magnetic properties, that means its capability of interacting with magnetic fields.

In the absence of external fields, there is no preferred orientation for a magnetic moment.

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\(^1\)The “hat” symbol will be used to indicate the quantum mechanical operators.
1.2 NMR phenomenon: a classical treatment

In the presence of a static magnetic field $B_0$, however, the energy of a magnetic moment $\mu$ depends on its orientation ($\theta$) relative to the direction of the applied field $B_0$ which is conventionally along $z$ axis.

Classically, the magnetic energy associated to the interaction between the individual nuclear magnetic moments corresponding to each nuclear spin and the static magnetic field $B_0$, called Zeeman interaction, can be expressed as:

$$E = -\mu \cdot B_0$$

The energy of the spins is thus minimized when the individual magnetic moment is aligned parallel to the magnetic field, as indicated by the negative sign. However, this alignment is opposed by the random thermal motion of the molecules. The randomizing effect of the thermal motion is not complete since the spin ensemble shows an energetic preference for the $z$-component of the magnetic moments to be aligned with the same direction of the field. As a consequence, the magnetic moments are aligned in such a way that, averaged over the spin ensemble, there is a slight net alignment of the moments parallel to the magnetic field. The probability of having a $z$-component of the magnetic moments parallel to the $z$-axis is higher than having it anti-parallel. This difference in probability, which is small in NMR due to the small energy difference between two adjacent energy spin levels (for the spin-$\frac{1}{2}$ case the difference of populations between the two adjacent energy levels divided by the total populations is $10^{-5}$ at room temperature), generates a macroscopic net magnetic moment different from zero for a spin ensemble, which is called magnetization.

In the absence of a magnetic field the spins are oriented randomly because all orientations have the same energy. Consequently there is no net magnetization for the spin ensemble. When a magnetic field is applied along the $z$-axis there is an energetic preference for the spin ensemble to be oriented parallel to the field, but in the beginning magnetic moments are still oriented randomly so there is no net magnetization. However, the nuclei start exchanging energy among each other and with the lattice, leading to the so-called relaxation towards thermal equilibrium, which is reached some time after the application of a static magnetic field to the spin ensemble. The process by which the spins comes to equilibrium is called relaxation and is illustrated in the Fig. 1.2.

The net magnetization corresponds to the vectorial sum of all the magnetic moments of the spin ensemble at thermal equilibrium and it results to be aligned along the $z$-axis; in these conditions it coincides with the $z$-component of the net magnetization, commonly

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$^2$The energy of this thermal motion is very much greater than the energy of interaction between a nuclear magnetic moment and the applied field, and so the thermal motion disrupts the alignment of the magnetic moments.

$^3$The collection of all the spin systems of a macroscopic sample can be called spin ensemble.
indicated as *longitudinal magnetization*. Mathematically speaking, the magnetization can be expressed as follows:

$$M = \sum_i \mu_i$$  \hspace{1cm} (1.3)

where $i$ indicates the $i$-th spin of the ensemble. From a physical point of view, $M$ considered as the nuclear contribution to the macroscopic magnetic moment of the sample\(^4\). In turn, each nuclear magnetic moment related to the nuclear spin $I$ is given by the Eq. 1.1. Hence, the net magnetization of the spin ensemble is then written as:

$$M = \gamma J$$  \hspace{1cm} (1.4)

where $J$ is the net spin angular momentum of the spin ensemble giving rise to the magnetization $M$.

The equation of motion of a spin angular momentum $I$ subject to a torque $T$, $\mu \times B_0$ arising from the interaction of the nuclear magnetic moment of a single spin and the static field $B_0$ is given as:

$$\frac{dI}{dt} = \mu \times B_0$$  \hspace{1cm} (1.5)

If we consider the classical picture\(^5\), where the nuclear magnetic moment precesses around the direction of the external magnetic field. The motion of the magnetic moment can be described either in a *laboratory frame* $(x, y, z)$ or in a *rotating frame* $(x', y', z')$ which rotates in the laboratory frame with an angular frequency $\omega$ and has the $z'$-axis parallel to $z$.

---

\(^4\)Every single nuclear contribution to the macroscopic magnetic moment of the sample does not behave exactly as $M$ of the vectorial model.

\(^5\)That is the magnetic moment of a single, identical and non interacting spin.
By combining Eq. 1.5 with the classical definition of nuclear magnetic moment \( \mu = \gamma I \), the equation of motion in the laboratory frame can be written as:

\[
\frac{d\mu}{dt} = \gamma \mu \times B_0
\]

or as motion of the magnetic moment in rotating frame plus the rotation of the rotating reference frame in laboratory system:

\[
\frac{d\mu}{dt} = \frac{\partial \mu}{\partial t} + \omega \times \mu
\]

by combining the Eq. 1.6 & 1.7, the rate of change of \( \mu \) in a frame rotating with the angular frequency \( \omega \) is then given by

\[
\frac{\partial \mu}{\partial t} = \gamma \mu \times \left( B_0 - \frac{\omega}{\gamma} \right)
\]

Eq. 1.8 tells that the motion of \( \mu \) in the rotating coordinate system obeys the same equation as in the laboratory system (Eq. 1.6), provided that the actual magnetic field \( B_0 \) is replaced by an effective field \( B_{\text{ef}} \):

\[
\vec{B}_{\text{ef}} = B_0 - \frac{\omega}{\gamma}
\]

When \( \omega = \omega_0, \frac{\partial \mu}{\partial t} = 0 \), therefore \( \mu \) remains fixed with respect to \( x, y, \) and \( z \) i.e. the magnetic moment is static. Therefore in the laboratory frame, the angular frequency is equal to the precessing frequency of the nucleus or the Larmor frequency, \( \omega_0 = -\gamma B_0 \). In NMR, the Larmor frequency \( \omega_0 \) is commonly referred to as angular frequency (expressed in [rad s\(^{-1}\)]) of the considered nucleus at the applied magnetic field strength \( B_0 \) with precession direction determined by the sign of \( \gamma \). The negative sign indicates that a nucleus with a positive \( \gamma \) has a negative Larmor frequency, that means the precession of the magnetization vector about the field corresponds to a clockwise rotation, as shown in the Fig. 1.3.

### 1.2.2 Effect of the rf field and the rotating frame

Coming to the alternative perspective of the classical approach in the NMR experiment, by looking at the Eq. 1.6, a magnetic moment \( \mu \) precesses about the direction of an external static magnetic field \( B_0 \) along the z-axis with angular frequency \( \omega \). In order to move the magnetization to the transverse plane, the NMR experiment includes a small, time-dependent, additional magnetic field \( B_1 \), rotating in the \( x - y \) plane in the same

---

\( ^6 \)It is important to note that the Eq. 1.6 holds true for a time-dependent B, not simply a static one.
sense and with the same angular frequency as $\mu$ of the precessing frequency. In practice, a linearly oscillating field is used, which is resolved into two components rotating in the opposite senses ($B_1^+$ and $B_1^-$) with a RF frequency ($\omega_{rf}$) same as that of the Larmor precession frequency ($\omega_0$). The component rotating in the same sense as $\mu$ (in this case, $B_1^-$) has a significant interaction with the magnetization, the other component can be disregarded. The motion of the field $B_1^-$ viewed in a fixed axes system or laboratory frame is shown in the Fig. 1.4.

Eq. 1.6 is still valid, provided that the total magnetic field is the sum of a time independent and time dependent term and thus $\mu$ obeys the equation.

$$\frac{d\mu}{dt} = \mu \times \gamma [B_0 + B_1(t)]$$  \hspace{1cm} (1.10)

In order to remove the time dependence of the $B_1$ field that makes easier to work out the effect of this field on the magnetization, $B_1$ is taken to be along the $x'$-axis in the rotating frame, which is illustrated in the Fig. 1.5.

As mentioned in the previous section this coordinate system is rotating about the $z'$-axis in the same direction as Larmor precession and assuming that it rotates with a same frequency as $\omega_{rf}$. Hence in this rotating set of axes $B_1$ appears to be static and
1.2 NMR phenomenon: a classical treatment

Figure 1.5: Schematic representation of motion of the field $B_1^-$ in a rotating frame. The field is rotating at $-\omega_rf$ about the $z$ axis, in this frame, the field $B_1^-$ appears to be static.

directed along the $x'$-axis. In this case:

$$\frac{\partial \mu}{\partial t} = \mu \times \gamma [B_0 + B_1 - \frac{\omega_r f}{\gamma}]$$  \hspace{1cm} (1.11)

Also can be written as:

$$\frac{\partial \mu}{\partial t} = \mu \times [z'(-\omega_r f + \gamma B_0) + x'\gamma B_1]$$  \hspace{1cm} (1.12)

There are two effects in making the transformation of Eq. 1.10 to Eq. 1.12. The first is associated with inclusion of a term $\omega_r f$, the component along the $z'$-axis and the second is associated with expressing the vectors $B_0$ and $B_1$ in terms of their components in the rotating frame and shows the conversion of $B_1$ from a rotating to a static field.

The Eq. 1.12 can be rewritten to emphasize the near-resonance condition, $\omega rf + \gamma B_0 \approx 0$, (assume $\gamma$ is positive) then \[1\]:

$$\frac{\partial \mu}{\partial t} = \mu \times \gamma [(B_0 - \frac{\omega_r f}{\gamma}) z' + B_1 x']$$  \hspace{1cm} (1.13)

$$= \mu \times B_{ef}$$  \hspace{1cm} (1.14)

where

$$B_{ef} = z'(B_0 - \frac{\omega_r f}{\gamma}) + B_1 x'$$  \hspace{1cm} (1.15)

In the Eq. 1.15, $(B_0 - \frac{\omega_r f}{\gamma})$ is the reduced field ($(\Delta B)$,the apparent magnetic field) along the $z$-axis in the rotating frame. If the rotating frame is at the Larmor frequency, the apparent magnetic field is zero. Physically, Eq. 1.13 really experiences a static magnetic field $B_{ef}$. The moment precesses in a cone of fixed angle about the direction of $B_{ef}$ at the angular frequency $\gamma B_{ef}$. The size of the effective field is given by, $B_{ef} = \sqrt{B_1^2 + (\Delta B)^2}$. This situation is illustrated in Fig. 1.6.

The angle between the $\Delta B$ and $B_{ef}$ is called the tilt angle and is denoted as $\theta$. If the resonance condition is met, $\omega_0 - \omega_r f = 0$, then $\theta = \frac{\pi}{2}$, i.e. the effective field is
simply $B_1$ and $M_0$ precesses or *nutates* in the $z' y'$ plane. If $B_0 > \frac{\omega_{rf}}{\gamma}$, the effective field has a positive $z$-component, but when $B_0 < \frac{\omega_{rf}}{\gamma}$, the effective field has a negative $z$-component.

### 1.2.3 On-resonance RF pulses

NMR experiments are carried out by using bursts or pulses of the field $B_1$. Thus the amplitude $B_1$ is time-dependent. Under the on-resonance condition, the effective field lies in the $x'$-axis and is equal to $B_1$. The *tilt angle* $\theta$ of the effective field is $\frac{\pi}{2}$ or $90^\circ$. In this condition, the precession frequency is $\omega_1$ for the $B_1$ field and when the RF field is applied for time $t_p$, the angle $\beta$ through which the magnetization is rotated to the $y'$ direction is:

$$\beta = \omega_1 t_p \quad (1.16)$$

$\beta$ is the *flip angle* of the pulse. If the flip angle is $90^\circ$, then it creates the conditions

$$M_{x'} = 0; \quad M_{y'} = M_0 \quad (1.17)$$

Similarly, a pulse which inverts $M_0$, is

$$M_{x'} = -M_0; \quad M_{x'} = 0; \quad M_{y'} = 0 \quad (1.18)$$
1.3 NMR phenomenon: the quantum mechanical approach

Figure 1.7: Three-dimensional representations of the motion of the magnetization vector during an on-resonance pulse: the bold line represents the path of the magnetization vector starting from the \( z' \) axis. The effective field lies along the \( x' \) axis; the magnetization therefore precesses in the \( y' z' \) plane. The rotation is in the counter clockwise about \( x' \), so the magnetization moves toward the \( -y' \) axis. In (a) the flip angle is 90°: the magnetization ends up along the \( -y' \); in (b) the pulse flip angle is 180° which places the magnetization along \( -z' \).

referred to as a 180°\( _x \) or \( \pi \)\( _x \) pulse. These conditions are illustrated in the Fig. 1.7.

These are non-equilibrium states for the spin system which will tend to return towards the equilibrium: the processes which bring back the magnetization to the equilibrium are referred to as relaxation which will be discussed later.

1.3 NMR phenomenon: the quantum mechanical approach

Though the vectorial model introduced previously for the description of the NMR phenomenon results to be appropriate because it allows a quite physical and “visual” picture of the principal aspects connected to the dynamics of non-interacting nuclear spins in the presence of either static or time-dependent fields, as well as the relaxation theory, this approach can result to be inadequate when interactions among the spins of the sample are taken into account. An alternative, more accurate description of the spin dynamics can be provided by quantum mechanics (QM).

1.3.1 Isolated nuclear spin in a static magnetic field

As already mentioned, the spin of a particle has the properties of an angular momentum which is not associated with any physical rotation. For nucleus the total spin angular momentum arises from the combination of the spin angular momenta of its constituting
elementary particles (neutrons and protons), which is performed with precise quantum mechanical rules. Quantum-mechanics assesses that the angular momentum is quantized. The quantization of the total spin angular momentum of a nucleus can be expressed by means of the following equations:

\[ \hat{I}_z |I, m_I\rangle = m_I |I, m_I\rangle \quad (1.19) \]

\[ \hat{I}^2 |I, m_I\rangle = I(I + 1) |I, m_I\rangle \quad (1.20) \]

where the \textit{kets} \( |I, m_I\rangle \) indicate the eigenstates of the operator \( \hat{I}_z \), corresponding to the \( z \)-component of the total spin angular momentum of the nucleus in a given axes frame. The nuclear spin quantum number \( I \) determines the total spin angular momentum of the nucleus, whose square value is represented by the operator \( \hat{I}^2 \). The \( I \) value corresponding to the lowest-energy combination of the spin angular momenta of all the individual particles constituting the nucleus is referred to as \textit{spin} of the nucleus. Depending on the nucleus, the quantum number \( I \) can take integer (0, 1, 2,...) or half-integer (1/2, 3/2, 5/2,...) values. The \textit{azimuthal} quantum number \( m_I \) can take all the \( (2I + 1) \) values \(-I, -I + 1, ..., I\) and defines the eigenvalue of the nuclear spin angular momentum along the \( z \)-axis.

Since both \( \hat{I}^2 \) and \( \hat{I}_z \) are Hermitian operators, the set of \( (2I + 1) \) eigenfunctions \( |I, m_I\rangle \) is orthonormal, and can be used as a basis set for a matrix representation of the spin operators.

In order to describe the NMR phenomenon in terms of QM rules, it is necessary to define the spin Hamiltonian in the presence of the static magnetic field \( B_0 \) only. In the absence of time-dependent interactions, the eigenstates and the energies of a nuclear spin can be obtained by solving the time-independent Schrödinger equation:

\[ \hat{H} |\psi_n\rangle = E_n |\psi_n\rangle \quad (1.21) \]

where \( \hat{H} \) is the Hamiltonian operator and \( E_n \) is the energy eigenvalue corresponding to the \( n \)-th eigenstate \( |\psi_n\rangle \).

As reminded in the beginning of the previous section, for an isolated nuclear spin in the presence of \( B_0 \), the energy operator that of the classical magnetic interaction between a magnetic moment \( \hat{\mu} \) and a static magnetic field; the corresponding Hamiltonian is:

\[ \hat{H} = -\hat{\mu} \cdot B_0 \quad (1.22) \]

commonly referred to as Zeeman Hamiltonian.

Considering the relation between \( \hat{\mu} \) and the spin angular momentum \( \hat{I} \) (Eq. 1.1), the Zeeman Hamiltonian can be written as:

\[ \hat{\mu} = -\gamma \hbar \hat{\mathbf{I}} \cdot B_0 \quad (1.23) \]
Following the NMR convention, in which a laboratory axes frame is chosen so that the static magnetic field is along the $z$ direction, the Hamiltonian results to be simplified to:

$$\hat{H} = -\gamma \hbar B_0 \hat{I}_z \quad (1.24)$$

Following the previous discussion about the quantization of the angular momentum, the time-independent Schrödinger equation for a spin in a static magnetic field $B_0$ is:

$$\hat{H}|I,m_I\rangle = -\hbar \gamma B_0 m_I |I,m_I\rangle \quad (1.25)$$

where $|I,m_I\rangle$ are the eigenstates of $\hat{I}_z$. The energy values of the spin eigenstates of a single nucleus in the presence of an external magnetic field can be obtained from the comparison of Eq. 1.21 & Eq. 1.25:

$$E_{mI} = -\hbar \gamma B_0 m_I \quad (1.26)$$

Therefore, for an isolated nuclear spin in presence of a static uniform magnetic field, $2I+1$ states are possible, often referred to as Zeeman states, each of them corresponding to an energy value depending on the nucleus ($\gamma$), the $m_I$ quantum number, and the magnetic field strength ($B_0$).

The energy difference between two consecutive states is, in angular frequency units [rad s$^{-1}$], the Larmor frequency $\omega_0 = \gamma B_0$, already introduced in the vector model description. The case of spin $I = \frac{1}{2}$ nuclei will be considered since it has a particular relevance in NMR, and in particular to this thesis. For a system constituted by a single spin - $\frac{1}{2}$ nucleus, the possible Zeeman eigenstates are commonly indicated as $|\alpha\rangle$ and $|\beta\rangle$, where:

$$|\alpha\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \\ 2 \end{pmatrix} \quad (1.27)$$

$$|\beta\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \\ 2 \end{pmatrix} \quad (1.28)$$

These eigenstates satisfy the following relationships:

$$\hat{I}_z|\alpha\rangle = \frac{1}{2}|\alpha\rangle \quad (1.29)$$

$$\hat{I}_z|\beta\rangle = -\frac{1}{2}|\beta\rangle \quad (1.30)$$

Eq. 1.29 indicates that a spin in the Zeeman eigenstate $|\alpha\rangle$ is polarized along the $z$-axis, and this corresponds to have a positive eigenvalue ($+\frac{1}{2}$) of the $z$-component of the spin angular momentum, as schematically represented in Fig. 1.8. Similar arguments
Figure 1.8: Representation of Zeeman eigenstates $|\alpha\rangle$ and $|\beta\rangle$: the arrows represent the polarization axis of the spin in the corresponding state.

are valid for the $|\beta\rangle$ eigenstate. The Zeeman eigenstates $|\alpha\rangle$ and $|\beta\rangle$ are characterized by energies:

$$E_\alpha = -\frac{1}{2}\gamma\hbar B_0 \quad (1.31)$$

$$E_\beta = \frac{1}{2}\gamma\hbar B_0 \quad (1.32)$$

respectively. The energy-levels diagram for the spin-$\frac{1}{2}$ case is represented in Fig. 1.9.

Figure 1.9: Representation of the energy levels for a spin-$\frac{1}{2}$ in a static magnetic field $B_0$.

Actually, $|\alpha\rangle$ and $|\beta\rangle$, being eigenfunctions of the Zeeman Hamiltonian, are the stationary states of the system which are not time dependent, but these are not the only possible states a spin can experience. Generally, the nuclear spin can also be in a superposition state $|\psi\rangle$, obtained as a linear combination of Zeeman eigenstates. For the spin-$\frac{1}{2}$ case, each of the states is expressible as:

$$|\psi\rangle = c_\alpha |\alpha\rangle + c_\beta |\beta\rangle \quad (1.33)$$

Quantum mechanics established that in the Zeeman states, the $z$ component of the spin angular momentum is well defined, while both the $x$ and $y$ components are undetermined.
Considering a particular superposition state:

$$| + x \rangle = \frac{1}{\sqrt{2}} |\alpha\rangle + \frac{1}{\sqrt{2}} |\beta\rangle$$

(1.34)

it is given that $| + x \rangle$ is only eigenfunction of $\hat{I}_x$, with eigenvalue $\frac{1}{2}$, $I_z$ and $I_y$ are undetermined in this spin state. Similarly, there will exist many superposition states in which all the three $\hat{I}$ components will be determined.

A spin state can be depicted with an arrow pointing along the direction in which the spin angular momentum is well defined, that is along the spin polarization. The particular spin states for which the spin polarization is along one of the cartesian axes is represented by using braket-notation as $| \pm i \rangle$, with $i = x, y, z$ and the sign being the sign of the $\hat{I}_i$ eigenvalue. The pictorial representations of $| + x \rangle$ and $| + y \rangle$ states is shown in Fig. 1.10, which cannot be inserted in the energy-levels diagram of Fig. 1.9, in fact, they are not eigenstates of $\hat{H}$, and for this reason they do not possess a well-definite energy eigenvalue.

A Zeeman eigenstate is different from a superposition state, since the former, in absence of time-dependent Hamiltonians, remains the same, as long as the Hamiltonian does not change, while the latter, even in absence of time-dependent Hamiltonians, it is subjected to a time evolution that transforms it into a different superposition state. Generally, the time-evolution of a superposition state is governed by the time-dependent Schrödinger equation:

$$\frac{d|\psi(t)\rangle}{dt} = -\frac{i}{\hbar} \hat{H} |\psi(t)\rangle$$

(1.35)

It is worth noting that the eigenstates of the time independent Hamiltonian $\hat{H}$ can also be treated as particular examples of superposition states. In fact, from Eq. 1.33 it follows that for the spin-$\frac{1}{2}$ case $|\psi\rangle = |\alpha\rangle$ when $c_\alpha = 1$ and $c_\beta = 0$, and $|\psi\rangle = |\beta\rangle$ when $c_\alpha = 0$.
and $c_\beta = 1$.

This discussion aims at singling out that the picture of spin precession in the presence of $B_0$ previously introduced with the vectorial model of NMR is only appropriate to describe the time-evolution of superposition states. Let consider two time points $t_a$ and $t_b$, with $t_b > t_a$, and assuming that the state of a system at $t_a$ is already known. By solving Eq. 1.35, it is possible to predict the state of a system at $t_b$. In particular, this equation is easily solved in the presence of the time-independent Zeeman Hamiltonian, as it is the case when $\hat{H} = \hat{H}^2$ and no rf field present. For this case, it results:

$$|\psi(t_b)\rangle = e^{-i\omega_0\tau \hat{I}_z}|\psi(t_a)\rangle$$  \hspace{1cm} (1.36)

with $\tau = t_b - t_a$

The time-evolution of the generic superposition state $|\psi(t_a)\rangle$ is thus determined by the operator:

$$\hat{R}_z(\omega_0\tau) = e^{-i\omega_0\tau \hat{I}_z}$$ \hspace{1cm} (1.37)

In general sense:

$$\hat{R}_k(\phi) = e^{-i\phi \hat{I}_k}$$ \hspace{1cm} (1.38)

with $k = x, y$ or $z$, is commonly referred to as rotation operator, since it introduces a rotation of the superposition state $|\psi\rangle$ around the $k$-axis of an angle $\phi$. Therefore, the operator defined in Eq. 1.37 generates a rotation around $z$ of the spin state $|\psi(t_a)\rangle$ of the angle $\omega_0\tau$.

Assuming and omitting the mathematical demonstration, it is interesting to report the result of the application of Eq. 1.36 to the Zeeman, as well as to the $|+x\rangle$, $|+y\rangle$, ... states: while $|\alpha\rangle$ and $|\beta\rangle$ remain unchanged by the effect of the rotation along the $z$-axis, all the superposition states are transformed in a different state. For an example, the time evolution of the $|+x\rangle$ state for a $\gamma$ - negative nucleus, in subsequent time steps of $\tau = -\frac{\pi}{2\omega_0}$, is:

$$|+x\rangle \rightarrow |+y\rangle \rightarrow |-x\rangle \rightarrow |-y\rangle$$ \hspace{1cm} (1.39)

Physically, for the spin initially in the $|+x\rangle$ state, this evolution corresponds to a precession motion of the polarization around the magnetic field direction, with angular rate $\omega_0 = \gamma B_0$. the time evolution of the $|+x\rangle$ state is depicted in Fig. 1.11.

This result obtained can be generalized to every superposition state of the system: whatever is the initial polarization of the spin, in presence of the external magnetic field, it will precess around the magnetic field direction at a frequency equal to the Larmor frequency and with rotation direction depending only by the sign of $\gamma$.

These results correlates with what we found by the vector model: in that semi-classical description the sample magnetization $M$ precesses around the $z$-axis at the
1.3 NMR phenomenon: the quantum mechanical approach

Figure 1.11: Precession motion of the spin polarization, corresponding to the time evolution of the $|+x\rangle$ spin state of a $\gamma$ negative nucleus, in presence of $B_0$. $\tau = -\frac{\pi}{2\omega_0}$.

Larmor frequency, while the quantum mechanics demonstrates that this is the motion of each spin which is not in a stationary (Zeeman) state.

In order to obtain a quantum mechanical description of the NMR phenomenon it is necessary to consider the effect of rf fields on the spin system which will be discussed in the following section.

1.3.2 The effect of a rf field on an isolated spin

A radio frequency (rf) field oscillating along the $x$-axis of the laboratory frame can be expressed as:

$$B_1(t) = B_1 \cos(\omega_{rf} t + \phi)e_x$$  \hspace{1cm} (1.40)

where $\omega_{rf}$ is the frequency of the oscillating field (corresponding to the reference frequency of the spectrometer), while $\phi$ refers to its phase. Similar to the semi-classical approach, also in the quantum mechanical calculation $B_1(t)$ can be decomposed into two counter-rotating magnetic fields with angular frequency $\omega_{rf}$. It is generally true that only the component rotating in the same direction as the Larmor precession of the spins, represented as $B_1^{rf}(t)$, affects the spin dynamics. Therefore, from the point of view of the effect generated by the rf field $B_1(t)$ on the NMR spectrum, the following approximation is valid:

$$B_1(t) \cong B_1^{rf}(t)$$  \hspace{1cm} (1.41)

and the resulting rf field $B_1(t)$ can be expressed in the laboratory frame as:

$$B_1(t) = \frac{1}{2}B_1[\cos(\omega_{rf} t + \phi)e_x + \sin(\omega_{rf} t + \phi)e_y]$$  \hspace{1cm} (1.42)
The Hamiltonian describing the interaction between an individual spin angular momentum \( I \) and the resonant component of the rf field is:

\[
\hat{H}_{rf}^{\text{I}}(t) = -\gamma \hbar \hat{I} \cdot \mathbf{B}_1(t) \tag{1.43}
\]

When a rf field \( \mathbf{B}_1 \) is present, the total Hamiltonian describing the energy of the spin system shows a time-dependence. Comparing the Eqs. (1.42 & 1.43), the term corresponding to the rf field Hamiltonian is:

\[
\hat{H}_{rf}^{\text{I}}(t) = -\frac{1}{2} \gamma B_1 [\cos(\omega_{rf} t + \phi)\hat{I}_x + \sin(\omega_{rf} t + \phi)\hat{I}_y] \tag{1.44}
\]

In particular, considering the Eq. 1.43, in the presence of both a static and a rf magnetic field (\( \mathbf{B}_0 \) and \( \mathbf{B}_1(t) \), respectively), the Hamiltonian can be expressed simply as:

\[
\hat{H} = \hat{H}_Z + \hat{H}_{rf}^{\text{I}}(t) \tag{1.45}
\]

\[
= -\gamma \hbar \hat{I} \cdot (\mathbf{B}_0 + \mathbf{B}_1(t)) \tag{1.46}
\]

It is necessary to remove the time dependence of \( \hat{H}_{rf}^{\text{I}} \), as previously discussed in the Section 1.2.2, by expressing it in a frame rotating around the \( z \)-axis in the same sense of the spin precession at the angular frequency \( \omega_{rf} \) as \( \mathbf{B}_1(t) \).

After some rearrangement, the expression of the total spin Hamiltonian given in Eq. 1.46 in the rotating frame becomes:

\[
\hat{H}_{\text{rot}} = (\omega_0 - \omega_{rf})\hat{I}_z + \omega_1 (\hat{I}_x \cos \phi + \hat{I}_y \sin \phi) \tag{1.47}
\]

where \( \omega_1 = \frac{1}{2} |\gamma B_1| \) is a measure of the rf field amplitude which is the nutation frequency\(^7\) and the superscript indicates that the Hamiltonian is expressed in the rotating frame.

As already stated in the vector model, \( \mathbf{B}_1(t) \) is provided by applying the radio-frequency rf pulse pulse, which is an oscillating field of duration in the order of \( \mu s \) to \( ms \), whose intensity, measured through its nutation frequency \( \omega_1 \), is of the order of ten to few hundreds of kHz.

Let us consider the application of a strong rf pulse of length \( \tau_\text{p} = t_\text{p} - t_0 \) and phase \( \phi = 0 \) on a non-interacting spin system. In the presence of a resonant rf field \( \omega_0 = \omega_{rf} \), as already noted that the corresponding Hamiltonian is:

\[
\hat{H}_{\text{rot}} = \omega_1 \hat{I}_x \tag{1.48}
\]

It can be shown that the effect of such a pulse on a generic spin state \( |\psi\rangle^{\text{rot}} \), where the superscript indicates that it is expressed in the rotating frame, can be described in the following way:

\[
|\psi(t_\text{p})\rangle^{\text{rot}} = \hat{R}_x(\beta_\text{p})|\psi(t_0)\rangle^{\text{rot}} \tag{1.49}
\]

\(^7\)The nutation is always positive.
where \( t_0 \) and \( t_p \) indicate the start and end time points of the pulse and \( \beta_p = \omega_1 t_p \) indicates the flip angle of the pulse which is introduced earlier. Its matrix representation on the Zeeman eigenbasis is given by [2]:

\[
\hat{R}_x(\beta_p) = \begin{pmatrix}
\cos \frac{1}{2} \beta_p & -i \sin \frac{1}{2} \beta_p \\
-i \sin \frac{1}{2} \beta_p & \cos \frac{1}{2} \beta_p
\end{pmatrix}
\] (1.50)

and it can be used to calculate the effect of the application of rf field expressed by Eq. 1.48 on a spin system prepared in an initial state \( |\psi(t_0)\rangle \). Let assume a spin in the Zeeman state \( |\alpha\rangle \) and an on-resonance radio-frequency pulse applied, at \( t = 0 \), along the rotating frame \( x \) axis with \( \beta_p = \frac{\pi}{2} \), that is a \((\pi/2)_x\) pulse. In consequence of this \( \frac{\pi}{2} \) rf pulse the spin polarization is rotated from the \( z \)-axis to the \( y \)-axis, pointing to the negative direction; in terms of spin state the initial stationary state \( |\alpha\rangle \) is transformed into the superposition state \( |-y\rangle \), as already discussed within the vector model. A representation of this effect is given in Fig. 1.12.

![Figure 1.12: Transformation of the \( |\alpha\rangle \) state into \( |-y\rangle \) by a \((\pi/2)_x\) pulse.](image)

If the rf pulse is then turned off, the spin polarization, under the influence of only \( B_0 \), will start to precess about its direction at the Larmor frequency. On a microscopic scale, the effect of an on-resonance \((\pi/2)_x\) pulse on a single spin in the \( |\alpha\rangle \) Zeeman state is the same as the magnetization evolution found within the vector model.

As already discussed in the vector model, the production of transverse magnetization by means of a suitable rf pulse, and the resulting oscillating electromagnetic field in the \( xy \) plane, is sufficient to explain the generation of the “macroscopic” NMR signal. On the other hand, until now, the QM description of the NMR phenomenon has concerned a single spin. However, to obtain an explanation of the macroscopic NMR phenomenon it is necessary to pass from the single spin description to the treatment of a multi-spin system.
1.3.3 Ensemble of spin - 1/2: Density matrix

The quantum mechanical description of an ensemble of identical and non-interacting spins would require to consider each individual spin and adding their contributions together, in order to calculate a macroscopic quantity like the magnetization. A detailed description of the quantum state of the spin ensemble can be obtained by introducing the *density operator* formalism which turns out to be a useful tool for the theory of NMR [4]. This approach avoids referring to the states of the individual nuclear spins, hence greatly simplifying the QM description of a spin state of macroscopic samples. With the aim of completing the schematic quantum mechanical description of the NMR phenomenon, it is necessary to introduce the basics of this formalism in this thesis and the very first results which can be obtained [2].

Let us consider a single spin - 1/2 in a generic superposition state:

$$|\psi\rangle = c_\alpha |\alpha\rangle + c_\beta |\beta\rangle$$  \hspace{1cm} (1.51)

Superposition *ket* states $|\psi\rangle$ are conveniently represented as column vectors whose elements are the coefficients of the linear combination defining $|\psi\rangle$ in terms of the Zeeman eigenstates:

$$|\psi\rangle = \begin{pmatrix} c_\alpha \\ c_\beta \end{pmatrix}$$  \hspace{1cm} (1.52)

On the contrary, the *bra* state $\langle \psi |$ can be expressed as a row vector:

$$\langle \psi | = (c^*_\alpha, c^*_\beta)$$  \hspace{1cm} (1.53)

where $c^*_\alpha$ and $c^*_\beta$ are the complex conjugates of $c_\alpha$ and $c_\beta$, respectively.

Given a generic $\hat{Q}$ operator describing a physical observable, the expectation value of $\hat{Q}$ is given by:

$$\langle \hat{Q} \rangle = \langle \psi | \hat{Q} | \psi \rangle$$  \hspace{1cm} (1.54)

this can be expressed in the vector-matrix representation of $|\psi\rangle$ and $\hat{Q}$ on the $|\alpha\rangle, |\beta\rangle$ basis, as:

$$\langle \hat{Q} \rangle = \begin{pmatrix} c^*_\alpha \\ c^*_\beta \end{pmatrix} \begin{pmatrix} Q_{\alpha\alpha} & Q_{\alpha\beta} \\ Q_{\beta\alpha} & Q_{\beta\beta} \end{pmatrix} \begin{pmatrix} c_\alpha \\ c_\beta \end{pmatrix}$$

$$= c_\alpha c^*_\alpha Q_{\alpha\alpha} + c_\beta c^*_\alpha Q_{\alpha\beta} + c_\alpha c^*_\beta Q_{\beta\alpha} + c_\beta c^*_\beta Q_{\beta\beta}$$  \hspace{1cm} (1.55)

An operator can be defined by multiplying the column vector $|\psi\rangle$ and the row vector $\langle \psi |$; its matrix representation is given by:

$$|\psi\rangle \langle \psi | = \begin{pmatrix} c_\alpha \\ c_\beta \end{pmatrix} \begin{pmatrix} c^*_\alpha & c^*_\beta \end{pmatrix}$$  \hspace{1cm} (1.56)
The expectation value of the operator \( \hat{Q} \) can be expressed using the operator \( |\psi\rangle\langle\psi| \) as follows:

\[
\langle \hat{Q} \rangle = Tr\left\{ |\psi\rangle\langle\psi| \hat{Q} \right\}
\]

(1.57)

Let us consider that the ensemble is constituted by two independent spins. Assuming, the first spin has state \( |\psi_1\rangle \) and the second spin has state \( |\psi_2\rangle \). In general, the determination of \( Q \) is still uncertain because of quantum indeterminacy. However the average outcome is the sum of the two expectation values:

\[
Q(\text{average}) = \langle \psi_1 | \hat{Q} | \psi_1 \rangle + \langle \psi_2 | \hat{Q} | \psi_2 \rangle
\]

(1.58)

which can be rewritten as:

\[
Q(\text{average}) = Tr\left\{ (|\psi_1\rangle\langle\psi_1| + |\psi_2\rangle\langle\psi_2|) \hat{Q} \right\}
\]

(1.59)

If there are \( N \) spins involved, then the expectation value of \( \hat{Q} \) will result to be:

\[
\langle \psi|\hat{Q}|\psi \rangle = \frac{1}{N} Tr\left\{ (|\psi_1\rangle\langle\psi_1| + |\psi_2\rangle\langle\psi_2| + |\psi_3\rangle\langle\psi_3| + \ldots) \hat{Q} \right\}
\]

(1.60)

where \( |\psi_i\rangle \) with \( i = 1, 2, 3, \ldots \) is the wavefunction representing the state of the \( i - th \) spin. It is possible to define the density operator \( \hat{\rho} \) from the Eq. 1.60

\[
\hat{\rho} = \frac{1}{N}(|\psi_1\rangle\langle\psi_1| + |\psi_2\rangle\langle\psi_2| + |\psi_3\rangle\langle\psi_3| + \ldots)
\]

(1.61)

this expression can also be written as:

\[
\hat{\rho} = |\psi\rangle\langle\psi|
\]

(1.62)

where the overbar represents the average over the \( N \) number of spins of the ensemble. By substituting \( \hat{\rho} \) in Eq. 1.60, \( \langle \hat{Q} \rangle \) is:

\[
\langle \hat{Q} \rangle = Tr\left\{ \hat{\rho} \hat{Q} \right\}
\]

(1.63)

The remarkable nature of the result obtained from Eq. 1.63 is that the expectation value of a physical observable, in macroscopic observation, can be deduced by combining only two operators with one representing the observable, and the other being the density operator itself, representing the state of the entire spin ensemble, independent of the number of spins it contains.

The matrix representation of the density operator \( \hat{\rho} \), for an ensemble of non-interacting spins - 1/2, on the \( (|\alpha\rangle, |\beta\rangle) \) basis, is called the density matrix and is represented as:

\[
\hat{\rho} = \begin{pmatrix}
\rho_{\alpha\alpha} & \rho_{\alpha\beta} \\
\rho_{\beta\alpha} & \rho_{\beta\beta}
\end{pmatrix} = \begin{pmatrix}
c_{\alpha} c_{\alpha} & \overline{c_{\alpha} c_{\beta}} \\
\overline{c_{\beta} c_{\alpha}} & \overline{c_{\beta} c_{\beta}}
\end{pmatrix}
\]

(1.64)
The *diagonal* elements of the spin density operator $\rho_{\alpha\alpha}$ and $\rho_{\beta\beta}$ are called the *populations* of states $|\alpha\rangle$ and $|\beta\rangle$. The *off-diagonal* elements $\rho_{\alpha\beta}$ and $\rho_{\beta\alpha}$ are called the *coherences* between states $|\alpha\rangle$ and $|\beta\rangle$.

The physical interpretation of the *populations* and *coherences* of the density operator is that: the difference between the populations $(\rho_{\alpha\alpha} - \rho_{\beta\beta})$ indicate the net longitudinal spin polarization of the sample, i.e. the magnetization in the direction of the $B_0$ field, while, without going into any detail, non-zero coherences indicate the presence of transverse spin polarization, which means non-zero magnetization in the direction perpendicular to $B_0$.

It is important at this stage to define a magnetization vector, $\mathbf{M}$, indicating the net magnetization of the sample with cartesian components $M_z$, $M_x$, $M_y$ related to the coherences $(\rho_{\alpha\beta}, \rho_{\beta\alpha})$. In analogy with the spin polarization for a single spin in a generic superposition $|\psi\rangle$ state, $\mathbf{M}$ provides not only a pictorial but also a physically meaningful representation of the state of the spin ensemble, mathematically described by $\hat{\rho}$.

At last, the real usefulness of the density operator $\hat{\rho}$ is clear when the values of its elements are known for a certain state of the ensemble. A particularly important state is that of thermal equilibrium which the spin system reaches when it is left unperturbed for long time. Quantum statistical mechanics establishes that, given a spin system with eigenstates $|\psi_i\rangle$, solutions of the time-independent Schrödinger equation (Eq. 1.21), at the thermal equilibrium:

1. The coherences $\rho_{ij}^{eq}$ between the eigenstates of the system are all zero:
   \[ \rho_{ij}^{eq} = 0 \quad \text{for } i \neq j \] (1.65)

2. The populations of the energy states obey the *Boltzmann distribution*:
   \[ \rho_{i}^{eq} = \frac{e^{-\frac{E_i}{k_B T}}}{\sum_k e^{-\frac{E_k}{k_B T}}} \] (1.66)

where $k_B = 1.38066 \times 10^{-23}$ J K$^{-1}$ is the *Boltzmann Constant*, and the sum is over all eigenstates. The Boltzmann distribution causes the lower energy $|\alpha\rangle$ state to be more populated than the higher energy $|\beta\rangle$ Zeeman state. It is worth pointing here that the population of a state does not indicate the fraction of spins which are ‘in’ that state. In a real sample, there are only few spins exactly in the states $|\alpha\rangle$ and $|\beta\rangle$, while the vast majority of the spins will be in a superposition state; $\rho_{\alpha\alpha}$ and $\rho_{\beta\beta}$ will therefore indicate the contribution, from all the spins, to the $|\alpha\rangle$ and $|\beta\rangle$ states respectively.
1.3 NMR phenomenon: the quantum mechanical approach

It is now easy to calculate the populations and coherences for an ensemble of spin \(-\frac{1}{2}\) nuclei at the thermal equilibrium. Beginning with the definition of Boltzmann factor, which is given by:

\[
B = \frac{\hbar \gamma B_0}{k_B T}
\]

Eq. 1.66 can be simplified by using some approximations:

\[
\exp\left\{-\frac{E_\alpha}{k_B T}\right\} = \exp\left\{\frac{1}{2} B\right\}
\]

\[
\exp\left\{-\frac{E_\beta}{k_B T}\right\} = \exp\left\{-\frac{1}{2} B\right\}
\]

Practically, for temperatures higher than a fraction of a kelvin degree, in the case of nuclear spins, the value of \(B\) is very small; therefore it is possible to expand the exponentials as a power series and considering only the first term:

\[
\exp\left\{-\frac{E_\alpha}{k_B T}\right\} \approx 1 + \frac{1}{2} B
\]

\[
\exp\left\{-\frac{E_\beta}{k_B T}\right\} \approx 1 - \frac{1}{2} B
\]

The populations of \(|\alpha\rangle\) and \(|\beta\rangle\) states at the thermal equilibrium is written as:

\[
\rho_{\alpha\alpha}^{eq} = \frac{1}{2} + \frac{1}{4} B
\]

\[
\rho_{\beta\beta}^{eq} = \frac{1}{2} - \frac{1}{4} B
\]

while, as already discussed, the coherences \(\rho_{\alpha\beta}\) and \(\rho_{\beta\alpha}\) are zero. The above approximation is called the high-temperature approximation.

Hence, for an ensemble of positive \(\gamma\) spin \(-\frac{1}{2}\) nuclei at the thermal equilibrium, the low-energy Zeeman state \(|\alpha\rangle\) is slightly more populated than the high-energy \(|\beta\rangle\) state. This signifies that the sample has a net positive longitudinal magnetization, while there is no transverse magnetization present, along the direction of the magnetic field. In the case of an ensemble of \(\gamma\) - negative nuclei, the net longitudinal magnetization is negative, which means against the direction of the magnetic field. In order to get some quantitative ideas of the energies involved, the difference in energies between the Zeeman states for an ensemble of protons in a magnetic field of 11.74 T is approximately \(3.3 \times 10^{-25}\) J, while the thermal energy at room temperature is \(k_B T \approx 4.1 \times 10^{-21}\) J. This shows that the thermal energy is several orders of magnitude bigger than the difference in energy between the two Zeeman states. Physically speaking, at the thermal equilibrium, since the difference between their populations is small (in this case, its in the order of \(10^{-4}\)),
there is just a small net longitudinal magnetization along the direction of the magnetic field.

The thermal equilibrium density matrix for isolated spin - 1/2 nuclei, is as follows:

\[
\rho^{eq} = \begin{pmatrix}
\frac{1}{2} + \frac{1}{4}B_0 & 0 \\
0 & \frac{1}{2} - \frac{1}{4}B_0
\end{pmatrix}
\] (1.74)

In terms of angular momentum operators, it is to verify that the density operator for an ensemble of spin - 1/2 nuclei at the thermal equilibrium is:

\[
\hat{\rho}^{eq} = \frac{1}{2} \hat{I} + \frac{1}{2} B \hat{I}_z
\] (1.75)

This thermal equilibrium density operator is important for obtaining a straightforward microscopic description of NMR phenomenon. A term which describes a magnetic field \( B_1(t) \) oscillating in a direction perpendicular to \( B_0 \) can be introduced into the Hamiltonian of the system and can be transferred the mathematical treatment applied in case of single spin into the density operator formalism. After verifying the transformation occurred to the density operator, the effect of \( B_1(t) \) field on the spin ensemble can be obtained.

The calculations, omitted for the sake of simplicity, demonstrate that the effect on the spin ensemble of the normal on-resonance (\( \frac{\pi}{2} \)) rf pulse is to equalize the populations of the two Zeeman states and transform the initial population difference into coherences. The physical meaning of this result is that, in the rotating frame, the longitudinal magnetization becomes null, while a transverse magnetization created along \(-y\) will be equal in magnitude to the initial \( M_z \).

When the rf pulse is turned off, the sample net transverse magnetization resumes its precessional motion around the external magnetic field \( B_0 \) at the Larmor frequency, hence generating the macroscopic NMR signal.

### 1.4 NMR signal and the simplest NMR experiment

From the practical viewpoint, the simplest NMR experiment, as seen in the previous sections, consists of a pulse. As already said, the application of a rf pulse might confer to the spin system a non-zero transverse magnetization. The precession of the transverse magnetization on the \( xy \) plane corresponds to a tiny magnetic field oscillating, for instance, along the \( x \) direction. This oscillating magnetic field induces a small (but detectable) oscillating rf voltage into a coil whose axis is placed along the \( x \) axis of the laboratory fixed frame, as represented by the Fig. 1.13.
1.4 NMR signal and the simplest NMR experiment

The electric current induced in the coil is the NMR signal, which is amplified and detected. The resulting intensity vs time pattern is called Free Induction Decay (FID), which corresponds to the time-domain NMR spectrum shown in Fig. 1.14, where the rf pulse is represented by a rectangle pulse and the decay of the NMR signal with time is correlated to the presence of the relaxation processes, as it will be discussed in the next chapter. A generic NMR experiment consists in a sequence of rf pulses and time delays, referred as pulse sequence.

In general, the time-domain representation of the spectrum is uninterpretable, and so it is necessary to find a way of generating frequency-domain spectrum representation from the time-domain signal. Fourier Transform is a relatively simple mathematical procedure through which the NMR spectrum is obtained from the FID. In fact, the time and frequency constitute a Fourier-pair, and it is possible to obtain frequency-spectrum \( I(\omega) \) from the FID \( F(t) \), by means of the following relationships [7]:

\[
F(t) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} I(\omega) \ e^{i\omega t} \ d\omega \quad (1.76)
\]

\[
I(\omega) = \int_{-\infty}^{+\infty} F(t) \ e^{-i\omega t} \ dt \quad (1.77)
\]

This means that the same information about the spin system is in principle contained both in the frequency - spectrum and in the FID.
1.5 Nuclear spin interactions

So far we have discussed the ensemble of non interacting nuclear spins, for which it is possible to obtain a detailed quantum mechanical description, which in turn allows a “microscopic” explanation of the basic NMR phenomenon to be obtained. This situation obviously very far from reproducing the complexity of a real sample. A nuclear spin, placed in a real environment is indeed subjected to many interactions with other nuclei and electrons in its own molecule and also with the surroundings. The interactions experienced by the nuclear spins can be divided into external and internal depending on whether they are produced by an external system generating magnetic or electric fields or they are caused by the sample itself, respectively [4].

Normally, the local magnetic and electric fields produced by the molecular environment are some orders of magnitude smaller than the static field $B_0$, so from a quantum mechanical point of view, the effect of nuclear spin interactions can be assessed by the perturbation theory which considers the Zeeman interaction, that is the interaction between the nuclear spin and an external magnetic field $B_0$, to be the dominant interaction.

The internal Hamiltonian can contain different terms, corresponding to the different internal interactions experienced by the nuclear spins, which can be treated as perturbations of the Zeeman terms.

The chemical shift interaction or shielding interaction represents the indirect magnetic interaction between the external magnetic field and the nuclear spins through the involvement of electrons: in fact, the external magnetic field $B_0$ induces currents in the electron clouds surrounding the nuclei, which in turn generate an induced magnetic field. This secondary field is directly proportional to the static field $B_0$. Although the magnitude of this secondary field is much smaller with respect to $B_0$, its effects are large enough to generate detectable variations in the spin precession frequency.

The direct dipole-dipole or through-space interaction corresponds to the classical coupling between magnetic dipoles. In fact, every spin magnetic moment generates a magnetic field with which a second spin can interact. The interaction is mutual, without the involvement of electron clouds. This interaction can be either intra- or inter-molecular: in the case of solution systems, this interaction is averaged to its isotropic value, zero, due to molecular tumbling, while in the case of solid systems this is the major cause for the line broadening which will be discussed in following.

The J-coupling or indirect dipole-dipole coupling represents the magnetic interaction of nuclear spins with each other, through the involvement of bonding electrons: its presence is a direct manifestation on the NMR spectrum of the chemical bonds.
All the mentioned internal interactions have a purely magnetic nature. However, nuclei with spin $I > \frac{1}{2}$ experience a non-spherical distribution of the electric charge in the nucleus producing an electric quadrupole moment that can interact with the electric field gradients originated by the nuclear and electronic charge distributions. This interaction is called quadrupolar interaction and possesses an electric nature. The quadrupolar interaction will not be discussed in the following, since no quadrupolar nuclei have been investigated in this thesis work.

The interactions introduced so far have a major influence on the NMR spectrum of diamagnetic substances: however, further interactions are involved in paramagnetic substances where the interactions between the unpaired electron spins and the nuclear spins of surrounding atoms can give rise to several observable NMR phenomena: hyperfine shifts, paramagnetic relaxation and residual dipolar coupling by magnetic alignment [8]. The interactions which mainly contribute to these peculiar spectral effects arise from the electron Zeeman interaction, Fermi-contact coupling and the electron-nuclear dipolar or pseudo-contact coupling [9].

Even if, especially for specific interactions, the density matrix formalism, introduced in the previous section, allows a quantum mechanical description of interacting multiple-spin systems to be obtained, here, considering the aims and the contents of the thesis, I will completely omit the description as well as the results of this advanced theoretical method. However, the understanding of even the simplest Solid State NMR spectrum requires the most important features of the nuclear spin interactions to be known.

A quite simple way of approaching the description of the nuclear spin interactions, and of their basic implications on a real spectrum, is to consider the spin Hamiltonian of a single nuclear spin placed in a “real” environment: this can be built up by starting from the Zeeman Hamiltonian, which describes the interaction between the nuclear spin and an external static magnetic field, and adding, as further Hamiltonian operators, all the main interactions involving the spin in its environment [2, 4]. Indicating the Zeeman Hamiltonian with $\hat{H}_0$ and a generic interaction Hamiltonian with $\hat{H}_{int}$, the system Hamiltonian can be then expressed as:

$$\hat{H} = \hat{H}_0 + \sum_{int} \hat{H}_{int}$$ (1.78)

On the model of the Zeeman interaction, every other one can be seen as an interaction between the nuclear magnetic moment and a local magnetic field generated by the environment; therefore, in terms of Hamiltonians, each interaction can be written as:

$$\hat{H}_{int} = -\gamma \hbar \mathbf{I} \cdot \mathbf{B}_{loc}$$ (1.79)
where $B_{\text{loc}}$ can be always expressed as:

$$B_{\text{loc}} = A_{\text{loc}} \cdot J$$

(1.80)

where $A_{\text{loc}}$ is a second rank tensor describing the interaction and its spatial orientation dependence, and the vector-operator $J$ can be considered as the last origin of $B_{\text{loc}}$ [4].

In the vast majority of the cases the Zeeman interaction remains the most important one: this means that the Hamiltonian of the system can be written, as a good approximation, as the Zeeman Hamiltonian corrected at the first order by the various $\hat{H}_{\text{int}}$. More explicitly, from the perturbation theory, this means that the stationary states of the system, eigenstates of the Hamiltonian, remain the eigenstates of the Zeeman Hamiltonian, while their energies are corrected to the first order. This implicates that, besides the Zeeman term ($\hat{H}_0$), only the secular parts of the various $\hat{H}_{\text{int}}$, that is the ones which commute with $\hat{H}_0$, are included in the Hamiltonian of the system since they are the only ones contributing to the first order correction to energy. In formulae:

$$\hat{H} \cong \hat{H}_0 + \sum_{\text{int}} \hat{H}_{\text{sec}}^{\text{int}} \quad \text{where} \quad [\hat{H}_0, \hat{H}_{\text{sec}}^{\text{int}}] = 0$$

(1.81)

This approximation can be expressed in a more qualitative and physical way, which could result to be useful in some cases, having recourse to the expression of $\hat{H}_{\text{int}}$ in terms of interaction between the nuclear magnetic moment and local magnetic fields generated by the spin environment (Eq. 1.79) [4]. As seen in the case of the isolated, as well as of the ensemble of non interacting spins, $B_0$ determines the energy levels of the system, while $B_1$, oscillating perpendicular to $B_0$ at the Larmor frequency, induces population transfers between the Zeeman states. Since the external static magnetic field ($B_0$) is always orders of magnitude larger than any local field related to a spin interaction ($B_{\text{loc}}$), it is reasonable to believe that only two kinds of $B_{\text{loc}}$ will have some non-negligible effect on the spin and will be therefore included in the Hamiltonian. The first are the $B_{\text{loc}}$ aligned in the $B_0$ direction ($z$-axis of the laboratory frame), which, for similarity with it, are expected to slightly modify the energy levels of the spin, the latter are the $B_{\text{loc}}$ precessing in the $xy$ plane around the $z$-axis at an angular frequency close to the Larmor frequency, which will act in a similar way as $B_1$.

In the following, I will consider one interaction at a time; the effect of each interaction can be obtained by finding the eigenvalues of the correspondingly perturbed Hamiltonian and then it can be conveniently expressed in terms of modification of the unperturbed Larmor resonance frequency of the spin.

In the case of spin-$\frac{1}{2}$ nuclei, the NMR phenomenon can be approximatively \(^8\) seen

\(^8\)Actually, as seen in Subsection 1.3.3, the rigorous description given by the density matrix treatment,
as a transition from the state \( |\alpha \rangle \) to the state \( |\beta \rangle \), giving rise to a peak in the NMR spectrum at a frequency equal to the Larmor frequency. Therefore, in the case of spin-\( \frac{1}{2} \) nuclei, finding the modification of the resonance frequency by effect of each interaction, will allow the corresponding effect on the spectral signal to be directly obtained. As already said the case of spin \( I > \frac{1}{2} \) nuclei will not be considered here.

### 1.5.1 Shielding Interaction

The shielding interaction involves the nuclear spin and the local magnetic field produced, in consequence of the presence of the external static magnetic field, by the electrons surrounding the nucleus.

The Hamiltonian \( \hat{H}_{\text{int}} \) for the shielding interaction is [10]:

\[
\hat{H}_{\text{cs}} = \gamma \hbar \mathbf{\hat{I}} \cdot \mathbf{\sigma} \cdot \mathbf{B}_0
\]  

(1.82)

Where \( \mathbf{\sigma} \) is the shielding tensor, the local magnetic field is \( \mathbf{B}^{\text{loc}} = \mathbf{\sigma} \cdot \mathbf{B}_0 \) and the ultimate source of the local magnetic field is \( \mathbf{B}_0 \) itself.

Applying the perturbative approach, the secular term of \( \hat{H}_{\text{cs}} \) results to be:

\[
\hat{H}_{\text{cs}}^{\text{sec}} = \gamma \hbar \sigma_{zz} \mathbf{B}_0 \hat{I}_z
\]  

(1.83)

and the corresponding resonance frequency for the \( |\alpha \rangle \rightarrow |\beta \rangle \) or, in general, the \( |m\rangle \rightarrow |m-1\rangle \) transition, is:

\[
\omega = \omega_0 (1 - \sigma_{zz})
\]  

(1.84)

where \( \omega_0 \) is the Larmor frequency and \( \sigma_{zz} \) the \( zz \) component of the \( \mathbf{\sigma} \) tensor, written in the laboratory axes frame.

For all the nuclear spin interactions, it is convenient to express the interaction tensor rather than in the laboratory axes frame, in its principal axes frame (PAF), which is, by definition, the axes frame in which the tensor is diagonal (the diagonal elements being referred to as principal components). By expressing \( \sigma_{zz} \) in terms of the \( \mathbf{\sigma} \) principal components, \( \sigma_{11}, \sigma_{22}, \sigma_{33} \), the resonance frequency, corrected by the shielding interaction results to be [10]:

\[
\omega = \omega_0 \left[ (1 - \sigma_{11}) \sin^2 \theta \sin^2 \phi + (1 - \sigma_{22}) \cos^2 \theta \sin^2 \phi + (1 - \sigma_{33}) \cos^2 \theta \right]
\]  

(1.85)

where \( \theta \) and \( \phi \) are the polar angles which define the orientation of the external magnetic field \( \mathbf{B}_0 \) in the \( \mathbf{\sigma} \) PAF.

Given a certain nucleus in a molecule, the principal axes frame of its shielding tensor is more complex.
Figure 1.15: Polar angles, $\theta$ and $\phi$, defining the orientation of $B_0$ in the $\sigma$ Principal Axes Frame (1, 2, 3).

has a fixed orientation within the molecule, therefore, provided to neglect molecular motions, also the orientation of $B_0$ in that frame is well defined.

However, in a powder sample, the molecules can randomly assume all the possible orientations with respect to $B_0$, each orientation corresponding to a different couple of $\theta$, $\phi$ angles. Therefore, the observed resonance signal of a nucleus in a powder sample will result from the integral over all the possible molecular orientations of the resonance frequency expressed as a function of $\theta$, $\phi$ (Eq. 1.85). The integral result is referred to as lineshape function, or, more commonly, as powder pattern.

Independently on the obtainment of the analytical expression for the powder pattern, it results important to locate some critical points as “shoulders” and “divergences”. In the case of the powder pattern arising from the shielding interaction, the critical points are, in frequencies [10]:

$$\omega_1 = \omega_0 (1 - \sigma_{11}) \quad (1.86)$$
$$\omega_2 = \omega_0 (1 - \sigma_{22}) \quad (1.87)$$
$$\omega_3 = \omega_0 (1 - \sigma_{33}) \quad (1.88)$$

Assuming the recommended convention of ordering the $\sigma$ principal components so that $\sigma_{11} \leq \sigma_{22} \leq \sigma_{33}$ [11], $\omega_1$ and $\omega_3$ result to be the shoulders and $\omega_2$ the divergence of the powder pattern. The meaning of “shoulder” and “divergence” is illustrated in Fig. 1.16, in which a generic powder pattern is shown.

From Equation 1.85, it is easy to verify that $\omega_i$ is the resonance frequency of the molecules oriented so that the principal axis $i$ is parallel to $B_0$.

Besides the shielding tensor, the chemical shift tensor is useful and widely used. In
solution NMR, where, due to the averaging effect of the molecular motions, the chemical shielding interaction loses its orientation dependence, determining only a scalar correction to the resonance frequency, the chemical shift is defined as [11]:

$$\delta[\text{ppm}] = \left( \nu_s - \nu_{\text{ref}} \right) / \nu_{\text{ref}} \times 10^6$$

(1.89)

where $\nu_s$ and $\nu_{\text{ref}}$ are the resonance frequencies (in Hz) of the observed nucleus in the sample and in a reference compound, respectively.

Similarly, the absolute shielding is defined as [11]:

$$\sigma[\text{ppm}] = \left( \nu_{\text{nucl}} - \nu_s \right) / \nu_{\text{nucl}} \times 10^6$$

(1.90)

where $\nu_{\text{nucl}}$ is the frequency of the bare nucleus.

By combining these two last equations, it is easy to obtain that:

$$\delta = \frac{\sigma_{\text{ref}} - \sigma_s}{(1 - \sigma_{\text{ref}})}$$

(1.91)

Being usually $|\sigma_{\text{ref}}| \ll 1$,

$$\delta \cong \sigma_{\text{ref}} - \sigma_s$$

(1.92)

Coming back to a solid sample, a corresponding chemical shift tensor $\delta$ can be defined, with principal components:

$$\delta_{11} = \sigma_{\text{ref}} - \sigma_{11}$$

(1.93)

$$\delta_{22} = \sigma_{\text{ref}} - \sigma_{22}$$

(1.94)

$$\delta_{33} = \sigma_{\text{ref}} - \sigma_{33}$$

(1.95)
where $\sigma_{\text{ref}}$ is the absolute shielding of a reference compound, and $\sigma_{11}, \sigma_{22}, \sigma_{33}$ are the principal components of the $\sigma$ tensor.

According to the conventional order adopted for the $\sigma$ principal components, the chemical shift principal components are ordered so that $\delta_{11} \geq \delta_{22} \geq \delta_{33}$. Many different conventions are reported in the literature for expressing the shielding and chemical shift tensors; the one so far and in the following reported has been recently advised in the literature [11] for its less ambiguity with respect to some older conventions.

Following ref. [11], the chemical shift tensor can be described by three parameters:

- the isotropic chemical shift $\delta_{\text{iso}}$
  \[
  \delta_{\text{iso}} = \frac{1}{3} \text{Tr} \delta = \frac{1}{3}(\delta_{11} + \delta_{22} + \delta_{33})
  \]  

- the span $\Omega$
  \[
  \Omega = \sigma_{33} - \sigma_{11} = \delta_{11} - \delta_{33} > 0
  \]
  which expresses the breadth of the powder pattern, and is sometimes referred to as chemical shift anisotropy, CSA;

- the skew $\kappa$
  \[
  \kappa = 3 \frac{(\sigma_{\text{iso}} - \sigma_{22})}{\Omega} = 3 \frac{(\delta_{22} - \delta_{\text{iso}})}{\Omega}
  \]  

whose meaning is better clarified by the following examples:

The skew is restricted to values between $-1$ and $+1$; the limit values have a particular physical meaning: they correspond to the cases in which the chemical shift, or equivalently, the shielding tensor, is axially symmetric, which in turns arises from an axial symmetry at the nuclear site.

In terms of components, an axially symmetric $\sigma$ tensor has two of the three principal components identical, and one, relative to the direction of the symmetry axis, different. The skew value, obtainable from the experimental powder patterns, allows the unique component, and consequently the two equal components, to be unambiguously identified. Two cases are possible:

- $\kappa = 1$ means $\delta_{11} = \delta_{22}$, or, equivalently, $\sigma_{11} = \sigma_{22}$, therefore the unique component of the $\delta$ tensor is the least shifted, that is $\delta_{33}$ (or, considering the $\sigma$ tensor, the most shielded);

\footnote{The span and the skew are conveniently defined such that they are the same for the shielding and the chemical shift tensors.}
1.5 Nuclear spin interactions

Figure 1.17: Shielding ellipsoids corresponding to skew values $\kappa = \pm 1$. The principal axes of the ellipsoids coincide with the $\sigma$ principal axes and their length is proportional to the corresponding shielding value.

- $\kappa = -1$ means $\delta_{22} = \delta_{33}$, or, equivalently, $\sigma_{22} = \sigma_{33}$, therefore the unique component of the $\delta$ tensor is the most shifted, that is $\delta_{11}$ (or, considering the $\sigma$ tensor, the least shielded).

The shielding tensor is often depicted as an ellipsoid, fixed within the molecule and centered on the nucleus, with principal axes coincident with the $\sigma$ principal axes, and length of the axes proportional to the corresponding shielding values. Therefore, the shielding tensor can be depicted as a prolate ellipsoid, for a nucleus with $\kappa = 1$, as an oblate ellipsoid for a nucleus with $\kappa = -1$ (Fig. 1.17).

In Fig. 1.18 the powder patterns for a nucleus with $\kappa = \pm 1$ are shown. It is worth to notice that the shoulders and the divergences correspond to the resonance frequencies of the molecules with unique shielding principal axis (that is symmetry axis for the nuclear site) oriented parallel and perpendicular to the $B_0$ direction, respectively. The higher intensity of the divergences reflects the fact that while infinite molecular orientations allow the unique shielding axis to be perpendicular to the $B_0$ direction, only one leads it to be parallel to $B_0$.

It is clear that, even the only interaction so far considered, the shielding interaction, causes a large broadening of the resonance signal of a nucleus in a solid sample. In particular it gives rise to a powder pattern, which, by definition, is a broad signal resulting from the resonance frequencies corresponding to all the possible molecular orientations with respect to the static magnetic field direction. This kind of induced line-broadening is related to the classification of the shielding interaction as an inhomogeneous interaction.
1.5.2 Dipolar Interaction

The dipolar interaction is the direct interaction among the magnetic moments $\mu$ of the nuclei.

The Hamiltonian describing the dipolar interaction between two nuclear spins, $\hat{I}$ and $\hat{S}$, can be expressed in tensorial form as:

$$\hat{H}_{dd} = -2\hbar \hat{I} \cdot D \cdot \hat{S} \quad (1.99)$$

where $D$ is the dipolar coupling tensor which describes the interaction and, in particular, its spatial dependence.

Apart from multiplicative constants, Eq. 1.99 has the general form of Eq. 1.79, with the local magnetic field $B_{loc} = DS$, whose ultimate source is therefore the nuclear spin $\hat{S}$.

If written in its PAF, the $D$ tensor is always axially symmetric, with the unique principal axis aligned with the internuclear vector $r_{IS}$; its principal components can be written as $-d/2, -d/2, d$ where:

$$d = \hbar \left( \frac{\mu_0}{4\pi} \right) \frac{1}{r^3} \gamma_I \gamma_S \quad (1.100)$$

$\mu_0$ is the magnetic permeability of a vacuum and $r$ is the internuclear distance for the pair of nuclei considered [4]. Moreover $D$ is a traceless tensor, feature which determines...
1.5 Nuclear spin interactions

the lack of dipolar coupling contributions to solution NMR spectra\(^\text{10}\).

The dipolar interaction Hamiltonian, \(\hat{H}_{dd}\), can be conveniently expressed in polar coordinates in the laboratory axes frame; in such form, the only variables result to be the \(\theta\) and \(\phi\) angles, which define the orientation of the internuclear vector \(\mathbf{r}_{IS}\) in the laboratory axes frame.

Considering only the secular part of \(\hat{H}_{dd}\), which determines the first order corrections to the Zeeman Hamiltonian, it results to be different if either an homonuclear or an heteronuclear case is considered.

- for the heteronuclear dipolar interaction

\[
\hat{H}_{sec}^{dd} = -\left(\frac{\mu_0}{4\pi}\right) \frac{\gamma_I \gamma_S \hbar^2}{r^3} [A]
\] (1.101)

- for the homonuclear dipolar interaction

\[
\hat{H}_{sec}^{dd} = -\left(\frac{\mu_0}{4\pi}\right) \frac{\gamma^2 \hbar^2}{r^3} [A + B]
\] (1.102)

where \(A\) and \(B\), terms of the so called “dipolar alphabet”, which also includes other non secular terms, are:

\[
A = \hat{I}_z \hat{S}_z (3 \cos^2 \theta - 1)
\] (1.103)

\[
B = -\frac{1}{4} [\hat{I}_+ \hat{S}_- + \hat{I}_- \hat{S}_+] (3 \cos^2 \theta - 1)
\] (1.104)

where \(\hat{I}_\pm = \hat{I}_x \pm \hat{I}_y\) and \(\hat{S}_\pm = \hat{S}_x \pm \hat{S}_y\).

The difference between the heteronuclear and the homonuclear cases can be qualitatively explained in terms of local magnetic fields generated by the nuclear spin \(S\) and acting on \(I\), or viceversa. Indeed, the \(B\) term can be shown to be equivalent to a local magnetic field oscillating at the Larmor frequency of the spin \(S\), \(\omega^S_0\), in a direction perpendicular to the static field \(B_0\); therefore it will significantly affect the spin \(I\) only in the homonuclear case, in which \(\omega^S_0 = \omega^I_0\).

1.5.2.1 Heteronuclear dipolar interaction

When an heteronuclear spin pair is considered, the eigenfunctions of the Zeeman Hamiltonian are the product Zeeman states \(|\alpha\alpha\rangle, |\alpha\beta\rangle, |\beta\alpha\rangle, |\beta\beta\rangle\), with energies:

\[
E_{m_I, m_S} = -\hbar B_0 (m_I \gamma_I + m_S \gamma_S)
\] (1.105)

\(^\text{10}\)However, in solution NMR spectra, dipolar couplings contribute to the relaxation processes.
Figure 1.19: Powder pattern for a spin involved in a two-spin heteronuclear dipolar interaction. The two transition powder patterns and their sum (thick line) are shown.

For each spin, two degenerate transitions are possible, which give rise to the NMR signal, resonating at Larmor frequency of the spin considered.

The $\hat{H}_{dd}$ corrections to the energies of the product Zeeman states result to be:

$$E_{dd} = -d\hbar(3\cos^2\theta - 1)m_I m_S$$

(1.106)

where $d$ has been defined in Equation 1.100 and $\theta$ is the polar angle between $r$ and $B_0$.

It can be easily verified that, for each nucleus, this removes the degeneration of the two transitions; combining into the same formula the two corrected resonance frequencies, it results, for the spin $I$:

$$\omega_I = \omega'_I \pm \frac{1}{2} d(3\cos^2\theta - 1)$$

(1.107)

and a completely analogous expression can be written for the $S$ spin.

As in the case of the shielding interaction, the resonance frequency depends on the molecular orientation, and in particular on the orientation of the internuclear vector, with respect to the static magnetic field $B_0$.

It can be shown that the orientation dependence, expressed by the $(3\cos^2\theta - 1)$ term, is the same as for an axially symmetric chemical shift tensor, for which the only important angle is the polar angle between the unique chemical shift principal axis and the magnetic field direction.

Therefore, for each transition, by integrating the dipolar corrected resonance frequency (Eq. 1.107) over all the possible molecular orientations, a powder pattern of the same shape as the ones already shown for the axially symmetric chemical shift tensors (Fig. 1.18), is obtained.

In Fig. 1.19 the two transition powder patterns, as well as the observable powder pattern, resulting from their sum, are shown.
1.5 Nuclear spin interactions

1.5.2.2 Homonuclear dipolar interaction

In the case of the dipolar interaction between like spins, due to the presence of the $B$ term in $\hat{H}_{dd}^{\text{sec}}$ (Eq. 1.99), a distinction, not necessary in the heteronuclear case, has to be made between the interaction involving only two spins, and the interaction among more than two spins.

When a two-spin interaction is considered, it is still possible to find stationary states which are eigenfunctions of both the Zeeman Hamiltonian $\hat{H}_0$ and the secular dipolar Hamiltonian $\hat{H}_{dd}^{\text{sec}}$, even if, for the presence of the $B$ term, they are no longer the product Zeeman states. By correcting the energy levels for $\hat{H}_{dd}^{\text{sec}}$, a powder pattern completely analogous to the one of the heteronuclear case is obtained.

When a dipolar interaction among three or more spins is considered, $\hat{H}_{dd}^{\text{sec}}$ results from the sum of $[A + B]$ over all the possible spin pairs of the system:

$$A = \sum_{j<k} \hat{I}_{\text{jz}_j} \hat{I}_{\text{zk}_j} (3 \cos^2 \theta_{jk} - 1)$$

$$B = \sum_{j<k} -\frac{1}{4} [\hat{I}_{\text{+j}} \hat{I}_{\text{-k}} + \hat{I}_{\text{-j}} \hat{I}_{\text{+k}}] (3 \cos^2 \theta_{jk} - 1)$$

where $j$ and $k$ run on the interacting nuclear spins.

It can be shown that, in this case, it is not possible to find stationary states which are, at the same time, eigenfunctions of all the terms of the Hamiltonian $\hat{H}_0 + \hat{H}_{dd}^{\text{sec}}$ [4]. In an approximative way, it can be said that the eigenstates of the system, by effect of the $B$ term, continuously change during the time, as well as their energies do.

This continuous time fluctuation of the energy levels implicates a line broadening of the spin resonance signals, which is intrinsically different from the inhomogeneous line broadening caused by the chemical shift and heteronuclear dipolar interaction anisotropy. The homonuclear dipolar interaction among three or more spins and the line broadening which generates, are classified as homogeneous.

The homogeneous homonuclear dipolar interaction is often the most important factor affecting a proton NMR spectrum in the solid state: in consequence of it, the observed signals are broad lines, with typical linewidths of several tens of kHz.

1.5.3 Indirect spin-spin interaction

This interaction, more commonly referred to as $J$ coupling, involves, as in the case of the already described dipolar interaction, two or more nuclear spins. Indeed the $J$ coupling is sometimes indicated as indirect dipole-dipole coupling, where the adjective
indirect emphasizes that, in this case, the interaction among the spins is not directly among the nuclear magnetic moments through the space, but it is mediated by the surrounding electrons. Completely omitting the detailed theoretical description, first given by Ramsey in 1953 [12,13], the mechanism of this interaction can be qualitatively imagined as a perturbation induced by a nuclear spin on the surrounding electrons, which, through the chemical bonds framework, is transmitted to other nuclei.

The Hamiltonian describing the indirect spin-spin interaction has the same form of $\hat{H}_{DD}$ (Eq. 1.99); the molecular orientation dependence is contained in a second-rank tensor, $J$, which, like the direct dipolar coupling tensor $D$, is diagonal. On the other hand, differently from $D$, $J$ is not traceless; for this reason this interaction is observable also in solution NMR, where it gives rise to the common splittings of the signals, known as $J$ couplings. The anisotropic part of $J$ is usually treated together with the dipolar interaction: a global coupling constant can be measured and, apart from very heavy nuclei for which it could become really relevant, the $J$ contribution to the direct dipolar coupling is usually very small ($< 10\%$). Nevertheless, experimental methods for determining the anisotropy of $J$ are reported in literature [14,15], their role being very important especially for studies aimed to accurately measure molecular structural data.

1.5.4 Paramagnetic interaction

Nuclear spins can interact with electron spins, however in diamagnetic systems these interactions are negligible since paired electrons with nuclei interactions have equal but opposite in sign, which therefore cancel out.

In order to have a non-negligible effect of the nuclear-electronic spins interaction we must deal with paramagnetic systems, having unpaired electrons. In this case, the nuclear-electronic spins interaction can take place through two distinct mechanisms:

i) classical dipolar mechanism;

ii) Fermi contact mechanism

The second mechanism only occurs whenever the probability density of the electron at the nucleus is non-zero. There are basically two conditions because this can happen: the unpaired electron and the coupled nucleus must belong to the same molecule, and the unpaired electron must occupy an orbital which does not show a node at the nucleus (i.e. a s or s-like orbital). These conditions are quite rare to be simultaneously met, and anyway they are not met in the systems investigated in this thesis, so we will no longer discuss the Fermi contact mechanism in the following.

The classical dipolar mechanism can be described by an Hamiltonian which is equal to
the Hamiltonian describing the dipolar interaction between two nuclear spins, provided
that we substitute the nuclear gyromagnetic ratio with the electronic one:

$$\hat{H}_{D_{en}} = -\frac{\gamma_n \gamma_e \hbar}{2} \hat{I}_Z \hat{S}_Z (3 \cos^2 \beta - 1)$$ (1.110)

in this case, \( r \) represents the electron-nucleus distance and \( \beta \) the angle between the
vector \( r \) and the direction of \( B_0 \).

It is obvious that the energy of the spin system arising from this interaction depends
on the spin state of the electron, in addition to that of the nucleus. In this sense, the
behaviour of the electron is very different from that of the nucleus, since:

a) the two Zeeman electronic levels are separated by an energy much higher than the
two Zeeman nuclear levels, and therefore the population of the two Zeeman electronic
levels can significantly differ, contrary to what takes place for nuclei;

b) the two Zeeman electronic states can very rapidly interchange, as due to the
typically very short electron \( T_1 \), thus giving rise to an “average” situation, as seen from
the nucleus standpoint.

On the basis of these considerations, the electron-nucleus dipolar Hamiltonian can
be simplified in the following way:

$$\hat{H}_{D_{en}} = -\frac{\gamma_n \hbar}{2} \langle \mu_e \rangle \hat{I}_Z (3 \cos^2 \beta - 1)$$ (1.111)

where \( \langle \mu_e \rangle \) is the time average of the electronic polarization.

It must be noticed that, contrary to what happens for the nuclear-nuclear dipolar in-
teraction, this interaction has an isotropic term differing from zero. This implies, for
instance, a shift of the NMR lines in solution-state spectra.

### 1.6 Difference between NMR in solids and liquids

Both liquid and solid samples can be studied by NMR spectroscopy. However, the kind
of information that can be extracted on these classes of systems is different because of
their different physical properties, and in particular molecular dynamics. Liquids are
systems characterized by a high molecular mobility, while in solids it is much restricted.

As mentioned in the previous section, each nuclear interactions has peculiar features,
however all of them have the common behaviour of being anisotropic, that is they depend
on the molecular orientation, in particular with respect to the “quantization axis” aligned
with the static magnetic field \( B_0 \). In other words, the nuclear resonance frequency, as
determined by a certain interaction, is a function of the molecular orientation: in a
powder solid sample, all the possible molecular orientations are present and a powder pattern, rather than a single resonance line, results from the integral of the frequency function over the molecular orientation distribution.

However, the role of the interactions anisotropy is strongly modulated by the physical state of the sample: the fast brownian motions of the molecules in a liquid average out the anisotropy of the interactions, since the time scale of the motions present in liquids is faster than the time scale of NMR; the spectrum contains only the isotropic parts of the interactions, resulting in narrow signals (linewidth of the order of Hz). The narrow signals observed in solution are determined by the isotropic chemical shifts and the scalar couplings.

In principle, a solid sample is completely different from a liquid. In a real solid sample many inequivalent are present nuclei and, for each of them, the spin interactions could be different that is different chemical shift, different dipolar interactions, etc., thus making the spectrum a complex superimposition of many different powder patterns. Due to the considerable breadth of typical powder patterns, approximately of the order of $10^4$ Hz, it is easy to imagine that the solid state NMR spectrum would result as a broad and involute pattern, from which the extraction of the information would be completely unfeasible.

Despite this lack of resolution does not prevent several important studies to be performed, as, to cite only examples contained in the thesis, low-resolution proton NMR experiments described in Subsection 2.6.2, most of the potentialities of solid-state NMR spectroscopy have been exploited since the development and the combined application of a set of special techniques, which allowed the anisotropy of the interactions to be partly or completely eliminated, and a so called “high-resolution” spectrum to be obtained. These techniques are introduced in the next section.

### 1.7 High-resolution solid-state NMR

The birth of the “modern” solid-state NMR is commonly fixed at 1976, when three, singly developed, fundamental techniques, the Magic Angle Spinning (MAS), the High-Power Decoupling (HPD or, equivalently, DD) and the Cross-Polarization (CP) were first combined, allowing $^{13}$C high-resolution NMR spectra to be obtained on powder samples [16]. While the first two techniques (MAS and DD) strictly affect the spectral resolution, the Cross Polarization acts strongly improving the sensitivity of dilute spins (such as $^{13}$C).
1.7 High-resolution solid-state NMR

1.7.1 Magic-angle spinning (MAS)

The magic-angle spinning \([17,18]\) consists in a fast macroscopic rotation of the sample about an axis oriented at a magic angle with respect to the magnetic field \(B_0\) direction (Fig. 1.20). It requires a special experimental setup for the sample holder (rotor), as well as an opportune pneumatic system, both of them nowadays routinely present in NMR spectrometers equipped for solid-state studies. The magic-angle spinning is a brilliant device which reproduces, on solid samples, the effect of the fast brownian motions in the liquids.

Without going into theoretical details, the principle of MAS can be illustrated by considering the effect on the shielding interaction. As shown in Section 1.5.1, at the first order, the shielding tensor \((\sigma)\), written into the laboratory frame, can be reduced to the sole \(\sigma_{zz}\) component, with the \(z\)-axis along the static magnetic field direction. If a “rotor axes frame” is defined such as the \(z^R\)-axis is along the sample rotation direction (Fig. 1.20), it can be proved that \(\sigma_{zz}^{lab}\) is equal to \([4]\):

\[
\sigma_{zz}^{lab} = \sigma_{iso} + \frac{1}{2} \left[ (3 \cos^2 \alpha - 1)(\sigma_{zz}^R - \sigma_{iso}) \right. \\
+ \sin^2 \alpha \left[ \frac{1}{2}(\sigma_{xx}^R - \sigma_{yy}^R) \cos(2\omega_R t) + \sigma_{xy}^R \sin(2\omega_R t) \right] \\
+ \sin(2\alpha)[\sigma_{xz}^R \cos(\omega_R t) + \sigma_{yz}^R \sin(\omega_R t)]
\] (1.112)

where \(\omega_R\) is the sample spinning angular frequency and the orientation of \(B_0\) into the rotor axes frame is defined by the polar angle \(\alpha\) and \(\beta\), the last being equal to \(\omega_R t\) (Fig. 1.20).

Eq. 1.112 contains one time-independent term (the first two addenda of the sum) and
one time-dependent term (the last two addenda). If the spinning frequency is much greater (approximately at least 3 or 4 times) than the chemical shift anisotropy, which practically corresponds to the powder pattern breadth in frequency, the time-dependent term can be neglected.

The remaining time-independent part contains the isotropic chemical shift and an angular term (not by chance reminiscent of the orientation dependence factor of the spin interactions), which only depends on the $\alpha$ angle between the $z^R$ axis and $B_0$. Setting $\alpha$ at the magic angle, $54.74^\circ$, the angular term is null and $\sigma_{zz}$ becomes equal to $\sigma_{iso}$. Therefore, the magic-angle spinning averages out the anisotropy of the shielding interaction, whose contribution to spectrum is simply reduced, as in solution NMR, to the isotropic shielding (or, equivalently, the isotropic chemical shift).

Since all the interactions contribute to the spin Hamiltonian, at the first order, only through their $zz$ component, it can be demonstrated that the result just shown for the shielding interaction is generalizable to all the spin interactions. In the case of the quadrupolar interaction, when second-order effects have to be taken into account, the magic-angle spinning cannot completely average out the anisotropy of the interaction, but the central transition linewidth can be considerably reduced.

The assumption that the spinning frequency largely exceeds the interaction anisotropy is actually a quite strong limitation for the MAS “magic” effect. Several technical problems prevent to freely raise up the spinning frequency: at present, the maximum MAS frequency achieved is 70 kHz, while on the best performing probeheads available for commercial spectrometers such limit is reduced to 35-40 kHz. At the routine MAS frequencies, depending on the nucleus and the interactions anisotropy, the previous assumption can be no longer applicable; when the MAS frequency does not largely exceed the interaction anisotropy, the time-dependent term of Eq. 1.112 cannot be neglected and, as a consequence, magic-angle spinning cannot completely average out the interactions anisotropy.

The consequences on the NMR spectrum strongly depend on the character of the interaction considered. In the case of inhomogeneous interactions, as the chemical shift, the heteronuclear and two-spin homonuclear dipolar interactions, the powder pattern is transformed in a series of narrow signals: one of them is the isotropic signal, while the others, arising from the time-dependent term, appear at frequencies which differ from the isotropic signal by an integer multiple of the spinning frequency. The latter signals are called *spinning sidebands* (ssb): their intensity profile reproduces the static powder pattern, and, the higher the spinning frequency is, the fewer the spinning sidebands are. Differently from
the isotropic signal, the ssb positions depend on the spinning frequency; therefore, by acquiring spectra at different spinning rates, they can be easily recognized. The effect of the MAS frequency on a chemical shift powder pattern is shown in Fig. 1.21.

On the other hand, if homogeneous interactions are considered (as homonuclear dipolar couplings involving more than two spins), when the spinning frequency does not largely exceeds the static signals linewidth, the magic-angle spinning effect on the spectrum is very scarce. In particular, if the spinning frequency \( \omega_R \) is much less than the static linewidth \( \Delta \omega \), the signal is almost unaffected by magic-angle spinning; in an intermediate regime in which \( \omega_R \approx \Delta \omega/4 \), very broad spinning sidebands appear. The effect of the magic-angle spinning on a signal affected by homonuclear dipolar interaction is shown in Fig. 1.22.

Going into some more practical considerations, magic-angle spinning plays an essential role in the obtainment of solid-state high resolution spectra of nuclei for which the homonuclear dipolar interaction is not dominant; this happens with the so called “dilute spins”: \(^{13}\)C and \(^{29}\)Si are two common examples for which homonuclear dipolar

![Figure 1.21: Effect of the magic-angle spinning frequency on a chemical shift powder pattern. The spectra refer to an axially symmetric chemical shift tensor, with isotropic chemical shift equal to 0 and anisotropy of 5 kHz.](image-url)
Figure 1.22: Effect of the magic-angle spinning frequency on a signal broadened by homogeneous homonuclear dipolar interactions. $\Delta \omega$ and $\omega_R$ are the signal static linewidth and the spinning frequency, respectively.

lar interactions can be almost neglected. In most cases, magic-angle spinning, at the available spinning frequencies, is able to average out the chemical shift anisotropy of the different signals; therefore, provided to remove the heteronuclear dipolar couplings (see following subsection), high-resolution spectra of these nuclei can be obtained.

On the other hand, the $^1$H nucleus is the most important case in which the magic-angle spinning is often not sufficient to obtain high resolution spectra: the high natural abundance and the usually numerous presence in most common compounds, cause the homonuclear dipolar interactions to dominate the proton spectra. Due to their large anisotropy and homogeneous character, the commonly available spinning frequencies often do not allow high resolution spectra to be straightforwardly obtained.

A more detailed description of the experimental aspects concerning the observation of the nuclei investigated in this thesis is reported in Sections 2.5-2.6.

1.7.2 High-power decoupling (HPD)

In the case of dilute spins ($^{13}$C, $^{29}$Si, ...) the main cause of line-broadening is often the heteronuclear dipolar interaction with abundant spins, usually protons. Even if the nature of the heteronuclear dipolar interaction is mainly inhomogenous, in the case in
which the abundant spins are involved in an homonuclear dipolarly coupled network, an homogeneous contribution in the dilute spin spectrum is present; in particular this results in an homogeneous line-broadening which, as described in the previous subsection, cannot be usually removed by magic-angle spinning at the available spinning frequencies. Fortunately, by the employment of high-power decoupling (HPD), sometimes also referred to as dipolar decoupling (DD), all the effects of the heteronuclear dipolar couplings can be removed, so allowing high-resolution spectra of dilute spins to be obtained. In its simplest form high-power decoupling consists of a continuous radio-frequency irradiation, Continuous Wave (CW) decoupling, applied at the resonance frequency of the abundant spins coupled with the dilute ones to be observed; the rf power which has to be employed is somehow proportional to the strength of the heteronuclear dipolar coupling, therefore, even if the idea is exactly the same as the decoupling employed in solution NMR (for removing the $J$ couplings), in the solid state an rf power hundreds of times stronger is currently used\textsuperscript{11}. The scheme of the simple pulse sequence employed for the acquisition of an X spectrum in which a CW proton decoupling is employed is reported in Fig. 1.23. More evolute high-power decoupling pulse sequences have been developed and successfully applied, two important examples being the two-pulse phase-modulated (TPPM) \[19\] and the SPINAL \[20\] sequences. Most of the proton-decoupled spectra reported in this thesis have been acquired applying a CW decoupling sequence (except 2D experiments, where TPPM decoupling sequence were used), which resulted efficient enough for removing heteronuclear dipolar couplings for the systems here investigated.\textsuperscript{11}

\textsuperscript{11}It is worth to notice that a rigorous explanation of high-power decoupling would require to have recourse to the average Hamiltonian theory, which can be found in reference \[4\].
1.7.3 Cross-polarization (CP)

Unlike magic-angle spinning and high-power decoupling, cross-polarization [21–26] does not act on the spectral resolution, but it is very useful, sometimes indispensable, for the obtainment of dilute spin spectra with a good signal to noise ratio. Indeed, dilute spins are troubled both by low natural isotopic abundance and by long $T_1$ relaxation times, which, as better described in the next section, determine the time delay between two consecutive scans; for both these reasons a spectrum with a good signal to noise ratio can take a very long time to be recorded.

Cross-polarization acts on this problem, by allowing a magnetization (polarization) transfer to be realized from abundant to dilute spins, exploiting the heteronuclear dipolar interactions. Commonly, the abundant spins are protons, but, in principle, any other abundant spin can be used ($^{19}$F for instance).

Even if a theoretical treatment of cross-polarization is possible and necessary for a rigorous discussion, considering the aims and the contents of the thesis, I am just interested in explaining, very qualitatively, the idea at the basis of this technique and in highlighting some aspects which will be often used in discussing the experimental results of the thesis [4].

Experimentally, cross-polarization, as high-power decoupling, requires the presence of at least two channels on the spectrometer. The CP pulse sequence (Fig. 1.24) consists in a $90^\circ_x$ pulse on the $^1$H channel, followed by the simultaneous application of two contact pulses along the $-y$ direction, on both the $^1$H and the X channels, for a time called contact-time.

After the $90^\circ_x$ pulse, a proton magnetization $M(H)$ in the $-y$ direction is created.
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Reminding that, from the vector model, in the rotating frame $M$ precesses around $B_1$, the effect of the $-y$ contact pulse will be to simply lock the proton magnetization $M(H)$ along the $-y$ axis (the magnetic field corresponding to the contact pulse is indicated as spin-lock field).

The alignment between $M(H)$ and the spin-lock field $B_1(H)$ suggests a parallelism with the equilibrium situation of a generic magnetization $M$ in a static field $B_0$: the $B_1(H)$ direction ($-y$) can be considered as a quantization axis, as well as the $B_0$ direction in an equilibrium situation. Within this parallelism, $^1H$ spin states ($|\alpha_H^*\rangle, |\beta_H^*\rangle$) can be defined in the rotating frame, their energy gap being, in angular frequency, $\omega_1(H) = \gamma_H B_1(H)$.

In order to realize cross-polarization, the simultaneous contact pulse acting on the $X$ spins has to be set so that the Hartmann-Hahn matching condition is satisfied:

$$\gamma_H B_1(H) = \gamma_X B_1(X) \quad (1.113)$$

In this condition the frequencies of the $^1H$ and $X$ rotating frames are equal: $\omega_1(H) = \omega_1(X)$; therefore, the energy gap between the $^1H$ and the $X$ spin states in the rotating frame is the same and, therefore, an energy exchange between the $^1H$ and $X$ spin systems is possible.

After the contact pulse, the $^1H$ energy distribution is out of equilibrium: the transverse magnetization aligned with the spin-lock field $B_1(H)$, equal in magnitude to the initial magnetization aligned with $B_0$, is too much for the thermal equilibrium established by $B_1(H)$, always much smaller than $B_0$ ($\gamma B_0/2\pi$ is of the order of MHz, while $\gamma B_1/2\pi$ is of the order of kHz); in terms of spin states this means a population excess for the $|\alpha_H^*\rangle$ state.

The heteronuclear dipolar interaction, expressed (in angular frequency units) by:

$$\hat{H}_{HX} = -\sum_{j<k} d_{jk}(3\cos^2\theta_{jk} - 1) \hat{I}_j^z \hat{I}_k^z \quad (1.114)$$

where $d_{jk} = h (\mu_0/4\pi) r_j^{-3} \gamma_j \gamma_k$ is the dipolar-coupling constant for the $j$th $^1H$ and $k$-th $X$ spins (Eqs. 1.100, 1.101), contains only $\hat{I}_z$ operators: being the quantization axis, in the rotating frame, perpendicular to $z$, $\hat{H}_{HX}$ cannot affect the net energy of the system. On the other hand, it can allow the spin system to reach an equilibrium situation, transferring the energy arising from $|\alpha_H^*\rangle \rightarrow |\beta_H^*\rangle$ transitions to the $X$ spin states, by inducing $|\beta_X^*\rangle \rightarrow |\alpha_X^*\rangle$ transitions.

In such an energy redistribution, due to the Hartmann-Hahn matching, the net energy of the H-X spin system is unchanged. Correspondingly, the system net magnetization is unaltered, but it has been redistributed between H and X, as well: the energy exchange between the H and X spin states corresponds to a decrease of the $^1H$ transverse magnetization in favour of the creation of an X transverse magnetization, which, in the end,
gives rise to a detectable X resonance signal.

Creating X magnetization by transfer from the abundant \(^1\)H spins system rather than by direct X excitation provides, at least, two important advantages: the X low natural abundance is by-passed and it is not necessary to employ a long time delay between two consecutive scans, being the recovering of the equilibrium magnetization along \(B_0\) dictated by the proton \(T_1\) instead of the longer X \(T_1\).

In the reported approximated description of the cross-polarization, the homonuclear dipolar interaction among the protons has not been cited: nevertheless it is involved in the process, especially allowing the energy redistribution among protons\(^{12}\).

From a practical point of view, the set-up of a CP experiment requires the Hartmann-Hahn matching condition to be established: this is usually realized by fixing the amplitude of \(B_1(H)\) and repeating the experiment varying the amplitude of \(B_1(X)\), or vice-versa. Apart from deviations, possible when the experiment is performed with MAS, the matching is indicated by the reached maximum intensity of the X signal. For a given HX couple, the Hartmann-Hahn condition is usually set on a reference compound and then employed for the different samples.

A very important aspect to consider is the “dynamics” of the cross-polarization process, which practically means that, once that the Hartmann-Hahn matching is satisfied, the intensity of a certain X signal is still function of the contact time. In simple cases, that is when it is possible to assume that \(T_{1p}(X) \gg T_{XH}\) and \(T_{1p}(H) \gg T_{XH}\), the X magnetization \((M)\) vs the contact time \((t_c)\) follows the equation [28]:

\[
M(t_c) = M_{eq} \left( e^{-\frac{t_c}{T_{1p}(H)}} - e^{-\frac{t_c}{T_{XH}}} \right)
\]

where \(T_{XH}\) is a time constant called cross-polarization time, \(T_{1p}(H)\) is the proton spin-lattice relaxation time in the rotating frame, which will be described in the next section, and \(M_{eq}\) is the ideal maximum value that \(M\) would reach in absence of relaxation. The plot of this function is reported in Fig. 1.25. In an approximative way it can be said that the rate of the magnetization transfer is proportional to \(1/T_{XH}\), while its decay is mainly regulated by \(T_{1p}(H)\). Indeed, considering that \(T_{XH}\) is usually shorter than \(T_{1p}(H)\):

- for very short contact times, \(t_c \ll T_{XH}\),

\[
M(t_c) \approx M_{eq} \frac{t_c}{T_{XH}}
\]

that is \(M\) linearly increases with \(t_c\), the line slope being \(\frac{M_{eq}}{T_{XH}}\);

\(^{12}\)It is worth to mention that beside the quantum mechanical approach, cross-polarization has been also explained with a thermodynamic model [27].
1.7 High-resolution solid-state NMR

Figure 1.25: Trend of the X signal intensity vs the contact time as expected by Equation 1.115. This plot has been obtained assuming $M_{eq}=100$, $T_{XH}=5$ ms and $T_{1ρ}(H)=50$ ms.

- for very long contact times, $t_c \gg T_{XH}$

$$M(t_c) \approx M_{eq}e^{-\frac{t_c}{T_{1ρ}(H)}}$$  \hspace{1cm} (1.117)

that is $M$ exponentially decays with $t_c$, the exponential decay being regulated by $T_{1ρ}(H)$.

Therefore, for each X nucleus in a given molecule, the contact time value at which the maximum polarization transfer is realized, depends on both these two time constants. While the explanation of the spin-lattice relaxation time $T_{1ρ}(H)$ is postponed to the next section, $T_{XH}$ can be approximatively inversely related to the strength of the X-H heteronuclear dipolar interaction.

For an XH couple, the dipolar coupling is determined both by structural factors ($d \propto \frac{1}{r^3}$), such that the shorter the internuclear distance is, the stronger the dipolar coupling is, and by dynamic factors: molecular motions can, to a variable extent, average the anisotropy of the dipolar interaction, decreasing its strength; therefore, the internuclear distance being the same, nuclei in more mobile molecular environments usually show longer $T_{XH}$, while short $T_{XH}$ are indicative of more rigid molecular environments.

In practice, when a CP spectrum has to be acquired on a real sample, the $t_c$ value is chosen in order to realize, when it is possible, a sufficiently good polarization transfer for all the different X signals. On the other hand, the different CP dynamics for different X nuclei allows the CP experiment to be used as a selective technique: playing with the $t_c$ value, signals arising from either more mobile or more rigid molecular environments can be selected.
1.8 Relaxation

In the two following subsections I would like to report the very basic elements of relaxation in solid-state NMR, especially with the aim of providing a brief theoretical reference for the next chapters, in which relaxation times will be included in the description of the experimental approach to the study of organic-inorganic multicomponent materials and in the discussion of the results. An extensive treatment of relaxation in solids can be found in ref. [7].

1.8.1 Relaxation times $T_1$, $T_2$, $T_1\rho$

The term relaxation always refers to a process by which a system comes back to the thermodynamic equilibrium state after a perturbation.

The relaxation processes occurring in NMR can be quite easily introduced by having recourse to the vector model.

The conclusion of Subsection 1.2.2 has been that the magnetization $M$ of a spin system in an external static magnetic field $B_0$ (along $z$), first aligned, at the equilibrium, with $B_0$ and then flipped into the $xy$ plane by a $90^\circ$ rf pulse, after the pulse is turned off, precesses in the $xy$ plane around $B_0$ so generating the NMR signal at $\omega = \omega_0$.

However, this is not an equilibrium state for the system: $B_0$ is again the only magnetic field present, therefore $M$ should be aligned with it and no transverse magnetization should be present. Both the recovering of the $M_z$ component back to the initial equilibrium value and the nulling of the transverse magnetization ($M_x$ and $M_y$ components), vs time, are in principle exponential processes, regulated by the $T_1$ and $T_2$ relaxation times, respectively.

Strictly speaking, $T_1$ and $T_2$ are contained in the Bloch equations, which describe the time evolution of the magnetization $M$ in a generic magnetic field $B$:

$$\frac{dM}{dt} = \gamma M \times B - \frac{M_\perp}{T_2} + \frac{(M_0 - M_{||})}{T_1}$$

(1.118)

where $M_{||}$ and $M_{\perp}$ are the $M$ projections in the $xy$ plane and along the $z$ axis, respectively, and $M_0$ is the equilibrium magnetization in presence of the only static field $B_0$. $T_1$ is the longitudinal or spin-lattice relaxation time, while $T_2$ is the transverse or spin-spin relaxation time. For both of them, the second name is related to the relaxation mechanism: while longitudinal relaxation involves the energy exchange between the spin system and the environment (the crystal lattice, for a crystalline solid), transverse relaxation only involves energy exchanges among the spins, leaving unchanged the total energy of the spin system.

The corresponding quantum mechanical “translation” is that spin-lattice or longitudinal
1.8 Relaxation

Relaxation concerns the evolution of the spin state populations back to the Boltzmann distribution values, while spin-spin or transverse relaxation concerns the decay of the coherences (Subsection 1.3.3).

The easiest practical manifestations of $T_1$ and $T_2$ can be found in the basic NMR experiment ($90^\circ$ pulse - acquisition). The NMR signal prior to the Fourier transform, that is the electric current oscillating at the Larmor frequency (Subsection 1.2.3), exponentially decays with time constant equal to $T_2$; the detectable decaying-oscillating signal, in the time domain, is the so called Free Induction Decay (FID) (Fig. 1.14).

On the other hand, since $T_1$ determines the restoring rate of the equilibrium longitudinal magnetization after an rf pulse, it is clear that, in a multi-scans experiment, in order to flip, in every scan, the entire equilibrium magnetization, a time delay longer (usually five times) than $T_1$ has to be waited between two consecutive scans.

In solid-state NMR a third relaxation time plays an important role: the spin-lattice relaxation time in the rotating frame, $T_1 \rho$, already introduced in Subsection 1.7.3. The situation occurring, for example, during the contact time of the CP sequence, in which a magnetization $M$, initially in equilibrium with a static magnetic field $B_0$ and then flipped, by an rf pulse, in the $xy$ plane, is forced to remain aligned, in the rotating frame, along a spin-lock field $B_1^{SL}$, is not an equilibrium situation. As already said in Subsection 1.7.3, $B_1^{SL}$ is much weaker than $B_0$, and, consequently, $M$ tends to assume an equilibrium reduced magnitude equal to $\left(\frac{B_1^{SL}}{B_0} M_0\right)$, which is often negligible with respect to $M_0$, where $M_0$ is the equilibrium magnetization magnitude in presence of $B_0$ only. This relaxation process is again exponential and the time constant is the spin-lattice relaxation time in the rotating frame,$T_1 \rho$ .

1.8.2 Relaxation times and molecular motions: the simplest model

Given a certain spin system, all the relaxation times are closely related to the nuclear interactions which contribute to the system spin Hamiltonian, their fundamental trait d’union in most cases being the molecular motions.

In NMR, a generic relaxation process occurs thanks to the effect of time-fluctuating magnetic fields, which directly arise from the time modulation of the spin interactions exerted by the molecular motions. As far as spin-$\frac{1}{2}$ nuclei in diamagnetic systems are concerned, the dipolar interaction is usually the most important source of relaxation, followed by the chemical shift, while separate considerations must be done for those systems in which paramagnetic centers are present. The relaxation times of nuclei quite

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13Actually, this is rigorously true for a liquid; as it will be shown in the following, the situation is much more complicated in solids.
close in space to these centers (typically at a distance of a few Å, which is however dependent on the concentration of the paramagnetic centers themselves) are mainly affected, and in particular sensibly shortened, by the electronic-nuclear dipolar interaction. The different relaxation times are affected in different ways. For instance, the nuclear $T_1$ is strongly affected by the fluctuation of the electronic-nuclear dipolar interaction arising from spin exchange among different unpaired electrons, which is effective at frequencies of the order of the nuclear Larmor frequency. This mechanism is therefore somehow different from the more common dipolar (or CSA) mechanism, where the fluctuations at the Larmor frequency are typically caused by molecular motions. It must be noticed that the contribution to the spin-lattice relaxation rate arising from the direct paramagnetic interaction is very important, and typically it overwhelms the other relaxation contributions, but only at very short distances from the paramagnetic centers, since it depends on $r^{-6}$, $r$ being the unpaired electron-nucleus distance.

Coming back to a more general treatment, relaxation in NMR is usually approached in a statistical way, by first introducing the time correlation function, $G(\tau)$ of a generic time-dependent local magnetic field $b(t)$, arising from the fluctuating spin couplings:

$$G(\tau) = \langle b(t) \cdot b(t + \tau) \rangle \quad (1.119)$$

where $\langle \rangle$ indicates an average over an equilibrium ensemble.

$G(\tau)$ is defined such as to describe the correlation between the local field values at time $t$ and $t + \tau$, and it is considered independent of $t$.

Particularly useful is the Fourier transform of the correlation function:

$$J(\omega) = \int_{-\infty}^{\infty} G(\tau) e^{-i\omega\tau} d\tau \quad (1.120)$$

the so called spectral density function, which expresses the power available for the relaxation over the whole frequency “spectrum”. Through the spectral densities, the measurable relaxation times can be related to the molecular motions parameters, somehow contained into the correlation function. Within the Redfield theory [1, 9], which strictly speaking would be applicable only in “fast motion” regimes (this aspect will be better discussed in the following), the different relaxation rates, inverse of the respective relaxation times, can be indeed expressed as linear combinations of spectral densities:

$$R_k = \frac{1}{T_k} = \sum_i c_i J(\omega_i) \quad (1.121)$$

A very simple expression of the correlation function was introduced by Bloembergen, Purcell and Pound in 1948 [29], within the so called BPP theory for the NMR relaxation.
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Figure 1.26: Curves of the spectral density $J(\omega)$ vs $\omega$, as provided by the BPP theory (Eq. 1.123), calculated for three different values of correlation time, $\tau_c$.

By assuming to consider a random motion and an ensemble of equivalent dynamic unities, $G(\tau)$ can be expressed as:

$$G(\tau) = \langle b^2 \rangle e^{-\frac{\tau}{\tau_c}}$$

(1.122)

where $\langle b^2 \rangle$ is the mean squared value of $b$ and $\tau_c$ is the correlation time, which is a time constant describing the decay of the correlation in the $b$ fluctuations. Even if this is not rigorous, sometimes it can be useful to establish an over-simplified relation between $\tau_c$ and some time constant typical of the motion (as, for instance, the period of a rotation). The spectral density corresponding to the BPP expression of $G(\tau)$ is:

$$J(\omega) = \langle b^2 \rangle \frac{2\tau_c}{1 + \omega^2 \tau_c^2}$$

(1.123)

In Fig. 1.26 $J(\omega)$ is plotted for three different values of $\tau_c$; it is noticeable that the spectral density is almost constant for, approximatively, $0 \leq \omega \leq \frac{1}{\tau_c}$, and then it decreases. From a physical point of view, this means that most of the power for relaxation is provided at frequencies less than or equal to the “frequency” of the $b(t)$ fluctuations.

As previously said, the dipolar interaction is the most important source of relaxation for spin-$\frac{1}{2}$ nuclei; the homonuclear dipolar interactions will be the most important source of relaxation for an ensemble of abundant spins (as $^1$H), while the heteronuclear ones will be dominant in the relaxation of dilute spins (as $^{13}$C). In the following I will report some results concerning only the case in which the relaxation is determined by homonuclear dipolar couplings.

When relaxation is determined by homonuclear dipolar couplings, the relaxation
rates \( R_1, R_2, R_{1\rho} \), result to be:

\[
R_1 = \frac{1}{T_1} = \frac{3}{2} K_I \left[ J_1(\omega_0) + J_2(2\omega_0) \right] \tag{1.124}
\]

\[
R_2 = \frac{1}{T_2} = \frac{3}{2} K_I \left[ \frac{1}{4} J_0(0) + \frac{5}{2} J_1(\omega_0) + \frac{1}{4} J_2(2\omega_0) \right] \tag{1.125}
\]

\[
R_{1\rho} = \frac{1}{T_{1\rho}} = \frac{3}{2} K_I \left[ \frac{1}{4} J_0(2\omega_1) + \frac{5}{2} J_1(\omega_0) + \frac{1}{4} J_2(2\omega_0) \right] \tag{1.126}
\]

where:

\[
K_I = \left( \frac{\mu_0}{4\pi} \right)^2 \gamma I h^2 (I + 1) \tag{1.127}
\]

with \( \mu_0 \) the magnetic permeability of a vacuum.

Assuming to consider an isolated pair of spins, with internuclear vector \( r \) constant in modulus and subject to isotropic rotational diffusion, \( \langle b^2 \rangle \) can be calculated for the different \( J_i \) contained in Eqs. 1.124–1.126. Then, by expressing the various spectral densities according to the BPP theory (Eq. 1.123), the relaxation rates result to be:

\[
R_1 = \frac{1}{T_1} = \frac{2}{5r^6} K_I \left[ \frac{\tau_c}{1 + \omega_0^2 \tau_c} + \frac{4\tau_c}{1 + 4\omega_0^2 \tau_c} \right] \tag{1.128}
\]

\[
R_2 = \frac{1}{T_2} = \frac{3}{5r^6} K_I \left[ \frac{\tau_c}{1 + \omega_0^2 \tau_c} + \frac{5}{3} \left( \frac{\tau_c}{1 + \omega_0^2 \tau_c} \right) + \frac{2}{3} \left( \frac{\tau_c}{1 + 4\omega_0^2 \tau_c} \right) \right] \tag{1.129}
\]

\[
R_{1\rho} = \frac{1}{T_{1\rho}} = \frac{2}{5r^6} K_I \left[ \frac{3}{2} \left( \frac{\tau_c}{1 + \omega_0^2 \tau_c} \right) + \frac{5}{2} \left( \frac{\tau_c}{1 + \omega_0^2 \tau_c} \right) + \frac{\tau_c}{1 + 4\omega_0^2 \tau_c} \right] \tag{1.130}
\]

Looking at the frequencies present in the different relaxation rate formulae, which descend from the respective spectral densities contained in Eqs. 1.124–1.126, and considering the meaning of the spectral density functions as well as the previously mentioned rough parallelism between \( \tau_c \) and a motional time constant, it can be easily guessed that the two spin-lattice relaxation processes, characterized by \( T_1 \) and \( T_{1\rho} \), are determined by molecular motions with characteristic frequencies of the order of magnitude of \( \omega_0 \) (Larmor frequency) and \( \omega_1 \) (\( \omega_1 = \gamma B_1 \), where \( B_1 \) is the spin-lock field), respectively, while the spin-spin relaxation, regulated by \( T_2 \), results to be affected by molecular motions both at \( \omega_0 \) and at very low frequencies, in principle at zero frequency (actually, as better explained in the following, \( T_2 \) measurements in the solid state cannot be used
Figure 1.27: Curves of $T_1$, $T_2$, $T_{1\rho}$ vs the correlation time, $\tau_c$, as provided by the BPP theory for an isolated couple of protons, separated by 0.1 nm. The $T_1$ trend is calculated at two different values of $\omega_0$, 30 and 300 MHz, while the $T_{1\rho}$ trend is calculated assuming a spin-lock frequency $\omega_1=100$ kHz.

for studying very slow molecular motions). In Fig. 1.27, the three relaxation times are plotted vs the correlation time $\tau_c$.

Even if a more proper description of the temperature dependence of the various relaxation times requires the assumption of a certain model, in the simplest case, for example, the Arrhenius law:

$$\tau_c = \tau_\infty e^{E_a/kT}$$  \hspace{1cm} (1.131)

(where $\tau_\infty$ is a temperature independent parameter and $E_a$ is the motion activation energy), considering that, in general, the correlation time will decrease by increasing the temperature, an approximate idea of the temperature trends of relaxation times can be obtained by the curves reported in Fig. 1.27. The very “right” part of the plot (short $\tau_c$) can be considered representative of the motional situation in liquids, while the very left (long $\tau_c$) can be indicative of rigid solid systems. As it can be guessed by the plot, what happens in practice is indeed that, in liquids, that is under extreme narrowing conditions ($\omega_0^2\tau_c^2 \ll 1$), $T_1$, $T_{1\rho}$ and $T_2$ are often equal and do not depend on $\omega_0$, while, in solids, $T_2$ is usually considerably shorter than $T_1$ and $T_{1\rho}$. Moreover, $T_2$ is expected to have a monotonic trend with the temperature, while both the $T_1$ and $T_{1\rho}$ curves pass through a minimum, raised and shifted to shorter $\tau_c$ with increasing $\omega_0$. In discussing these trends, some considerations on the effective applicability of Eqs. 1.128–1.130, are necessary. As
already mentioned, the Redfield theory, from which the expression of relaxation rates in terms of spectral densities (Eq. 1.121) descends, is strictly valid when $\tau_c \ll T_1, T_2$ [1]. In rigid solid systems this condition is usually not satisfied for $T_2$. What happens in practice is that $T_2$'s are usually in the very left part of the curve reported in Fig. 1.27, where the experimental trend (solid line) deviates from the hypothetical Redfield-BPP trend (dashed line) and $T_2$'s are therefore insensitive to molecular motions (and thus to the temperature); in particular, this happens when the motion correlation time $\tau_c$ exceeds the so called rigid-lattice limit, that is for $\tau_c$ larger than the inverse of the static linewidth (usually of the order of $10^{-5}$ s$^{-1}$). Also considering that, even when $T_2$'s out of the rigid lattice limit are measured, effects other than dynamic might affect their values (the static field inhomogeneity for example), it descends that quantitative studies of molecular motions by means of variable temperature $T_2$ measurements in the solid state are difficult and not common. Nevertheless, $T_2$ measurements can provide useful semi-quantitative information concerning, in general, the degree of molecular mobility of different regions in a sample. In this thesis, for example, proton $T_2$ measurements have been widely employed to single out motionally distinct regions of a sample (see also Subsection 2.6.2): considering that, out of the rigid-lattice regime, $T_2$ always monotonically increases with decreasing $\tau_c$, shorter $T_2$ values could be related with sample domains characterized by a minor degree of molecular mobility, while longer $T_2$'s could be considered indicative of more mobile sample fractions.

As far as $T_1$ and $T_{1\rho}$ are concerned, as already said for $T_2$, in most solid systems their values can be found in the slow motions side (left part of the curves reported in Fig. 1.27) and usually Eqs. 1.128–1.130 do not suitably describe the trend with $\tau_c$ of $T_1$ and $T_{1\rho}$. On the other hand, differently from $T_2$'s, variable temperature $T_1$ and $T_{1\rho}$ measurements allow molecular motions to be accurately characterized also in the solid state. Indeed, even when some slow motions do not match requirements on which the Redfield theory is based, due to the occurrence of spin diffusion (described in the next subsection), fast relaxing nuclei present in relatively mobile molecular fragments or phase domains “drive” the spin-lattice relaxation processes of all the other nuclei: the actually measured $T_1$ and $T_{1\rho}$ values are averaged values, which result to be closer to the shorter intrinsic ones (see also Subsection 2.6.2, in particular the parts dealing with the experimental measurement of proton $T_1$ and $T_{1\rho}$). For these reasons the trend of measured spin-lattice relaxation times, contrary to what happens for $T_2$, can be usually reproduced by means of suitable motional models. BPP curves (Fig. 1.27), even though not fully adequate, might provide an approximate idea of the real $T_1$ and $T_{1\rho}$ trends vs $\tau_c$. Actually, in order to accurately characterize molecular motions from relaxation time measurements, the BPP theory, derived for the strongly ideal system of an isolated pair
of spins for which the homonuclear dipolar interaction is the main source of relaxation, has to be overcome. For the analysis of both protons and heteronuclei relaxation times, theoretical and semi-empirical models have been developed which take into account a major degree of “reality”, as, for example, the simultaneous presence of several motions, the distribution of correlation times and the correlation among motions. Analogously, beside the Arrhenius law, more complicated equations for the temperature dependence of the relaxation times can be applied. Therefore, the experimental trends of the various relaxation times can be much more complicated than those provided by the BPP theory (for a reference review see ref. [30]; for an example of experimental approach to an extensive relaxation study see ref. [31–33]).

As far as this thesis is concerned, relaxation times data obtained by high- as well as low-resolution experiments are analyzed by either qualitative or quantitative way, are useful in investigating and discussing the molecular dynamics of the systems studied, especially in terms of the existence of motionally distinct domains; this aspect is better described and exemplified in Sections 2.5-2.6.

1.8.3 Spin diffusion

This expression indicates an important process, which can strongly affect the nuclear relaxation behaviour of solid systems, consisting in a spatial diffusion of nuclear magnetization occurring without diffusion of matter. The origin of this process lies in the $B$ term of the homonuclear dipolar interaction Hamiltonian (Eq. 1.38), also called flip-flop term. The effect of the $B$ term on a pair of dipolarly coupled spins is to exchange their polarizations: if, for example, the first spin is in the $|\alpha\rangle$ Zeeman state and the second in the $|\beta\rangle$ state, under the effect of the $B$ term the situation is reversed; it is important to notice that this exchange process does not alter neither the energy nor the net magnetization of the system.

By extending the flip-flop process from a single spin pair to a network of like spins, a spatial diffusion of the magnetization is realized. Because, at short times, the time evolution of the spatial distribution of the magnetization can be described by a diffusion equation, the process is referred to as spin diffusion. The just mentioned diffusion equation is:

$$\frac{\partial M(r,t)}{\partial t} = D \frac{\partial^2 M(r,t)}{\partial^2 r}$$  \hspace{1cm} (1.132)

where $M(r,t)$ is the magnetization, function of both the spatial coordinates and time, and $D$ is the spin diffusion constant. From the universal random walk result, $D$ can be expressed as:

$$D = \langle r^2 \rangle / n\tau$$  \hspace{1cm} (1.133)
where $\langle r^2 \rangle$ is the main square diffusive path length, $\tau$ is the time for a step in the random walk and $n = 2, 4, 6$ for diffusion in 1, 2, 3 dimensions, respectively (actually, in dependence on the geometrical models assumed to describe the morphology of the systems, especially polymers, $n$ can range from 1 to 6) [7].

Being originated from the homonuclear dipolar couplings, spin diffusion is particularly important in abundant spin systems, where it strongly affects the nuclear spin relaxation behaviour. Indeed, in most organic systems, the measured proton $T_1$ and $T_{1\rho}$ values do not correspond to their intrinsic values, that is the values hypothetically measurable in absence of spin diffusion, being instead intermediate values between the shortest and the longest intrinsic $T_1$ and $T_{1\rho}$, respectively (see also Subsection 2.6.2, in particular the parts concerning the experimental measurements of proton $T_1$ and $T_{1\rho}$).

The reason for this is that the spin diffusion allows the fast relaxing nuclei to act as relaxation sink for the close longer relaxing nuclei; the extent of the averaging process, which can be complete, so determining a unique average $T_1$ and $T_{1\rho}$ value to be measured, or partial, so allowing more different relaxation times values to be detected, depends on the time the spin diffusion is let to proceed, on the spin diffusion rate and on the degree of homogeneity of the sample. Provided to know the first two factors, spin diffusion can be used as a probe for investigating the heterogeneity of a sample: this is the idea of the Goldman-Shen experiments, in which the spin diffusion is used to determine the different domain sizes of a sample [34]. An approximate estimate of the heterodomain sizes present in a sample can be drawn by the proton $T_1$ and $T_{1\rho}$ measurement. By substituting, in Eq. 1.133, $\tau$ with $T_1$ or $T_{1\rho}$ and taking some good reference values from polymer studies, in which spin diffusion has been extensively studied, as $n = 6$, a $D$ of $10^{-16} \text{m}^2\text{s}^{-1}$ for the laboratory frame and half of this for the rotating frame [7], and $T_1$ and $T_{1\rho}$ typical values of 700 ms and 10 ms, respectively, the corresponding maximum diffusive path lengths result to be of the order of 20 nm and 2 nm, respectively. This means that an efficient $T_1$ or $T_{1\rho}$ relaxation sink can relax neighbouring nuclei located at a maximum distances of about 20 nm and 2 nm, respectively. Still considering these approximate values, if more than one $T_1$ or $T_{1\rho}$ values are measured, it means that heterogeneities of average sizes larger than, respectively, 20 nm and 2 nm, exist.

It is important to remark that, being a process involving $|\alpha\rangle \leftrightarrow |\beta\rangle$ transitions, the spin-spin relaxation time, $T_2$, is not affected by the spin diffusion; moreover, spin diffusion has a negligible effect on the relaxation of dilute spin systems; therefore the intrinsic, site specific, $T_1$ and $T_{1\rho}$ values for dilute spins can be measured.
Chapter 2

A solid-state NMR approach to the study of interfacial interactions in organic-inorganic multicomponent materials

This chapter constitutes of two parts; the first one is devoted to a brief introduction of the systems which can be included in the general definition of organic-inorganic multicomponent materials and to a description of the solid-state NMR experiments exploited in the literature for studying these materials and in particular their interfacial properties. In the second part I will discuss the solid-state NMR experimental approach followed in this thesis. In particular, I will focus on the categories of systems that have been dealt with in this thesis and on their key properties which can be investigated by solid-state NMR.

2.1 Organic-inorganic multicomponent materials - an Introduction

Organic-inorganic multicomponent materials (OIMM), under the general definition, include a wide variety of systems which are currently attracting an extraordinary interest in both academic research and applications. In this thesis I will use the following definition for OIMM: every system in which an organic component coexists with an inorganic one and gives rise to recognizable separated domains whose average sizes of either or both components range from nano- to micrometers and, in particular, their combination
A solid-state NMR approach to the study of interfacial interactions in organic-inorganic multicomponent materials plays an essential role in determining the final properties of the whole material [35]. This definition excludes, for instance, materials like organometallic compounds, where organic and inorganic moieties are mixed at a molecular level, as well as materials where the combination of organic and inorganic components does not result in significantly different properties with respect to those of at least one of the components.

Hence leaving out the organometallic compounds, in the following I will discuss those systems which are of interest to the thesis, that are commonly referred to as composite or multicomponent materials, which are obtained by modifying, chemically or just through a proper micro- or nano-dispersion either organic or inorganic matrix obtaining a “material” and forming recognizable organic and inorganic domains, whose size is larger than molecular. In all these systems the properties of each component are affected by the presence of the others, and, importantly, their combination with the most desirable properties of both (e.g., thermal stability, stiffness, and spatial order of the inorganic components; chemical reactivity, tunability, molecular flexibility, and processability of the organic components) are crucial to the obtainment of a final “composite” material with new and improved properties. In all these materials, the interfaces between the components, where the most important interactions take place, play a significant role in determining the final properties of the whole material.

Apart from these important common features, typical OIMM include a wide variety of systems differing from many factors; for instance: the chemical nature of the organic and inorganic components, the kind of interface existing among them, the absolute and relative dimensions of their domains. By suitably combining these factors, materials with very different final properties can be designed.

The organic-inorganic interface is a very essential part of OIMM since its characteristics play a crucial role in determining the properties of the final material. Considering the wide variety of OIMM, a straightforward definition of “interface” is difficult to be given. For instance, there are systems in which the organic-inorganic interface can be quite easily recognized and separated from the individual components. On the other hand, there are systems in which the organic and inorganic components are intimately mixed and it is very difficult to clearly distinguish individual domains; in these cases the interface is often considered to be spread over the entire material. Another important variable is the nature of the interactions occurring at the organic-inorganic interface: covalent or hydrogen bonds, ion-dipole or van der Waals interactions can be established. Moreover, the interface can be “static”, when the organic and inorganic components are steadily bonded, or “dynamic”, if temporary weak interactions are established which change in time.

This thesis focuses on organic-inorganic multicomponent materials which have been designed for a specific purpose. Their application properties often strictly depend on
the nature and type of interfacial interactions between the organic and inorganic components in these materials. The study of the nature and type of interfaces existing among these components results in a better understanding of these materials and, consequently, helpful in improving the final properties of the whole material. The common features as well as the differences between organic-inorganic multicomponent materials having different nature and kinds of interfaces are exemplified in the following by citing the categories to which the systems studied in the thesis belong.

Submicrometer-sized silica particles encapsulated in poly(methyl methacrylate) can be considered as an example of organic-inorganic multicomponent material: this system is constituted by spherical silica core-shell particles with an average particle size of \( \approx 180 \text{ nm} \) functionalized with the grafting agent 3-(trimethoxysilyl) propyl methacrylate (TMSPM) and an outer coating of poly(methyl methacrylate) (PMMA) with an approximate thickness of 10 nm. Encapsulation of the inorganic particles within polymers has many applications, whereby surface characteristics of the core are altered by coating with a polymer layer. For this kind of systems, the organic and inorganic moieties usually have chemical bonding between each other with the help of grafting agents which are generally organo-silanes, containing simple or complex alkyllic chains as well as the Si-X termination (with, often, X = methyl or ethyl groups), which undergo hydrolysis and are able to react with silanol groups present on the silica surface, forming Si-O-Si bonds. In this case, the organo-silane employed was TMSPM which forms the bonding with the silica surface through its silane part while the acrylate part of the organic chain is supposed to bind with PMMA. A very schematic representation of a core-shell particle is reported in Fig. 2.1.

In these systems the organic and inorganic components form two distinguishable but strongly bonded “phases”, whose interface is made by chemical bonds; the inorganic components act as the core and the organic component forms the coating over the core surface, which can be considered the most active part of the material. The SSNMR study of this core-shell system is reported in Chapter 3.

A second example of organic-inorganic multicomponent material studied in this thesis is an organometallic complex (guest) incorporated into mesoporous silica nanoparticles, which generally act as host. This system comprised of the inorganic matrix made of mesoporous silica nanoparticles which are functionalized or in other words organically modified by the functionalizing agents (3-aminopropyltriethoxysilane (APTES) and ethoxytrimethylsilane (ETMS)) and then organic complex ([Y(DBM)₃ Phen] complex) which has been incorporated into the pores of the organically modified silica matrix.
A solid-state NMR approach to the study of interfacial interactions in organic-inorganic multicomponent materials

Figure 2.1: Schematic picture of a core-shell particle.

The functionalizing agents have been employed to form a chemical bonding with silanol groups of the silica nanoparticles as well as forming weak van der Waals interactions or hydrogen bonds with the guest organic complex through their alkylic chains. In this kind of systems, there are only weak interactions or sometimes hydrogen bonds (depending on the functionalizing agents used) present between the organometallic complex and the organically modified inorganic matrix. However, the interface between these components can be recognized and separated by studying the interactions occurring between the organic and the inorganic moieties. The schematic representation of this kind of guest/host systems with the inorganic nature of the matrix is shown in the Fig. 2.2. The SSNMR study of this material is reported in Chapter 4.

In the following, we will look at a different group of organic-inorganic multicomponent materials in which the organic component is quantitatively predominant contrary to the above two systems. These materials are provided by the several kinds of filled polymers: this expression refers to all those composites prepared by variously “dispersing” a particulate compound (filler) into a polymer matrix in order to improve several chemico-physical and mechanical properties of the polymer (barrier toward gases, solvent and heat resistance, stiffness etc.,).

Many variables exist among these materials, as the size and the shape of the filler particles (from micro- to nano-scale) as well as their chemical nature (clays, silica etc.). It is worthy noting that often also the fillers themselves can be considered organic-inorganic multicomponent materials: indeed it is a common practice to treat the fillers with organic modifiers, with the aim of improving the compatibility, as well as the in-
The first one is represented by organically modified bentonite clay particles dispersed in the polymer matrix. A very schematic picture of this type of systems with the modified clays in the polymer matrix is shown in Fig. 2.3. Natural bentonite clays are layered silicates constituted by inorganic platelets (or layers) made of one sheet of aluminium cations ($\text{Al}^{3+}$) in octahedral coordination with oxygen anions and hydroxyl groups and two outer tetrahedral silica sheets. The thickness of a clay platelet is $< 1\, \text{nm}$. Cation isomorphic substitutions, as well as some cation vacancies, generate a partial negative charge, which is usually balanced by the absorption of sodium ions ($\text{Na}^+$) on the platelets surface. These systems show a strong hydrophilic character in water, but this character can be quite easily converted to organophilic by exchanging the sodium ions with organic cations; for instance in this case dioctadecyl dimethyl ammonium cations, that have long aliphatic chains, were used. This change from hydrophilic to organophilic character is mainly aimed at improving the interactions between clay platelets and polymer in the final nano-composites. Moreover, long aliphatic chain ammonium cations were used in order to obtain nano-composite with exfoliated morphology which in turn improves the interactions between the inorganic particles and the organic matrix. In order to further facilitate the interfacial interactions between organically modified clay and polymer, 3-(trimethoxysilyl)propyl methacrylate (TMSPM) was also used which usually forms chemical bond with the silanol groups present on the edges of the modified clay as well as bonds to polymer with its organic part. In this kind of systems, it is possible to recognize and separate the interface between the organically modified inorganic particles and the polymer matrix.
A solid-state NMR approach to the study of interfacial interactions in organic-inorganic multicomponent materials

Figure 2.3: Sketch of a polymer matrix in which clay platelets are dispersed; microcomposite with clay tactoids micron in size (a), exfoliated (b) and, intercalated (c) polymer-clay composites morphologies.

Several kinds of interactions occur in this system, in which the ammonium ions form ionic interaction with the inorganic clay particles while TMSPM possibly forms covalent bonds with the modified clay particles and the organic matrix. As already stated, the filler particles themselves can be considered as OIMM, since the presence of both ammonium cations and TMSPM serves as the modifiers for the clay surface and thereby forms the organic and inorganic moieties within the clay platelets. The NMR study of clay/polymer nano-composites formed from organically modified bentonite fillers dispersed in the polyethylene matrix will be discussed in Chapter 6.

The second example of this type of organic-inorganic multicomponent materials is represented by an inorganic silica as filler for a polymer (synthetic rubber) matrix: this material has particularly commercial importance in the field of tyres. It is still not deeply understood the interface between the organic phase and the inorganic filler, play a crucial role in determining the properties of the final composite material. In Fig. 2.4 a sketch of a polymer matrix filled with silica particles is reported.

The composite was prepared by forming inorganic silica particles in situ within the polymer matrix by a sol-gel process which gave an average size of silica particles in the micrometer range. The interactions at the interface between silica and polymer are expected to be mainly weak van der Waals interactions. Though the composites were formed by the sol-gel process, the interface between organic and inorganic components in this system could be identified due to well formed silica particles. In order to improve the interfacial interactions between the organic and the inorganic phases, in some cases
2.2 Organic-inorganic multicomponent materials and solid-state NMR

Figure 2.4: Sketch of a polymer matrix in which particulate fillers are dispersed.

A silanizing agent was employed which in this case was octyl triethoxy silane (OTES), is supposed to bind with the silanol groups of the silica filler and to form weak interactions with polymeric chains. The NMR study of these filler/polymer composite, is reported in Chapter 5.

2.2 Organic-inorganic multicomponent materials and solid-state NMR

The wide variety of the organic-inorganic component materials, exemplified in the previous section, clearly shows that the applications of their macroscopic properties are strongly dependent on their microscopic properties and in particular on the nature and dimensions of organic-inorganic interfaces, mechanisms of interaction between organic and inorganic components, and structural and dynamic properties of either or both the organic and inorganic phases. However, it must be outlined that the inorganic component is often constituted by crystalline or amorphous phases, which do not experience strong modifications in passing from their pure state to the OIMM, apart from the regions at the interface with the organic domains. On the contrary, the organic component often exhibit changes in both their interfacial and bulk properties\(^1\), which deserve to be investigated.

Solid-state NMR spectroscopy is, in general, a very powerful tool to have access to information, at a molecular level, on solid systems, concerning both their chemical structure and their dynamic properties; moreover, it can be applied to almost all the solid systems, from the more crystalline to the completely amorphous ones.

On the other hand, the possibility of obtaining such information is strictly dependent

\(^1\)An example for this kind of composites is the one obtained by sol-gel processes, where the organic or inorganic domains are built from suitable monomers rather than derived from preformed organic or inorganic components.
on the presence of different NMR active nuclei (i.e. with spin different from zero) in the organic and inorganic components, but also with a sufficiently good sensitivity; besides it has to be noticed that solid-state NMR is a bulk technique, that is it cannot provide information on spatially distinguished parts of a sample, the response being a global information concerning the whole system.

The potentialities of the application of solid-state NMR spectroscopy in studying organic-inorganic multicomponent materials are promising and attractive; in particular, it is important the possibility of obtaining information, at a molecular level, on such complex systems, which can be valuable in understanding and then controlling several of their properties, often macroscopically evident, arising from still unclear microscopic mechanisms.

Considering the variety of the systems, such properties can be the most different, as well as the corresponding microscopic/molecular aspects to investigate. Just to cite two extremely different examples: for a composite comprised of inorganic porous silica and guest organic molecules, it can be important to understand the changes in dynamic properties in both organic and inorganic domains passing from their pure forms to the composites, while for a polymer-filler composite, in order to control and improve the mechanical properties of the material, it can be mostly important to get some insights into the polymer-filler interactions. From a microscopic point of view, as already said, all these systems are composed by one or more organic and inorganic components and the interfaces among them always play an important role which is the major focus of this thesis.

Regarding these important features, solid-state NMR provides several means for studying these materials, which can be grouped in two separated points:

- on one side there is the possibility of observing many different nuclei at the interfaces, from those more characteristics of the organic component (\(^{13}\text{C}, \; ^1\text{H}, \ldots\)), to those more typical of the inorganic ones (\(^{29}\text{Si}, \ldots\));

- on the other side, several different nuclear parameters can be investigated, each of them providing a different kind of molecular information; just to cite some examples, the isotropic chemical shifts, obtainable by high-resolution spectra, provide important information on the chemical structure of the material, while by the measurement and analysis of the relaxation times, molecular motions can be investigated; in between these two extremes, many high-resolution, so called, “selective” techniques allow structural and dynamic information to be simultaneously obtained.
Each of the elements cited in these two points could constitute, by itself, an independent research topic; in this sense, solid-state NMR is a continuously growing technique, in which many efforts are devoted to the theoretical, as well as technological development of new methodologies aimed to obtain more detailed and refined structural and dynamic molecular information. On the other hand, it has to be said that it is difficult to perform such detailed studies on complex “real” systems, as the organic-inorganic multicomponent materials, that is complex systems in which several components and/or phases coexist, which are not “simplified” by special treatments, as selective isotopic enrichments.

Due to their noticeable present interest, solid-state NMR has being employed in the study of organic-inorganic multicomponent materials. Despite the importance of SSNMR for the study of OIMM, only a few reviews have been published on this topic [35, 36], some of them concerning specific OIMM classes: polymer/clay nanocomposites [37, 38], sol-gel derived materials [39, 40], guest molecules or metal ions confined in porous silica materials [41, 42] and silica based polymers [43]. In the literature, beside deep studies, actually still not common, concerning specific aspects of these systems, many quite limited studies, often consisting in few standard high-resolution spectra, are present. Actually, papers reporting a quite complete, even if standard, solid-state NMR characterization are still relatively few.

2.3 The approach of this thesis

The objective of the thesis is to obtain structural and dynamic information on several organic-inorganic multicomponent materials, presented as examples, especially concerning their interfaces between different components, by the set-up and the application of a possible methodological approach, consisting in a combination of a choice of consolidated NMR techniques, which have been applied to different nuclei.

It is necessary to state that the measurement of quantitative structural data nor the detailed study of the molecular motions were out of the scope of this study, while we wanted to focus on obtaining feasible and comprehensive structural and dynamic characterization at the interfaces between organic and inorganic domains.

The fundamental idea was to exploit the possibilities provided by solid-state NMR, which have been previously described in the Section 2.2, in investigating several nuclei as well as different nuclear parameters. In fact, in presenting the employed approach, it seems quite convenient to make a division, based on the kind of nuclei investigated, which can be differentiated as protons ($^1$H) and “heteronuclei” (X).

The following part of this chapter is devoted to a description of the NMR “tech-
A solid-state NMR approach to the study of interfacial interactions in organic-inorganic multicomponent materials

niques” employed in this thesis. Both the applied techniques with their pulse sequences, and the information acquired by the respective nuclear properties are examined, together with both the high- and low-field NMR instruments used. These techniques are described in a quite general way, with the aim of providing a sort of reference for all the different experimental cases; indeed, due to the variety of the systems investigated, the experimental approach has been differently set-up and modulated for each distinct situation.

2.4 Spectrometers

The experimental work presented in this thesis has been performed on two spectrometers which are described in the following.

2.4.1 High-Field Instrument

A Varian Infinity Plus 400 MHz double-channel spectrometer has been used for all the high-resolution and part of the low-resolution (static) experiments performed at the Dipartimento di Chimica e Chimica Industriale of the Università di Pisa. The spectrometer is equipped with three multinuclear probes:

- CP-MAS 7.5 mm HX probe: the sample volume is 450 µL and the maximum spinning achievable is 7 kHz;

- CP-MAS 3.2 mm HX probe: the sample volume is 11 – 22 µL and the maximum spinning speed achievable is 25 kHz;

- a goniometric probehead for static measurements, with sample holders with an outer diameter of 5 or 10 mm

The spinning rate is controlled through a Varian/Chemagnetics spin-rate controller apparatus. For both 7.5 and 3.2 mm probes zirconium oxide rotors are used: teflon, or boron nitride spacers and end caps as well as Kel-F drive tips are available for the 7.5 mm probe, while the material used for all the removable parts of the 3.2 mm rotors is Vespel.

Both proton and heteronuclear channels are equipped with 1 kW amplifiers. The 90° minimum pulse lengths achievable with this assembly are 4 µs, 1.7 µs and 2.5 µs for both $^{13}$C and $^1$H on 7.5 mm, 3.2 mm and goniometric probes, respectively.
2.5 X nuclei investigation

2.4.2 Low-Field Instrument

Some of the relaxation times measurements at low resolution were acquired from a single-channel Varian XL-100 spectrometer interfaced with a Stelar-DS acquisition system. The magnetic field is produced through an electro-magnet which allows to reach the maximum Larmor frequency of 100 MHz on $^1$H nuclei. The spectrometer is equipped with a 5 mm static probe and a high-power amplifier, while no typical high-resolution devices, like MAS facility, are present. This probe allows to tune the $^1$H Larmor frequency up to the maximum value of 30 MHz.

The hardware allows a maximum digitalization rate of 1 MHz, that determines a minimum time interval between two consecutive points to the FID (the dwell time) equal to 1 $\mu$s: for solid systems, this usually allows to have a sufficient number of points describing the FID before it decays after $T_2$ relaxation. The 90° pulse is about 2.5 $\mu$s.

2.5 X nuclei investigation

By the term “X nuclei” here I mean those nuclei with spin-$\frac{1}{2}$ but different from protons which can be present in organic-inorganic multicomponent materials, more importantly at the interfaces between the components. In the following, I will describe in particular the experimental approach employed in this thesis for observing $^{13}$C and $^{29}$Si nuclei.

The observation of both these heteronuclei has been carried out by means of high-resolution techniques, that is by the combined application of the two “tools”, magic-angle spinning (MAS) and high-power decoupling (HPD), which, as described in Section 1.7, allow the anisotropy of the nuclear interactions to be averaged out, and a “liquid-like” spectrum of a solid sample to be obtained. Apart from the standard techniques for the structural characterization, additional techniques were employed only on $^{13}$C nucleus in order get insights about the dynamics of the systems which will be discussed in the following experimental subsections denoting only the $^{13}$C nuclei.

By employing the techniques described in the following, both structural and dynamic molecular information can be obtained. In particular, as better exemplified in the description of the various techniques, structural information, concerning both the chemical and geometrical structure of the systems, can be obtained by observing the isotropic chemical shifts and by employing two-dimensional correlation techniques, while dynamic information concerning either conformational properties or more general indications on the mobility of the different molecular domains, can be extracted by the application of suitable “selective” techniques, by the two-dimensional WISE technique, and by the measurement of several relaxation times.
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Figure 2.5: Single Pulse Excitation pulse sequence allowing the quantitative detection of X nuclei, with $^1$H high-power decoupling.

2.5.1 Single-pulse excitation

The scheme of the Single pulse excitation (SPE), or in other terms Direct excitation (DE) is shown in Fig. 2.5.

After the application of a $90^\circ$ pulse on the X channel, the FID is immediately acquired, while simultaneously HPD is active on the proton channel. A 4-step phase cycling of the $90^\circ$ is applied [2].

The practical applicability of this technique strongly depends on the sensitivity of the X nucleus to observe, which is determined both by the natural isotopic abundance and by the population difference between the initial and the final states of the transition, that is, for spin-$\frac{1}{2}$ nuclei, the $|\alpha\rangle$ and $|\beta\rangle$ spin states.

The population difference is decided by the Boltzmann distribution (Eqs. 1.72–1.73) and therefore, at a fixed temperature, by the sole Larmor frequency $\omega_0 = \gamma B_0$. It is evident that the sensitivity is increased by working at higher magnetic field strengths ($B_0$) while, at fixed field, it is determined by the magnetogyric ratio of the nucleus to observe ($\gamma$).

A quantity directly related to the NMR signal intensity of a particular nucleus, in natural abundance, is the receptivity [44], defined as:

$$\text{receptivity} = |\gamma|^3 x I (I + 1)$$

(2.1)

where $x$ is the natural abundance, expressed as a mole fraction in %.

The relative receptivities for the X nuclei observed in the thesis, with respect to that of proton, are reported in Table 2.1.

Due to the low receptivities of several X nuclei, the SPE technique is often very time
Table 2.1: Properties of the spin-$\frac{1}{2}$ X nuclei investigated in the thesis [44].

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Natural Abundance $x$ [%]</th>
<th>Magnetogyric ratio $\gamma$ [$10^7$ rad s$^{-1}$ T$^{-1}$]</th>
<th>Relative receptivity(^a) $D_P$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1$H</td>
<td>99.9885</td>
<td>26.7522128</td>
<td>1.000</td>
</tr>
<tr>
<td>$^{13}$C</td>
<td>1.07</td>
<td>6.728284</td>
<td>$1.70 \times 10^{-4}$</td>
</tr>
<tr>
<td>$^{29}$Si</td>
<td>4.6832</td>
<td>-5.3190</td>
<td>$3.68 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

\(^a\)Nuclear receptivity relative to that of proton (see Subsection 2.5.1).

consuming since usually, in the solid-state, it is necessary to wait for a sufficient time between one scan and the following one (D\(_1\) in Fig. 2.5 called the relaxation delay) in order to allow the longitudinal magnetization to completely relax to the thermal equilibrium via spin-lattice relaxation. However, this technique remains the simplest way to obtain a quantitative solid-state NMR spectrum in which the ratios among the peak areas reflect the ratios among the amounts of the respective nuclear sites.

As previously explained (Subsection 1.8.1), the recovery of the longitudinal magnetization is governed by the spin-lattice relaxation time T\(_1\): even if it is not possible to make general considerations on the relaxation times of X nuclei, it is clear that long T\(_1\)’s mean longer times for a quantitative SPE spectrum to be collected. Nevertheless, the acquisition of quantitative X spectra is sometimes very important, especially in elucidating the result of a certain chemical treatment or the kinetics of a reaction. A clear example of this is reported in Chapter 5.

Furthermore, the SPE pulse sequence can be employed also as a “mobility-selective” technique. In fact, I have already shown (Subsection 1.8.2) that spin-lattice relaxation times are very sensitive to molecular dynamics in the MHz regime. With reference to the BPP curves shown in Fig. 1.27, it is possible to state that, in solids, molecular motions are usually in the slow-motion side of the BPP curve (i.e. T\(_1\) decreases by decreasing the correlation time of the motion that means by increasing temperature) or, at most, in the intermediate regime (in proximity of the T\(_1\) minimum). Consequently, in spite of the non monotonic trend of T\(_1\) with correlation time, the statement that in solids rigid environments are characterized by much longer T\(_1\)’s than mobile environments, has a quite general validity.

Therefore, coming back to the SPE technique, the application of suitable short recycle delays can lead to the suppression, by saturation\(^2\), of the signals arising from nuclei in more rigid environments. In this sense, for each nuclear site giving rise to a signal, the

\(^2\)If the longitudinal magnetization is not allowed to recover, the difference between the $|\alpha\rangle$ and $|\beta\rangle$ states tends to zero, and eventually the 90° rf pulse does not produce any signal.
information on its chemical environment provided by the chemical shift can be combined with an indication on the dynamics of the environment itself.

In order to remove both probe and rotor background signal, instead of SPE, the *depth* pulse sequence [45] was used, only in the case of $^{13}$C, for the acquisition of the direct excitation spectra reported in this thesis. The *depth* sequence allows to obtain information equivalent to those extracted through the application of SPE pulse scheme.

### 2.5.2 Cross Polarization

*Cross Polarization* (CP) has been already introduced and described in Subsection 1.7.3. Despite this technique does not give quantitative results, it is the most frequently used technique in solid-state NMR of X nuclei since it often dramatically increases the sensitivity of the observed nuclei and reduces the total time of the experiment in comparison with an equivalent number of scans in SPE. Quantitative CP-MAS experiments can be performed too, but they require the knowledge of the characteristic CP time $t_{XH}$ and $^{1}H_{T_{1p}}$, as described in Subsection 1.7.3.

### 2.5.3 NQS

Through the *Non Quaternary Suppression* (NQS) technique it is possible to isolate signals corresponding to quaternary $^{13}$C nuclei from those relative to carbons which have directly bonded protons [46, 47]. The NQS sequence, shown in Fig. 2.6, comprised of a simple CP followed by a delay $D_{1}$: during this delay, the $^{13}$C transverse magnetization generated through CP can evolve under the presence of heteronuclear dipolar couplings, since no HPD is applied on the $^{1}H$ channel. After a $180^{\circ}$ pulse, a second delay of the same length $D_{1}$ is applied, during which only the transverse magnetization components that evolve under interactions different from the heteronuclear couplings are refocused,
2.5 X nuclei investigation

since HPD is present on the $^1$H channel during this delay. The $^{13}$C signal is then acquired during HPD in order to guarantee the high resolution.

As a consequence, only those carbons that do not have nearby protons contribute to the spectrum, since in both the D$_1$ delays their evolution is independent of the presence of heteronuclear dipolar couplings. With the exception to this case, methyl carbons contribute to NQS spectrum due to its fast rotations which averages out the anisotropic interactions.

2.5.4 Delayed Cross Polarization

The delayed cross polarization or T$_2$-selective cross polarization pulse scheme is shown in Fig. 2.7. This experiment allows the indirect measurement of the $^1$H spin-spin relaxation times through the observation of the X nucleus [48]. As far as the interest of this thesis is concerned, this technique was exploited only on $^{13}$C nucleus. After a first $90^\circ$ pulse applied on resonance in order to avoid offset-generated effects, the transverse magnetization of protons evolve under T$_2$ during the delay $\tau$: the application of a $180^\circ$ pulse followed by a second delay of the same length of the previous allows the refocusing of the different transverse magnetization components. The signal created in this way on the proton channel is transferred through CP to the $^{13}$C channel, where it is detected in the presence of HPD. By increasing $\tau$, the intensity of the $^{13}$C signal reflects the progressive decay of the non-refocusable components of the spin magnetization: these components are lost because of the incoherent evolution generated by the stochastic molecular motions. The time constant describing this decay is the $^1$H T$_2$.

Considering that the proton T$_2$ is expected to monotonically decrease with the decrease of the molecular mobility (Subsection 1.8.1), by properly selecting the value of $\tau$ it is possible to cancel out the contributions to the magnetization arising from $^{13}$C nuclei more strongly dipolarly coupled with protons characterized by very short T$_2$ values, which usually correspond to rigid environments.
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2.5.5 Inversion recovery

This pulse sequence [49] has been used in this thesis solely for the measurement of $^{13}$C $T_1$, and it is shown in Fig. 2.8.

An initial $180^\circ$ pulse is applied directly on the $^{13}$C channel in order to flip the longitudinal magnetization along the $-z$ direction. A delay $\tau$ is left in order for the magnetization to start recovering towards its equilibrium state by means of spin-lattice relaxation, then a $90^\circ$ pulse is applied, which flips the magnetization again on the $xy$ plane: the $^{13}$C signal is then detected in the presence of HPD. The intensity of the acquired signal, which reflects the direction of the longitudinal magnetization, is negative for small values of $\tau$ and becomes more and more positive as $\tau$ is increased until a plateau is reached. This behaviour can be described by means of the equation:

$$y(\tau) = a\{1 - \left[1 - b(1 - e^{-\frac{\tau}{T_1}})\right] e^{-\frac{\tau}{T_1}}\}$$

where $a$ is a pre-exponential factor proportional to the equilibrium magnetization, $b$ is a parameter that takes into account the non-perfect inversion obtained after a $180^\circ$ pulse (equal to 2 in case of perfect inversion) and $c$ is the relaxation delay that allows the recovery of the magnetization between one scan and the following one. All these parameters, together with $T_1$, are obtained as best-fitting parameters after a non-linear least-squares fitting of the data set collected for increasing $\tau$ values by means of the function of Eq. 2.2. This sequence is particularly suitable for mobile environments, characterized by short $T_1$ relaxation times, while it can be too time consuming for more rigid environments, often characterized by longer $T_1$s.
2.5.6 Torchia

This pulse sequence [50] shown in Fig. 2.9, can replace Inversion recovery in the measurement of spin-lattice relaxation times of carbon nuclei having efficient magnetization transfer from surrounding protons during CP.

After the $^{13}$C magnetization is built-up through CP, a $90^\circ$ pulse brings it along the $z$-axis, where it is subject to spin-lattice relaxation. After a variable delay $\tau$, the remaining magnetization is flipped back onto the $y$-axis using a $90^\circ$ pulse and then acquired. The $^{13}$C signal is detected soon after the $90^\circ$ pulse in the presence of HPD. The value of $^{13}$C $T_1$ can be extracted by analyzing the signal intensity as a function of the delay $\tau$ by means of the following equation:

$$y(\tau) = \sum_i a_i e^{-\tau/T_{1i}}$$

where the sum over the different relaxation components $i$ takes into account the possibility of a multi-exponential behaviour.

The use of CP in this sequence may allow a considerable reduction in the experimental times with respect to the Inversion-Recovery technique, since $D_1$ must be greater than 5 times the proton and not the carbon $T_1$. The applicability of this pulse sequence is hence more likely for the measurement of $^{13}$C $T_1$ in rigid environments.

2.5.7 Variable spin-lock time for the measurement of $^{13}$C $T_{1\rho}$

The pulse scheme for the measurement of $^{13}$C $T_{1\rho}$ is shown in Fig. 2.10.

A $90^\circ$ pulse is applied on the $^{13}$C channel, immediately followed by a spin-lock pulse of length $\tau$, during which the $^{13}$C magnetization is locked along the direction
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Figure 2.10: Pulse sequence for the direct measurement of the spin-lattice relaxation times in the rotating frame ($^{13}$C $T_1$), $\tau$ indicates the spin-lock time.

of the applied magnetic field $B_1$ in the rotating frame. During $\tau$, the magnetization decays under the effect of spin-lattice relaxation in the rotating frame. The $^{13}$C signal is detected immediately after the end of the spin-lock pulse, in the presence of proton HPD. The value of the $^{13}$C $T_1$ can be obtained by examining the signal intensity as a function of the spin-lock time $\tau$ for the different nuclear sites by means of the following equation:

$$y(\tau) = \sum_i a_i e^{-\frac{\tau}{T_{1i}^p}}$$

where the sum over the different relaxation components $i$ represents the possibility of a multi-exponential behaviour.

2.5.8 Two-dimensional experiments

The precise description of two-dimensional NMR experiments would require to have recourse to the density matrix formalism, but, in this context, I just would like to give a “qualitative” explanation of the basic idea of a generic two-dimensional NMR experiment, and then show which kinds of information can be extracted, in particular, by the FSLG-HETCOR and WISE experiments performed in the work of this thesis.

Although a large multiplicity of two-dimensional, homo- as well as heteronuclear experiments exists, a general scheme, valid for even the most complicated pulse sequences, can be drawn, and it is reported in Fig. 2.11.

Foremost, a so called preparation pulse or, in general, pulse sequence is applied, in order to perturb the initial equilibrium state by creating a transverse magnetization; then, in the time period $t_1$ the magnetization is allowed to evolve under the effect of certain nuclear interactions, selected by means of suitable “tools” (usually another pulse
The mixing or transfer pulse sequence is aimed to transform the evolved magnetization in an observable magnetization, which again, under the effect of nuclear interactions, give rises to the time evolution in $t_2$, which is the usual acquired FID. If the same experiment is performed for different values of the time period $t_1$ (which is usually increased by a fixed increment), in principle a double time-modulation of the magnetization can be observed: at each value of $t_1$ the acquired FID is the result of the magnetization evolution in $t_2$, while, fixing a point in the FID and looking at the signals array as a function of the $t_1$ value, the magnetization time modulation, arising from the interactions selected to act in the $t_1$ period of each experiment, can be observed. By performing a double Fourier transform, a two-dimensional spectrum is obtained, in which the two frequency axes correspond to the two time dimensions $t_1$ and $t_2$ (in practice, the first dimension is usually relative to $t_2$, the second to $t_1$). If the interactions acting in the $t_1$ and $t_2$ periods are suitably chosen, then important structural and/or dynamic information can be obtained by the observation of the so called cross peaks, that is the signals appearing at certain couples of frequency values ($\nu_1$ and $\nu_2$).

### 2.5.8.1 FSLG-HETCOR

Like in solution NMR, the acronym HETCOR refers to an heteronuclear correlation two-dimensional experiment. As implicit in its name, this experiment involves two different nuclear species, in particular protons and X (dilute spin) nuclei. The general two-dimensional experiment pulse sequence reported in Fig. 2.11 has therefore to be split on a double H-X channel. The pulse sequence of the Frequency Switched Lee-Goldburg Heteronuclear Correlation (FSLG-HETCOR) [51] for the solid samples is shown in Fig. 2.12.

This sequence allows to correlate the isotropic chemical shifts of $^1$H and X nuclei that interact via heteronuclear dipolar coupling: since this interaction propagates through space, this technique can give information about the conformational properties of the...
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Figure 2.12: FSLG-HETCOR pulse sequence.

In the samples investigated [52–54], a 90° pulse is applied on the $^1$H channel to generate transverse magnetization; during the $t_1$ period, in presence of the FSLG multiple pulse decoupling sequence [55–57] which removes the homonuclear $^1$H-$^1$H dipolar couplings, letting therefore the magnetization to evolve only under the effect of the chemical shift interaction. This time constitutes the evolution time of the sequence, that is the first time interval at the end of which the signal is stored; $t_1$ is increased from one scan to the following one. Thereafter, the mixing pulse is applied which is a normal CP contact pulse that transfers the signal from protons to the dipolarly coupled X spins, through heteronuclear dipolar interaction. Finally, the X signal is then acquired during $t_2$, in presence of TPPM heteronuclear decoupling (see Subsection 1.7.2) on the proton channel.

Therefore, the 2D map is obtained after a double Fourier transform with respect to both $t_1$ and $t_2$: since during the first time interval the proton spins evolve under the action of the chemical shift interaction and during the second time interval the same happens for X spins, on the first and second dimension of the map, $^1$H-X isotropic chemical shifts values can be read, so allowing the cross peaks which arising from dipolarly coupled $^1$H-X spin pairs, to be assigned: the anisotropic contributions to the chemical shifts are averaged out through the application of MAS.

The intensity of the cross-peaks is directly related to the strength of the heteronuclear dipolar couplings involved, which in turn, as already described in the CP pulse sequence (Subsection 1.7.3), depends on both structural and dynamic factors: on one side, the dipolar coupling constant $d$ (Eq. 1.100) is inversely proportional to the cube of the internuclear distance\(^3\), on the other hand, molecular motions can reduce, to a variable extent, the dipolar couplings; the experiment results have to be therefore interpreted keeping in mind the combination of these two possible factors. In practice, often

\(^3\)The sensitivity of many 2D solid-state NMR experiments is usually for distances less than 10 Å.
the observable cross-peaks are due to the spatially closest \( ^1\text{H} \) and X nuclei, not subject to a strong molecular mobility.

It is important to emphasize that in the HETCOR experiment in the solid state the heteronuclear correlation is based on the dipolar interaction, differently from what happens in the HETCOR experiment in solution, where the correlation is due to the indirect spin-spin \( J \)-couplings. Therefore, in the solid-state, the obtainable structural information directly refers to the spatial arrangement of the molecule, rather than to the chemical connectivities.

### 2.5.8.2 WISE

This bidimensional experiment [58] as its name suggests is \( ^1\text{H} \) \textit{Wideline separation}, in which the proton signals obtained without homonuclear decoupling can be separated on the basis of the isotropic chemical shift of the X nuclei to which the protons are dipolarly coupled. It reveals differences in mobility in the different surroundings from \( ^1\text{H} \) line widths and so this experiment can be used to obtain site-specific dynamic information.

The pulse scheme of the WISE experiment is shown in Fig. 2.13. It starts with an 90° pulse on the protons, followed by an incremented proton evolution time defined in the \( (t_1) \) domain. By means of CP (Subsection 1.7.3) from protons to \(^{29}\text{Si}\), the \(^1\text{H} \) magnetization at the end of the evolution time is transformed into amplitude modulation of the X signal, which is probed in \( t_2 \) domain. The X nuclei FID is acquired in the presence of TPPM heteronuclear decoupling in the proton channel. Fourier transformation along \( t_2 \) yields the different intensity X spectrum. If the spinning frequency is less than the proton homonuclear coupling, a Fourier transform along the \( t_1 \) yields the broad-line NMR spectrum of the protons from which CP to X nuclei occurs.

Moreover, in the resulting 2D spectrum, the chemical structure is reflected from the
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X chemical shift values resolved through the application of MAS and for each of these resolved signals, corresponding to certain molecular moieties, the molecular mobility is characterized by the line shape of $^1$H signals, with narrow lines indicating high mobility, whereas broad proton lines correspond to restricted mobility.

In contrast to the heteronuclear correlation experiments where correlation among isotropic chemical shift values of X nuclei and protons can be established; in the WISE experiment, for every resolved X signals, it shows a proton wideline spectrum which reflects the homonuclear dipolar couplings of the protons in the proximity of the respective X nuclei. Moreover, in separating proton wideline spectra for different X signals, the WISE experiment does establish a correlation, between the chemical structure obtained from the X nuclei chemical shifts and the segmental mobility reflected by the proton line shapes. This basic pulse sequence can be modified in order to take into account the effect of spin diffusion process [59], however, this has not been employed to the particular samples of interest in this thesis, for which the mixing time is kept as short as possible in order to limit the redistribution of the $^1$H magnetization due to spin diffusion.

In this thesis, proton wideline spectra are separated for different $^{29}$Si positions which has been employed in the study of reinforced rubber with silica particles (see Chapter 5) with the aim of investigating mobility at the interfaces in the system.

2.6 $^1$H Investigation

The $^1$H nucleus has inherently much more favorable features with respect to many of the X nuclei, which would make it an optimum probe for the NMR investigation. It has a natural abundance of 99.99 %, the highest magnetogyric ratio among all the spin-$\frac{1}{2}$ nuclei ($\gamma = 26.75 \times 10^7$ rad s$^{-1}$ T$^{-1}$, Table 2.1) and also high protons density are present in all the organic systems, and in many of inorganic ones; indeed, for all these reasons, the $^1$H observation is the easiest and most routinary one in solution NMR.

On the other hand, in the case of solid-state NMR an additional element has to be considered, that is the presence of the homonuclear dipolar interaction (see Sub-subsection 1.5.2.2). Just the combination of the above listed proton features with the homonuclear dipolar interaction introduces a very high degree of complexity in the $^1$H solid-state NMR investigation.

In many of the commonly investigated molecular systems, due to the high proton “density”, a complex network of $^1$H-$^1$H homonuclear dipolar couplings exists, many of them being very strong (being $d \propto \gamma_H^2 r^{-3}$, Eq. 1.100) and involving much more than two spins; it is therefore easy to guess that a solid-state NMR $^1$H-spectrum of a static
2.6 $^1$H Investigation

powder sample often results as simply a very broad and unresolvable signal. Furthermore, the homogeneous character of the homonuclear dipolar interaction among more than two spins makes the magic-angle spinning, which, combined with the high-power decoupling, allows X high-resolution spectra to be obtained, much less effective for the $^1$H observation. Indeed, as already mentioned in Subsection 1.7.1, spinning frequencies sufficiently high to greatly exceed the anisotropy of the $^1$H-$^1$H dipolar interactions, as it would be necessary to the aim of obtaining a liquid-like spectrum, are still often not achievable on standard solid-state NMR spectrometers, while at intermediate spinning frequencies very broad spinning sidebands appear, but the isotropic signal component is not resolved (Fig. 1.22).

Since the beginning of solid-state NMR, many attempts have being devoted to the theoretical and experimental methods which could allow the homonuclear dipolar interactions to be eliminated, in order to obtain high-resolution $^1$H spectra, as well as suitably reintroduced with the aim of extracting the important structural information contained in them.

All these methods, which are complex pulse sequences, often referred to as multiple pulse sequences (one of them, the FSLG, have been cited in Section 2.5.8 for the HETCOR experiment), act on the spin part of the anisotropic interactions, differently from the magic-angle spinning, which intervenes on its spatial part.

Many of these methods have been introduced for stationary conditions, which have the demerits that the chemical shift anisotropy cannot be averaged out, and, due to many complex interference effects, the extension to MAS experiments has always been very troublesome. Only recently, theoretical approaches have been proposed to overcome these problems which have lead to the successful application of effective pulse sequences at high MAS frequencies [60,61].

These necessary developments are very powerful in the analysis of small molecules, while, on the other hand, their applicability is very limited to systems with high degree of complexity and “disorder”, as many materials of applicative interest, included the organic-inorganic multicomponent materials here investigated. Therefore, in the work of this thesis, as far as high-resolution proton spectra are concerned, I just had recourse to the acquisition of standard $^1$H-MAS spectra, which are described in the next subsection; on the other hand I employed some low resolution techniques, which are the topic of Subsection 2.6.2.

2.6.1 $^1$H-MAS

The $^1$H-MAS spectra reported in this thesis have been acquired with the simple single pulse experiment already described for the X nuclei observation (Subsection 2.5.1); ob-
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Figure 2.14: Single pulse sequence for the acquisition of $^1$H-MAS spectra.

viously, in this case, the excitation ($90^\circ$) pulse is applied on the $^1$H-channel and no decoupling is employed (Fig. 2.14).

Taking into consideration all the complications discussed before due to the homogeneous character of the homonuclear $^1$H-$^1$H dipolar interaction, the $^1$H-MAS spectra performed here on complex systems, acquired at the achievable spinning frequencies (the maximum limits being 7 kHz and 25 kHz on the two probeheads available on our Varian InfinityPlus 400 spectrometer in Pisa, described in the Subsection 2.4.1) are, in general, expected to be a superimposition of several signals, consequently resulting in broad spectral lines.

In complex systems like the ones discussed in this thesis, a large amount of protons in different environments are present and multiple domains exhibiting different average molecular mobilities exist. Moreover, the motional effects are expected to be very important in determining the appearance of the spectrum. On account of the averaging effect of molecular motions, the dipolar couplings involving protons located in sample fractions experiencing higher degree of molecular mobility can be sensitively reduced with respect to those among protons in very rigid fractions; this implies that the signals static linewidth ($\Delta \omega$) will be less for protons in mobile environments than for protons in rigid domains. Therefore, for mobile sample fractions the condition $\omega_R \gg \Delta \omega$ (Subsection 1.7.1) can be fulfilled at the achievable spinning frequencies ($\omega_R$), then resulting magic-angle spinning effectively averaging out the $^1$H-$^1$H dipolar couplings.

Generally, in practice, the MAS spectrum could be comprised of a very broad unresolved component, resulting from the contributions of the protons located in most rigid environments, on which the MAS effect will be in general negligible, and narrower components, arising from protons in more mobile sample fractions, which, in the most favorable cases, will show well resolved “liquid-like” isotropic signals.

Often the observed spectrum cannot be so sharply decomposed in just two components: in fact, a distribution of motionally different domains usually exists; moreover, a static proton signal, in addition to the strong homogeneous dipolar contribution, can
also be affected by inhomogeneous interactions (chemical shift anisotropy and homonuclear dipolar interactions between two isolated spins) on which the effect of MAS is intrinsically different (Subsection 1.7.1).

Therefore a correct interpretation of a $^1$H-MAS spectrum can be very complicated, but it can be sensitively facilitated by the combination with information obtainable by other experiments, as $X$ high-resolution and proton low-resolution experiments.

### 2.6.2 Low-resolution experiments

A totally different approach to the $^1$H high-resolution experiments which brings out the dynamic information of the system, is provided by the low-resolution or broad-line NMR techniques.

This approach results to be particularly useful in studying proton relaxation processes, and therefore in investigating some important molecular dynamic aspects of solid samples. The information obtained from the high-resolution measurement, that is the possibility of distinguishing proton signals on the basis of their isotropic chemical shift, is obscured by the homonuclear dipolar couplings, while this approach allows these problems to be completely by-passed.

Concerning the low-resolution experiments implicated in this thesis, the proton FID (Free Induction Decay) is observed in on-resonance conditions, that is the irradiation frequency is suitably calibrated to coincide with the resonance frequency of the protons. The oscillations of the FID, which would arise from the differences in the resonance frequencies of protons with different chemical shifts, are here negligible with respect to the linewidth because of the narrow proton isotropic chemical shifts dispersion which is especially occur at low magnetic fields. In these situations, the proton FID is essentially determined only by the homonuclear dipolar interactions and the data analysis is facilitated, as explained in the following description of the single experiments.

Experimentally, the low-resolution experiments described below in the FID analysis part, have been performed on a single-channel spectrometer (described in Subsection 2.4.2), operating at a low magnetic field strength (25 MHz as proton resonance frequency): the sensitivity is not a problem in the proton observation and, moreover, the low magnetic field strength further reduces the isotropic chemical shifts dispersion (which, contrary to the linewidth, does depend on the magnetic field strength), making the on-resonance condition easier to be attained simultaneously for all the protons. High-power amplifiers are necessary for having enough rf power to be able to irradiate the portion of the frequency-domain spectrum covered by the signal, which can variate between some kHz to some tens of kHz depending on the sample.

The advantages of being in such conditions come from the possibility of analysing
directly the on-resonance FID, without Fourier-transforming the time-domain data sets as it usually the case in high-resolution experiments. The observed on-resonance time decay of the NMR signal is a convolution of multiple contributions arising from nuclei affected by different decay rates, which in turn are connected to different dynamic behaviour: in fact, as discussed in (Section 1.8), the spin-spin relaxation time is the time constant related to the decay of the transverse magnetization component corresponding to the NMR signal of a given spin system which is detected as a FID component. For each observed component, this time constant is connected to the part of the homonuclear dipolar contribution left unaveraged by the motions, and its value is directly related to the dynamic properties of the fraction of nuclei responsible for that component. For these reasons, by means of the analysis of the shape of the on-resonance FID, described below, valuable quantitative information about the presence of regions of the sample experiencing different dynamic behaviours can be obtained.

2.6.2.1 FID analysis

In general, in solid samples, due to the strong dipolar interactions, the proton T\textsubscript{2} can be extremely short (few µs) and this gives rise to a practical problem in the FID acquisition: indeed, in every NMR experiment, between the end of the rf pulse and the beginning of the signal acquisition, a certain time interval, called dead-time and dependent on the spectrometer, the nucleus observed and the experimental conditions, has to be waited, in order to allow the coil to recover from the overload caused by the rf pulse. Due to the possibly very short \textsuperscript{1}H T\textsubscript{2}, in solid samples the FID can be mostly or completely decayed before the acquisition is started, with consequent loss of important information. This problem can be overcome by the application of suitable echo pulse sequences\textsuperscript{4}; eventually, different echo pulse sequences have been developed, in dependence on the spin system observed and on the information we want to obtain, but their basic concept is quite similar. The echo sequences employed in this thesis are the solid-echo \cite{62} and spin-echo or Hahn-echo \cite{63} pulse sequences, whose schemes are reported separately in Fig. 2.15 and 2.16, respectively.

By employing the solid-echo sequence, the rapid decay of FID which results in the broadening of NMR lines due to homonuclear dipolar interaction can be subdued. This sequence consists of a normal (90°) pulse, a subsequent time period τ (echo delay), and

\textsuperscript{4}In the case of the high-resolution proton observation, described in Subsection 2.6.1, the application of a normal SPE pulse sequence is often made possible by the better performances, that is shorter dead-time, of the high-resolution spectrometer and longer T\textsubscript{2} induced by MAS conditions, however, the loss of the very first part of the FID cannot be ruled out, and therefore, in general, the spectra cannot be taken quantitatively.
In addition to the effect of homogeneous contribution on FID, there are also inhomogeneous contributions which influence the fast decay of the FID causing inhomogeneous broadening in the Fourier-transformed spectrum due to the effect of chemical shift anisotropy, heteronuclear dipolar interactions and magnetic field inhomogeneity which could be overcome by the spin-echo sequence. Since the “purely-dynamic” $T_2$ only arises from homogeneous contributions, this sequence suits well at refocussing the inhomogeneous terms, thereby eliminate the inhomogeneous broadening which in turn results to the FID decay only related to $T_2$ time constant. However, in the solid state, inhomogeneous contributions to $T_2$ time constant can be neglected in majority of cases, except when very fast motions are present, which produces the slowly decaying $T_2$ components. With the particular relevance to the complex systems discussed in this thesis (see Chapter 5), having an inherent high degree of structural and dynamic complexities, often including both slow and fast motions, it can be necessary to employ both solid and spin echo sequences in order to take into account the complete motional range.
Spin-echo pulse sequence is the same as that of solid-echo except for the second refocusing pulse, which in this case is $180^\circ$ instead of $90^\circ$. This pulse sequence operates in a similar fashion to the solid-echo pulse sequence; it refocuses the dispersing transverse magnetization components a time $\tau$ after the $180^\circ$ refocusing pulse. The acquisition of the FID signal necessarily begins at time $\tau$ after the refocusing pulse and hence, no signal is lost due to a dead time delay and the maximum echo signal is formed at time $t=2\tau$. By varying the delays between the pulses, the amplitude of the transverse magnetization is measured as function of time $t=2\tau$. As already said, the limited proton chemical shift dispersion allows the FID to be observed in on-resonance condition; in such a way, the intensity of the first point of the FID is a measure of the whole spectrum intensity; therefore, for each $2\tau$ value, it will be not necessary to acquire the entire FID, but just the first part of it, with a considerable reduction of the acquisition and processing times.

Under these conditions, it is possible to quantitatively analyze the FID in terms of analytical functions, each of them representing a sample protons fraction characterized by a certain $T_2$ value. In practice, through a normal fit procedure, the linear combination of suitable functions which best reproduces the experimental FID is found. Such combination can be expressed in the general form:

$$F(t) = \sum_i w_i f_i(t)$$

(2.5)

where $f_i(t)$ are the analytical functions employed and $w_i$ their weight percentages (if $F(t)$ is normalized so that $F(0)=100$).

Beside additional parameters, peculiar of the various functions employed, each $f_i(t)$ is characterized by a certain $T_2$ value, which is obtained, together with the weight percentage $w_i$, as result of the fit.

Due to the already explained close relationship between proton $T_2$ and molecular mobility of the protons environment, by choosing the $f_i(t)$ among an ensemble of physically meaningful functions, this analysis allows motionally distinct domains of a sample to be singled out and characterized. A good reference for this kind of analysis can be found in [64], where, in a successful application to the study of the crystallinity of Polyethylene, an ensemble of employable meaningful functions is described, which then resulted to be successfully applicable to the analysis of several complex heterogeneous systems [65–67].

The employed analytical functions can be divided in those more suitable to the description of rigid or mobile sample fractions, originally identified with crystalline and amorphous phases of polymeric systems above $T_g$, respectively.

Gaussian, Pake and Abragamian functions result to be meaningful in describing the contributions to the FID arising from the more rigid domains.
2.6 $^1H$ Investigation

It is quite straightforward to consider Gaussian function that is suitable to describe sample rigid domains:

$$G(t) = \exp \left[ -\left( \frac{t}{T_2} \right)^2 \right] \quad (2.6)$$

Though I never had recourse Pake and Abragamian functions in this thesis, they must be mentioned for the sake of clear understanding on analytical functions used to define rigid sample environments.

The Pake function is the inverse Fourier transform of the analytical expression proposed by Pake [68] for the signal lineshape of a dipolarly coupled system of two spin-$\frac{1}{2}$, Gaussian-broadened by the dipolar interaction with other neighbours. The analytical expression, found by Look and co-workers [69] is:

$$P(t) = \sqrt{\frac{\pi}{6}} \exp \left[ -\frac{1}{2} \beta^2 t^2 \right] \left\{ \frac{\cos \alpha t}{\sqrt{\alpha t}} C \left( \sqrt{\frac{6\alpha t}{\pi}} \right) + \frac{\sin \alpha t}{\sqrt{\alpha t}} S \left( \sqrt{\frac{6\alpha t}{\pi}} \right) \right\} \quad (2.7)$$

where $C$ and $S$ are the Fresnell functions and $\alpha$ is a parameter related to the internuclear distance ($R_{HH}$) between the two dipolarly coupled spins:

$$\alpha = \frac{3\gamma^{2}h}{4R_{HH}^{3}} \quad (2.8)$$

while $\beta$ is the width of the Gaussian broadening function, which takes into account the dipolar interactions with the other protons. When the $\beta/\alpha$ ratio exceeds an approximative value of 0.7 the two-spins character of the function is overwhelmed by the Gaussian broadening, and, in the frequency domain, the spectral lineshape looses any doublet shape.

The so called Abragamian function can be considered as an approximate expression of Eq. 2.7, which was first used by Abragam [9] as a phenomenological expression of the $^{19}$F FID of CaF$_2$, and then resulted to well reproduce the FID of other regular, crystalline lattices [70].

As far as the more mobile domains are concerned, three other functions can be employed: exponential, Weibullian and Breretonian functions. The last one, actually never employed in the analyses reported in this thesis, is a quite complicated expression which has been theoretically derived in order to describe the dynamic of a polymer chain governed by a single relaxation time [71]; it resulted to well reproduce the FID of amorphous polymer phases, and Dadayli et al. [70] have empirically found that, even if this increases the number of parameters to be determined, the Brereton function can be approximated by the sum of a Weibullian function and one or two exponential functions.
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Figure 2.17: Inversion Recovery with solid-echo pulse sequence for the measurement of the low-resolution $^1$H $T_1$: $\tau_{echo}$ indicates the echo delay.

The Weibullian function is defined as:

$$W(t) = \exp \left[ -\left( \frac{t}{T_2}\right)^n \right]$$  \hspace{1cm} (2.9)

where the parameter $n$ ranges from 1 to 2, and the function, correspondingly, from a pure exponential to a pure Gaussian one. With respect to the exponential and Brereton functions, the Weibullian one results therefore suitable to reproduce FID contributions arising from domains with a character intermediate between very mobile and very rigid.

At last, it is important to notice that by combining FID analysis with $^1$H-MAS results it is often possible to relate motionally distinct domains of a sample with its different chemical components.

The low-resolution experiments discussed hereafter performed on a double-channel spectrometer which has been introduced previously in the Subsection 2.4.1 operating at a magnetic field of 400 MHz. Unlike FID analysis which has been performed at low-magnetic field, due to a large chemical shift dispersion of the signals, it is not possible to set exactly the on-resonance condition and so the FID has to be Fourier transformed and the integral of the different signals has to be picked-up in all these experiments.

2.6.2.2 Measurement of $^1$H $T_1$ using Inversion recovery with solid echo

In low-resolution conditions, by combining the solid-echo with classical pulse sequences employed in high-resolution, it is possible to measure proton spin-lattice relaxation times, both in the fixed ($T_1$) and in the rotating frame ($T_{1\rho}$).

As far as the $T_1$ is concerned, the pulse sequence employed is the Inversion Recovery with solid-echo, whose scheme is reported in Fig. 2.17.

The first $(180^\circ)_x$ rf pulse leads the magnetization to be aligned with $-z$, which, from a quantum mechanical point of view means that the spin state populations are inverted; during the time delay $\tau$ the spin-lattice relaxation occurs, through which the
magnetization tends to recover the initial equilibrium value; the \((90^\circ)_x\) pulse, applied at the end of \(\tau\), flips the partially relaxed magnetization into the \(xy\) plane, where, after the solid-echo, the signal is acquired.

Performing this experiment at various \(\tau\) values, the spin-lattice relaxation process can be monitored through the observation of the consequently variable signal intensity; therefore, fitting the trend of the signal intensity by means of a suitable analytical function, \(T_1\) can be determined.

2.6.2.3 Measurement of \(^1\)H \(T_1\) using Saturation recovery

*Saturation recovery* can be a valid alternative to direct Inversion recovery (IR) for the measurement of \(^1\)H \(T_1\) observing \(^1\)H in low-resolution conditions. The pulse scheme of the saturation recovery sequence is shown in Fig. 2.18.

In fact, IR needs to start with the sample at thermal equilibrium, which means waiting a relaxation delay which is at least 8-10 times the \(T_1\) value one wants to determine between one scans and the following one. Whereas saturation recovery can be a more rapid method of measuring \(T_1\) providing a different “equilibrium” condition, which can reliably achieved. In rigid solids, where often \(T_1 \gg T_2\), the repeated application of \(90^\circ\) pulses on the \(^1\)H rf channel at intervals greater than \(T_2\) but smaller than \(T_1\) “saturates” the \(^1\)H spin system, preparing the system in a state with no polarization.

Then, the \(^1\)H spin system evolves under the \(T_1\) relaxation, and the \(^1\)H \(T_1\) can be determined by sampling the magnetization at different time intervals. Since the measurements does not start from thermal equilibrium, the saturation sequence for the next scan can be applied immediately. The value of the spin-lattice relaxation time \(T_1\) for \(^1\)H nuclei can be extracted by analyzing the signal intensity as a function of the delays (\(\tau\)) by means of the following equation:

\[
y(\tau) = \sum_i a_i [1 - e^{-\frac{\tau}{T_i}}]
\]  

\(2.10\)
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Figure 2.19: Variable spin-lock time pulse sequence for the measurement of $^1\text{H} T_{1\rho}$ in low-resolution conditions.

where the sum of the different relaxation components $i$ takes into account the possibility of a multi-exponential behaviour.

As already said in Section 1.8, by variable temperature $T_1$ measurements, information concerning molecular motions with characteristic frequencies of the order of the Larmor frequency (MHz) can be obtained; on the other hand, reminding the strong influence of the spin diffusion on the proton spin lattice relaxation times, the simple $T_1$ measurement at a fixed temperature can provide indications about the degree of heterogeneity of the sample investigated: in particular the detection of more than one value of $T_1$ is indicative of the presence of heterogeneous domains with average linear sizes exceeding the order of few hundreds of Å in the sample.

Saturation recovery combined with solid echo was also employed in this thesis (see Chapter 6) which has been performed on goniometric probe introduced in the Subsection 2.4.1. The echo pulse scheme was introduced with the last 90° pulse as in the case of IR combined with solid-echo, that was discussed previously.

2.6.2.4 Measurement of $^1\text{H}$-$T_{1\rho}$ using variable spin-lock time

As already explained in Subsection 1.8.1, the spin-lattice relaxation time in the rotating frame $T_{1\rho}$ expresses the decaying rate to an equilibrium value (often negligible) of the transverse magnetization under the effect of a spin-lock field. The pulse sequence here employed for the measurement of the proton $T_{1\rho}$ is shown in Fig. 2.19.

After the first ($90^\circ_x$) pulse, a spin-lock pulse along $-y$ is applied for a $\tau$ time interval, during which the magnetization is decreased by the spin-lattice relaxation process in the rotating frame; the subsequent signal can be acquired. By performing the same experiment at different $\tau$ values, from the trend of the signal intensity vs $\tau$, the spin-lattice relaxation process in the rotating frame ($T_{1\rho}$) can be extracted as described in the Subsection 2.5.7 by means of Eq. 2.4.

As described in Section 1.8, measurements of the spin-lattice relaxation time in the
rotating frame at variable temperature allow information on molecular motions of characteristic frequencies of the order of the spin-lock field to be obtained (kHz regime); similarly to what already said for the proton $T_1$, even a single $T_{1\rho}$ measurement, at fixed temperature, provides useful information concerning the degree of heterogeneity of the sample under investigation. While it is very common to measure a unique average value of proton $T_1$ and it is not unusual to measure more than one averaged $T_{1\rho}$ values, due to the smaller $T_{1\rho}$ values, and the consequently smaller spatial scale (some tens of Å) on which the spin-diffusion is let to proceed for the spin-lattice relaxation in the rotating frame.

2.6.2.5 Multi-exponential relaxation decays: the PWRA

In many cases, especially in the presence of multi-exponential decays, a more reliable analysis of the data can be achieved by means of a specific method, which allows to completely interpret the relaxation of abundant spins in terms of dynamics, discarding the multi-exponential behaviour and thus eliminating effects, like spin diffusion, that can lead to a misinterpretation of the results. In particular, this method allows to largely simplify the $T_1$ or $T_{1\rho}$ analysis by taking into account the inverse of the Population Weighted Rate Average (PWRA) quantity, defined as follows [72]:

$$\text{PWRA} = \sum_i \frac{w_i}{T_{ki}}$$

(2.11)

where $w_i$ indicates the weight of the component with relaxation time $T_{ki}$, $i$ runs over the number of $T_k$ components, and $k = 1$ or $1\rho$. It must be noticed that $1/$PWRA is equal to $T_k$ in case of a monoexponential relaxation. In fact, as shown by Kenwright et al. [73], it is possible to demonstrate that the PWRA of the observed components is equal to the PWRA of the intrinsic relaxation components, which makes the PWRA connected with a given spin-lattice relaxation process in abundant spin systems completely independent of the presence of spin diffusion. Modelling the sample as a series of infinitesimal cells along the direction of the spin diffusion, the quantity of magnetization of a given cell at any instant can change in one of the following ways:

- it can increase thanks to a transfer of magnetization from a neighbouring cell by spin diffusion;

- it can decrease because of a transfer of magnetization towards a neighbouring cell caused by spin diffusion;
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- it can decrease because of a magnetization transfer to the lattice due to the presence of spin-lattice relaxation.

At any instant, however, the sum of the magnetization changes over the entire sample due to spin diffusion will not change the global magnetization of the system, but it will only redistribute it within the system, as already discussed in Subsection 1.8.3. Any change in the absolute value of magnetization will be only due to spin-lattice relaxation, and the instantaneous rate of loss (the effective relaxation rate) will be given by the sum over all the cells of the displacement from equilibrium of the magnetization multiplied by the intrinsic relaxation rate for that cell, corresponding to the PWRA of the observed components.
Chapter 3

Study of functionalized sub-micrometer sized SiO$_2$ particles encapsulated by a PMMA shell

Abstract

In this study, submicrometer-sized silica particles encapsulated by poly(methyl methacrylate) have been characterized by means of high-resolution solid-state NMR techniques. The organic-inorganic composite comprised of silica core-shell particles with a diameter of approximately 180 nm, functionalized with 3-(trimethoxysilyl)propyl methacrylate (TMSPM) and an outer coating of poly(methyl methacrylate) (PMMA) with an approximate 2 – 10 nm thickness, as shown by transmission electron microscopy, diffuse reflectance infrared Fourier transform spectroscopy, thermogravimetric analysis and differential scanning calorimetry. A systematic solid-state nuclear magnetic resonance study based on $^{29}$Si and $^{13}$C high-resolution techniques was performed herein for the sub-micrometer particles at the various stages of synthesis, thus characterizing their organic and inorganic components as well as their interface. The presence of TMSPM and PMMA was confirmed and the structural features of the TMSPM species characterized. Moreover, from a comparative study of functionalized silica samples with different average particle size, it was possible to reveal the significant effect of this parameter on the condensation reactions involved in the preparation of these materials.
3.1 Introduction

Nowadays there is a growing interest in composites containing both organic and inorganic components dispersed at a molecular level or as nanometric domains [74]. Polymer-inorganic composite materials can exhibit extraordinary properties which are frequently derived from the synergism between the properties of an inorganic material, such as optical, electronic and magnetic, combined with those of polymers, which include easy processing and good mechanical strength [75, 76]. The careful choice of both inorganic and organic components as well as of the processing route plays a key role to ensure the desired functional properties of the final material [77]. The properties of such materials, and consequently their actual and potential applications, are strongly dependent on their “molecular” properties, and in particular on the nature and dimensions of the organic-inorganic interfaces, the mechanisms of interaction between the organic and inorganic components, and the structural and dynamic properties of either the organic or inorganic phases. Understanding the characteristics of the organic-inorganic interface, the relative arrangement of components and, ultimately, their relationship with the composite properties, is an important goal for the research in this field.

To this aim, solid-state nuclear magnetic resonance (SSNMR) is a very powerful tool to provide information on molecular and supramolecular properties over large spatial and time scales. The knowledge of structural as well as dynamic properties, at a molecular level, of both the organic and inorganic components and especially of their interface offers an important tool to understand and correlate the microscopic mechanisms to the macroscopic properties [36]. Such information level can significantly help to design materials for specific purposes with improved properties.

Encapsulation of nano- or submicrometer-sized inorganic particles within polymers is desirable in many applications, whereby the surface characteristics of the cores are modified by coating with a polymer layer. Advantages of polymer encapsulation include improvement of particle dispersibility in organic media, stability enhancement, reduction of particle toxicity and the masking of taste and odor [78, 79]. Accordingly, polymer encapsulated inorganic particles can offer interesting properties for use within the biomedical or cosmetic fields, as novel textiles, paints, optics and electronics [80]. Although various inorganic materials are available in a form of nano-particles or submicrometer sized particles, silica is well known and widely used for its chemical stability, high surface area and easy availability [81]; moreover well-defined silica particles with spherical geometries can be considered as model colloids for the encapsulation process. Within the broad variety of available polymers, poly(methyl methacrylate) (PMMA) has been one of the most widely studied in the last decades due to its outstanding and
promising mechanical and chemico-physical properties. PMMA embedding inorganic or organically modified inorganic particles has been cast into films to yield enhanced functional properties [82]. In order to improve the affinity between the silica particles and the polymer, which greatly influences the final properties of these materials, the silica particles are often treated with silane coupling agents like 3-(trimethoxysilyl)propyl methacrylate (TMSPM), which couple with silica through their silyl groups while the organic part binds covalently or with weak interactions with the polymer chains [83]. A schematic representation of the nature of the composite interface is shown in Fig. 3.1 as an example.

Figure 3.1: Schematic representation of the nature of a composite organic-inorganic interface.

Numerous SSNMR studies have focused on functionalized silicas, particularly those obtained by means of silylation reactions with different silane coupling agents. Valuable structural information about the surface grafting of the coupling agents on the inorganic particles have been obtained by applying $^{29}$Si and $^{13}$C high-resolution techniques [84–94].

### 3.2 Materials, methods and aims

This study was carried out on sub-micrometer sized silica particles functionalized with TMSPM and encapsulated by a PMMA shell prepared by the group of Prof. A. Benedetti from the Department of Chemical Physics of Università Ca’ Foscari di Venezia and INSTN (Venice) [95]. In order to examine the morphology of the obtained organic-inorganic hybrid and to verify their chemical composition they also performed some characterizations using diffuse infrared Fourier transform (DRIFT) spectroscopy, Thermogravimetric analysis (TGA), Differential scanning calorimetry (DSC) and Transmission electron microscopy (TEM), some of which are reported here.

Dispersions of colloidal silica were prepared via the Stöber method [96], which produces spherical and monodisperse silica that was subsequently modified *in situ* using an excess of TMSPM by adaptation of literature methods [80,97,98]. This TMSPM-SiO$_2$ material was further used in the preparation of the composites with PMMA, which was
Study of functionalized sub-micrometer sized SiO$_2$ particles encapsulated by a PMMA shell

obtained through MMA polymerization in the presence of TMSPM-SiO$_2$ particles.

The structural formulae for TMSPM and PMMA are shown in Fig. 3.2 with the used labelling of carbon atoms.

![Figure 3.2: TMSPM(top) and PMMA (bottom) structures and carbon labelling.](image)

In this chapter, I present a systematic SSNMR study of the SiO$_2$-PMMA composite at the various stages of synthesis, commencing with the pristine silica particles (1), followed by their surface functionalization with the grafting agent, TMSPM, (2 & 3) and subsequent polymer encapsulation (4 & 5). In order to determine the effect of the silica particle size, two samples of functionalized silica particles with different average particle size, and hence, with different total surface area, were compared. Moreover in the final part of the chapter I will report the results of some SSNMR experiments carried out on composite obtained through the same procedure but applying stirring during the encapsulation (rather than obtained in static conditions).

The complete set of samples studied is presented in Table 3.1 which also includes PMMA (6), the extracted-TMSPM materials (7 & 8) and the TMSPM-SiO$_2$ composite (10) prepared under stirring. The samples (7 & 8) were prepared in order to investigate the role of TMSPM potentially not covalently bound to the surface of TMSPM-SiO$_2$. Sample (7) was obtained by extracting sample (2) by dissolution in hot CHCl$_3$ and drying the solid in vacuo. Then sample (8) was obtained by polymer encapsulation of sample (7). The results of this study and the experimental details have been reported in our recent paper [99].
### 3.2 Materials, methods and aims

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Sample</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>(^a)Stöber SiO(_2)</td>
</tr>
<tr>
<td>2</td>
<td>(^a)TMSPM-SiO(_2)</td>
</tr>
<tr>
<td>3</td>
<td>(^b)TMSPM-SiO(_2)</td>
</tr>
<tr>
<td>4</td>
<td>(^a,c)TMSPM-SiO(_2)/PMMA</td>
</tr>
<tr>
<td>5</td>
<td>(^a,d)TMSPM-SiO(_2)/PMMA-extracted</td>
</tr>
<tr>
<td>6</td>
<td>PMMA</td>
</tr>
<tr>
<td>7</td>
<td>(^a)Extracted-TMSPM-SiO(_2)</td>
</tr>
<tr>
<td>8</td>
<td>(^a)Extracted-TMSPM-SiO(_2)/PMMA</td>
</tr>
<tr>
<td>9</td>
<td>(^a)Stöber SiO(_2)</td>
</tr>
<tr>
<td>10</td>
<td>(^a,e)TMSPM-SiO(_2)/PMMA</td>
</tr>
</tbody>
</table>

Table 3.1: List of samples referred to in the discussion of this chapter.

\(^a\) Silica particle size of ca. 180 nm as determined by TEM.

\(^b\) Silica particle size of ca. 200 nm as determined by TEM.

\(^a\) Silica particle size of ca. 180 nm same as sample 1. This Stöber SiO\(_2\) was used for the preparation of sample 10.

\(^c\) This sample was obtained by the polymerization of MMA monomer onto functionalized SiO\(_2\) under static conditions.

\(^d\) This sample was obtained by extraction of sample 4, by dissolution in hot CHCl\(_3\) with the aid of sonication in order to remove PMMA not covalently bound to the surface of TMSPM-SiO\(_2\).

\(^e\) This sample was prepared as 4 but under stirring.
The aim of the solid-state NMR study is to especially investigate the structural properties of the interface present in the materials, and in particular those between silica and TMSPM and between TMSPM and PMMA. Solid-state NMR investigation involved 1D experiments on $^{13}$C and $^{29}$Si nuclei.

3.3 Results and discussion

The SSNMR study of samples 1 – 6 is presented in the following.

$^{13}$C

In Fig. 3.3 the $^{13}$C DE-MAS spectra of TMSPM-SiO$_2$ (200 nm, 3) and pristine SiO$_2$ (1) are reported, together with their signals assignment. The spectra of two samples of functionalized silica particles, TMSPM-SiO$_2$, with approximate particle sizes of 200 nm (3) and 180 nm (2, not shown) and pristine silica have been acquired by direct excitation of $^{13}$C nuclei using a short recycle delay of 2 s, which should favor the signals of carbon nuclei in mobile environments. All the expected TMSPM signals were observed for both of the functionalized silicas [90, 100], indicating not only the successful grafting of TMSPM onto silica but also that TMSPM moieties are quite mobile. The quite poor signal-to-noise ratio suggested that only a very small amount of TMSPM was effectively grafted onto silica, in agreement with previously published DRIFT-IR and TGA data, estimated to be about 1 wt% from the latter [95]. The peaks resonating at approximately 59 and 17 ppm (Fig. 3.3) could arise from TMSPM as well as from the ethoxy groups of unhydrolysed TEOS present in the silica matrix. Indeed, the presence of the latter was observed in the $^{13}$C spectrum of SiO$_2$.

The comparison between the $^{13}$C DE-MAS spectra of PMMA and composite 5, acquired with short recycle delay of 2 s, reveals the presence of some signals at about 60 – 70 ppm in the spectrum of the composite, not observable in the spectrum of PMMA, which can be ascribed to TMSPM and/or TEOS.

The $^{13}$C CP-MAS spectrum (Fig. 3.4) of PMMA shows the typical resonances of PMMA [100] which dominate also the CP-MAS spectrum of the composite 5. The absence of the TMSPM [C=CH$_2$] signals in both the $^{13}$C-DE and CP spectra of the composite could in principle suggest the formation of a bond between TMSPM and PMMA via a co-polymerization involving TMSPM double bonds and MMA, however, unfortunately, all the other TMSPM signals are also not clearly observable as a result of their superposition with either PMMA or unhydrolysed TEOS signals. Therefore, the apparent absence of TMSPM double bond signals could rather be due to a small signal to-noise ratio, ascribable to the very small amount of TMSPM in the composite, and
3.3 Results and discussion

Figure 3.3: $^{13}\text{C}$ DE-MAS spectra of (a) TMSPM-SiO$_2$ (200 nm, 3), (b) SiO$_2$ (1), (c) TMSPM-SiO$_2$/PMMA-extracted composite (5), and (d) PMMA (6). The signals assignment is reported using the atom labelling reported in Fig. 3.2. All the spectra were recorded with a MAS frequency of 5 kHz; spinning sidebands are marked with asterisks. The signal at $\approx$ 110 ppm in (b), (c) and (d) arises from incomplete suppression of the probe and rotor background signal. The signal at 30 ppm present in almost all the spectra is ascribable to an impurity.
Study of functionalized sub-micrometer sized SiO₂ particles encapsulated by a PMMA shell

Figure 3.4: $^{13}$C CP-MAS spectra of (a) PMMA (6), and (b) TMSPM-SiO₂/PMMA-extracted composite (5). The signals assignment is reported using the atom labelling reported in Fig. 3.2. All the spectra were recorded with a MAS frequency of 5 kHz; spinning sidebands are marked with asterisks.

therefore cannot be an evidence of the reaction between TMSPM and PMMA.

$^{29}$Si

In Fig. 3.5, the $^{29}$Si CP-MAS spectra of Stöber SiO₂ (180 nm, 1), TMSPM-SiO₂ (180 nm, 2), TMSPM-SiO₂ (200 nm, 3) and composite 5 are reported. As described in the Appendix A, silicon nuclei forming four and three Si–O bonds are conventionally indicated as $Q^4$ and $T^3$, respectively, where n is the number of oxygen atoms also bonded to other silicon atoms.

In the spectrum of Stöber SiO₂ signals due to $Q^4$ (≈−112 ppm), $Q^3$ (≈−103 ppm) and $Q^2$ (≈−94 ppm) silicon nuclei are present, which arise from fully condensed silicon nuclei, single silanols and geminal silanols, respectively. In the spectra of all the other samples, beside silica $Q$ peaks, signals arising from $T$ silicon nuclei are also observed between −80 and −50 ppm, and in particular at about −67 ppm ($T^3$) and −59 ppm ($T^2$), which can be exclusively attributed to TMSPM molecules involved in condensation reactions. A confirmation of the involvement of silica in the condensation reactions with TMSPM comes from the decrease of the $Q^3/Q^4$ and $Q^2/Q^4$ signals intensity ratios in passing from Stöber SiO₂ (sample 1) to the corresponding TMSPM-SiO₂ (sample 2), which indicates that both single and geminal silica silanols reacted with TMSPM molecules.
Figure 3.5: $^{29}$Si CP-MAS spectra of (a) Stöber SiO$_2$ (180 nm, 1), (b) TMSPM-SiO$_2$ (180 nm, 2), (c) TMSPM-SiO$_2$ (200 nm, 3) and (d) TMSPM-SiO$_2$/PMMA-extracted composite (5). In the inset an expansion of the T signals’ region of spectra (b), (c) and (d) is shown. All spectra were recorded with a MAS frequency of 5.8 kHz.
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However, it is likely that the covalent bonds formed by TMSPM molecules are not only with silica, but also with other TMSPM molecules, leading to TMSPM oligomeric structures covalently bound to the silica surface, as previously observed [87,90]. Furthermore, the simultaneous absence of T$^0$ and T$^1$ signals (expected to resonate at slightly higher frequencies) indicates that unbound TMSPM, as well as TMSPM molecules forming only a single Si-O-Si covalent bond, are not present.

Although the CP spectra are not strictly quantitative, it is possible to extract valuable information regarding the extent of condensation of silicon atoms by comparison of CP spectra for different samples. Indeed, by comparing the spectra of 2 and 3, it is possible to observe that in the former the ratio between the integrals of T$^3$ and T$^2$ peaks is clearly greater, indicating a larger condensation for TMSPM silicon atoms. Accordingly, also the ratio between the integrals of Q$^4$ and Q$^3$ peaks is higher in 2, where the signal of Q$^2$ silicons is substantially absent, while it is clearly detectable for 3. These results indicate that also the silica component underwent a higher degree of condensation in 2, as opposed to 3. Moreover, the ratio between the overall integral of the Q signals and that of the T signals is clearly different for the two samples, being about 8 in 2 and about 34 in 3, clearly indicating that in the former a much larger amount of TMSPM is present.

Therefore, it is possible to conclude that the smaller dimensions of silica particles, and hence greater surface area of the material, largely favor:

1. The presence of TMSPM on the surface of silica (a larger amount of TMSPM has been observed)
2. The grafting of TMSPM on the silica surface (higher condensation of silica atoms)
3. A higher probability of the condensation reaction occurring amongst TMSPM molecules (higher condensation of TMSPM silicon atoms),

From the $^{29}$Si CP-MAS spectrum of composite 5 (Fig. 3.5 (d)) it is possible to observe a ratio between the integrals of Q$^4$ and Q$^3$ signals similar to that of 2, which indicates a similar degree of silica condensation. As expected, this shows that the condensation of the inorganic component is not affected by the successive reaction with MMA in the TEOS medium. Nonetheless, the two $^{29}$Si CP-MAS spectra show a very different overall integral ratio between Q and T peaks (see Fig. 3.5), which in fact noticeably increases on passing from 2 to 5 (from about 8 to about 26). The possibility that this could be ascribed to the formation of additional silica during the polymer encapsulation process, due to the presence of TEOS as a solvent, was ruled out by observing that no silica was formed during the synthesis of PMMA, carried out using the same experimental conditions as reported previously [95]. Therefore, the change in the ratio between the integrals of T and Q signals seems to suggest a loss of TMSPM during the polymer-
3.3 Results and discussion

The condensation of MMA in the TEOS medium, for which the inorganic core particles become encapsulated by PMMA.

In order to understand if this loss could be due to the extraction of TMSPM-SiO$_2$/PMMA composite in hot CHCl$_3$, we also recorded the $^{29}$Si CP-MAS spectrum of the same composite which was not subjected to free polymer extraction (4, not shown). The results appeared similar to those of the composite after the extraction, thus ruling out the possibility that the loss of TMSPM could be due to the extraction itself, and rather supporting the hypothesis that it occurs during the PMMA encapsulation process.

This is further corroborated by the investigation of sample (7). If some TMSPM is lost during the encapsulation it is likely that it should be not covalently bound onto the silica surface. Therefore sample (7) was prepared by extracting sample (2) in hot CHCl$_3$ and its $^{29}$Si CP-MAS was acquired (see Fig. 3.6). The spectrum is similar to that of sample (2) but the relative intensity of TMSPM signals with respect to silica signals is reduced, in agreement with a certain TMSPM removal. However, both the extracted (7) and non extracted (2) TMSPM species show similar structure of the T signals, indicating similar condensation of TMSPM molecules in both the species. It could be reasonable to say that both the extracted and non extracted TMSPM species should be mostly oligomeric species, as indicated by the high condensation degree of T silicons and the absence of T$^0$ and T$^1$ silicons; moreover, it is very unlikely that a single

![Figure 3.6: $^{29}$Si CP-MAS spectrum of extracted TMSPM-SiO$_2$ (7). The spectrum was recorded with a MAS frequency of 6 kHz.](image-url)
TMSPM molecule can give rise to three covalent bonds with silica. Given the small amount of TMSPM in 7, the observation of its $^{13}$C and $^{29}$Si signals in 8, the PMMA encapsulated sample prepared from 7, was not possible.

Other characterization techniques were brought in to analyze the extracted samples (7 and 8) and to corroborate the SSNMR data.

**DRIFT – IR**

The DRIFT-IR spectra of (a) Stöber SiO$_2$ (1), (b) TMSPM-SiO$_2$ (2) and, (c) extracted-TMSPM-SiO$_2$ (7) are shown in Fig. 3.7.

![DRIFT-IR spectra](image)

Figure 3.7: DRIFT-IR spectra of (a) Stöber SiO$_2$ (1), (b) TMSPM-SiO$_2$ (2) and, (c) extracted TMSPM-SiO$_2$, (7).

The spectrum of 1 is characterized by the broad band visible between 3700 and 2700 cm$^{-1}$ attributed to OH stretching of surface silanols, and the region between 1600 and 400 cm$^{-1}$ which exhibits the absorption bands that correspond to the vibrational mode of siloxane links which has been evidenced by the Q$^4$ and Q$^3$ signals from $^{29}$Si CP-MAS spectrum. The spectrum of 2 indicates the presence of TMSPM, which is characterized by the C – H stretching vibrations between 2900 and 3000 cm$^{-1}$, and the C = O vibration band at 1700 cm$^{-1}$ which is in agreement with its parallel orientation to the SiO$_2$ surface that arises from hydrogen bonding between the carbonyl oxygen and surface silanols as previously noted [78,101,102]. A small shoulder visible at 1718 cm$^{-1}$ attests to the presence of TMSPM “free” carbonyl groups that are not involved in hydrogen bonding with the SiO$_2$ surface, as previously reported [102]. Following extrac-
tion of any unbound TMSPM to obtain 7, the characteristic C = O vibration band at 1700 cm\(^{-1}\) remains visible although less prominent, suggesting that TMSPM species are still present.

**TGA**

The thermogram depicted in Fig. 3.8 illustrates the mass loss of samples 1, 2, 7, 8. In the case of SiO\(_2\) (1), the loss is attributed to the removal of physisorbed and chemisorbed water, unhydrolyzed ethoxy groups which arise from the SiO\(_2\) precursor TEOS, and complete dehydroxylation [103]. In order to describe the difference in weight loss observed between 200 – 1000 °C, we found it necessary to exclude the percentage of water that was lost before reaching 200 °C. Therefore, by comparing the difference for thermograms of 1 and 2, it is possible to estimate a total amount of TMSPM of 0.9 %. A weight loss difference of 0.6 % between 2 and 7 is observed between 200 and 1000 °C, which can be attributed to TMSPM species which were most likely to be bound to the surface via hydrogen bonding only. The SSNMR data obtained for 2, showing an absence of T\(^0\) and T\(^1\) signals, suggest that these TMSPM species should be present as oligomers rather than as single molecules. The weight loss of composite 8 with respect to 7, which can be ascribed to PMMA, is about 1.6 %. This value is much less than what obtained for composites prepared from non extracted-TMSPM-SiO\(_2\) [95] which showed a weight loss of 4 % between 5 and 2.

![Figure 3.8: TGA of (a) Stöber SiO\(_2\) (1), (b) TMSPM-SiO\(_2\) (2), (c) extracted TMSPM-SiO\(_2\) (7) and, (d) extracted TMSPM-SiO\(_2\)/PMMA (8).](image-url)
DSC & TEM

The presence of PMMA in 8 is supported by differential scanning calorimetry (DSC) and TEM data. The DSC scan (Fig. 3.9) demonstrates the degradation of the polymer at 390°C in the composite (8) (curve a) which is in agreement with our reference sample of PMMA (6) (curve b), prepared by the method of Wang et al. [104].

Moreover, a certain degree of encapsulation of extracted TMSPM-SiO₂ by PMMA is shown by TEM (Fig. 3.10), albeit with less uniformity in the PMMA shell as compared with the micrograph of the non-extracted TMSPM-SiO₂/PMMA composite. In Fig. 3.10,
the presence of SiO$_2$ core particles without an apparent PMMA coating can also be noted.

These results support the loss of TMSPM, proposed on the basis of SSNMR data, occurring during the encapsulation reaction of non extracted TMSPM-SiO$_2$. In fact, oligomeric TMSPM species which are not covalently bound to the silica surface can be removed during the encapsulation process when TMSPM-SiO$_2$ is not preliminarily subjected to extraction. The presence of such oligomeric species does not interfere with the encapsulation process which is performed under static conditions in a TEOS medium, but rather, appears to increase the compatibility with MMA, which subsequently leads to greater degree of surface coverage by the polymer as it forms around the SiO$_2$ core to create a PMMA shell.

**Composites prepared under stirring**

As far as the second set of samples 9 and 10 are concerned, in which the composite encapsulation has been performed under stirring conditions, a composite's different morphology is evident from TEM (Fig. 3.11). It seems that, instead of a shell, PMMA forms a web that connects silica particles.

![Figure 3.11: TEM micrograph of TMSPM-SiO$_2$/PMMA composite 10.](image)

By SSNMR, we tried to investigate the changes in the interactions at the interface between the silica particles and the PMMA between the composites 5 and 10. In spite of their different morphology, the two composites show very similar $^{13}$C spectra (not shown). The $^{29}$Si spectra of 5, 9 and 10 (Fig. 3.12) show that the relative intensities of T with respect to Q is slightly higher in 10 than in 5, indicating the presence of a slightly higher amount of TMSPM in sample 10, but it is clear that the condensation
Study of functionalized sub-micrometer sized SiO$_2$ particles encapsulated by a PMMA shell

Figure 3.12: $^{29}$Si CP-MAS spectra of (a) Stöber SiO$_2$ (9), (b) TMSPM-SiO$_2$/PMMA (10) and, (c) TMSPM-SiO$_2$/PMMA (5).

of TMSPM silicons is similar both in 10 and 5. All the spectra presented in Fig. 3.12 show similar Q signals, indicating a similar silica condensation.

3.4 Conclusions

TMSPM functionalized SiO$_2$ particles embedded in a thin shell coating of PMMA were characterized by SSNMR at the various stages of synthesis. By means of $^{13}$C and $^{29}$Si high-resolution techniques it was possible to characterize the organic and inorganic components, as well as their interface, for both TMSPM functionalized silicas having different sizes and TMSPM-SiO$_2$/PMMA composites. The dimensions of silica particles were found to significantly affect the structural features of the obtained TMSPM-SiO$_2$, smaller dimensions favoring the condensation between silica and TMSPM as well as TMSPM self-condensation. SSNMR results on the PMMA encapsulated TMSPM-SiO$_2$ particles highlighted a loss of TMSPM occurring during the encapsulation process, which could be ascribed to the removal of oligomeric TMSPM species not covalently bound to the silica surface during the encapsulation of MMA onto the silica particles. The presence of such oligomers during the encapsulation process nonetheless appeared to favor the formation of the PMMA shell around the silica particles.
The SSNMR results on the TMSPM-SiO$_2$/PMMA composite prepared under stirring, in spite of its different morphology, suggested by TEM, showed spectra very similar to those of the other composite. Due to the very low amount of TMSPM in the silica matrix and also overlapping of the PMMA carbon resonances, it is quite difficult to investigate more in depth the interactions between TMSPM and PMMA, and to identify differences possibly related to the different morphologies.

3.5 Experimental

Solid-state $^{29}$Si- and $^{13}$C-MAS NMR spectra were recorded on the dual-channel Varian Infinity Plus 400 spectrometer described in Subsection 2.4.1, equipped with a 7.5 − mm CP-MAS probehead, working at 79.44 MHz for silicon-29 and at 100.56 MHz for carbon-13. $^{29}$Si CP-MAS spectra were recorded with a MAS frequency of 5.8 kHz, 60000 − 100000 transients, a recycle delay of 3 s and a contact time of 2 ms. $^{13}$C CP-MAS spectra were recorded with a MAS frequency of 5 kHz, 240 − 10000 transients, a recycle delay of 3 s, and a contact time of 2 ms. $^{13}$C-Direct Excitation (DE)-MAS spectra were recorded using a depth pulse sequence (described in Subsection 2.5.1) to suppress probe and rotor background signals; a MAS frequency of 5 kHz, 9000 − 42000 transients, and a recycle delay of 2 s were used. The $^{13}$C and $^1$H 90°-pulse lengths were 4.6 and 4.0 µs in all cases. All the $^{13}$C- and $^{29}$Si-NMR spectra were recorded under high power proton decoupling conditions. TMS was the primary chemical shift reference for all nuclei, while hexamethylbenzene and 3-(trimethylsilyl)- 1-propane-sulfonic acid sodium salt were used as secondary references for $^{13}$C and $^{29}$Si, respectively. All the experiments were performed at room temperature and using air as spinning gas.

On a ThermoNicolet Magna-IRTM, diffuse reflectance infrared Fourier transform (DRIFT) spectra were recorded in the range of 4000 − 500 cm$^{-1}$, at a resolution of 2 cm$^{-1}$ using a KBr background. Thermal analyses, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were recorded using alumina as the inert standard (Netzcsh STA 409). TGA and DSC analyses were collected consecutively, carried out with a temperature profile of 25 − 1000°C, a heating rate of 10°Cmin$^{-1}$, and an air to N$_2$ ratio of 2 : 1 with a flow of 10 nLmin$^{-1}$. Transmission electron microscopy (TEM) images were obtained with a JEOL JEM-3010, operating at 300 kV, equipped with a GATAN (Warrendale, PA, USA) Multi-Scan CCD camera model 794.
Chapter 4

Structural and dynamic study of an organometallic complex incorporated into mesoporous silica nanoparticles

Abstract

In this work, tris(dibenzoylmethanido)(o-phenanthroline)-yttrium(III) complex, APTES or ETMS functionalized mesoporous silica nanoparticles (MSNs) and composites made by incorporating the complex into APTES or ETMS functionalized mesoporous silica nanoparticles have been studied. This complex of diamagnetic yttrium is a model for luminescent europium complex, which in fact has many biological and electronic applications. Due to the paramagnetism and quadrupolar effects of europium nuclei, which broadens the NMR signals, thus causing big problems for the structural and dynamic analysis, a complex was prepared with an yttrium atom in place of the europium one. This complex is indeed expected to have very similar molecular properties due to the similar chemical behaviour and atomic radius of Y and Eu. With the aim of characterizing the structural and dynamic properties of the complex incorporated into functionalized silica nanoparticles, as well as their mutual interactions, several SSNMR techniques have been exploited. $^{13}$C and $^1$H MAS experiments were performed together with the measurements of $^{13}$C $T_1$ and $^1$H $T_1$ and $T_{1HP}$ at variable temperatures for the composites, the neat functionalized silicas (APTES-MSN and ETMS-MSN) and the complex. Additional detailed structural information concerning the functionalization of the silicas have
been obtained from $^{29}\text{Si}$ high-resolution spectra.

4.1 Introduction

Lanthanide complexes are among the most important luminescent materials due to the strong absorption of ligands and effective energy transfer from ligands to central metal ions [105]. Compared with the conventional luminescent materials, lanthanide complexes are a useful class of luminophores since they exhibit high photoluminescence efficiency along with a narrow emission spectrum, large Stokes shifts, and high color purity under ultraviolet excitation, which make them useful alternatives to radioactive probes and organic dyes [106, 107]. These characteristics made the lanthanide complexes a promising candidate for a variety of potential technological applications, such as in fluoroimmunoassays, spectroscopic structural probes in biologically important systems, optical amplification, energy harvesting devices, lightconversion molecular devices (LCMDs), and organic lightemitting diodes (OLEDs) [108–112]. Organic dyes, which represent the standard choice for biomarking and bioimaging applications, suffer disadvantages such as a broad emission band, superposition of excitation and emission spectra, and short fluorescent lifetimes and photobleaching. In contrast, the europium ions can be efficiently excited at 393 nm, while their efficient red-emission is far away peaked at 612 nm. This large Stokes shift allows an easy filtering of the light scattered by the sample and at the same time the narrow emission can be easily discriminated from the broad emission, so increasing the sensitivity in detection. Moreover for Eu$^{3+}$ ions, the emission lifetime is longer (around 1 ms).

In particular, lanthanide complexes with many kinds of ligands ($\beta$-diketones, aromatic carboxylic acids, and phenanthroline) show excellent emission properties, since these organic chromophore molecules often have large absorption coefficients in the ultraviolet-visible region and can function as ‘antennae’ [113]. It has long been observed that when such molecules are bound to europium ions, the energy absorbed by these molecules may be efficiently transferred to the central europium ion that in turn emits in the visible, thereby enhancing its luminescence according to the so-called “antenna effect”. The presence of these organic ligands can also serve as a shielding for the central ion from certain molecules which are known to quench the luminescence of europium ions, such as solvents containing OH-groups. The $\beta$-diketonate ligand which has been used in this study as the primary ligand, was among the first recognized suitable sensitizers [114]. In addition to this ligand, phenanthroline was used as a secondary ligand in order to tentatively improve the luminescence yield through the antenna effect. These kinds of lanthanide organic complexes have great potentials in photoelectronic application, such as laser materials [115], luminescence labels [116].
4.1 Introduction

However, lanthanide complexes have been excluded for long time from practical applications as phosphor devices mainly due to their poor photo and thermal stabilities, optical properties and low mechanical strength [107]. In order to improve the photo and thermal stabilities, optical properties (longer luminescence lifetime, stronger luminescence etc.) and mechanical strength, organic lanthanide complexes have been incorporated into host matrices like mesoporous materials [105], polymers [108], clays [106,117]. The mesoporous materials which are of interest in this study have been synthesized (by sol-gel method [118] or by using silica precursors with some modifications for a template) which entrap lanthanide complexes by ion-exchange [119], simple doping (no strong bonding between the organic and inorganic phases) or by covalent bond grafting method [120], because of their unique properties, for example, large, controllable pore sizes and high surface areas [121]. In this study mesoporous silica nanoparticles prepared with some modifications, i.e. using a surfactant template as the matrix, since the pore sizes of these mesoporous nanoparticles are large enough to encapsulate lanthanide complexes. The silica nanoparticles can present significant advantages such as high optical emission intensity, low toxicity, efficient surface functionalization for molecular recognition and cheap, fast and reliable production process [122]. In fact, in recent years these luminescent silica nanoparticles have stimulated great research interest for biological labelling [123], contrast reagents for magnetic resonance tomography [124], and sensors for biology and medicine [122].

Xu et al. [125] were the first to use MCM-41 (mesoporous silica) as a host for a luminescent europium \( \beta \)-diketonate complex. The silica is sometimes modified with the silanizing/functionalizing agents (3-aminopropyltriethoxysilane (APTES), ethoxy trimethyl silane (ETMS), N-(3-trimethoxysilyl) ethylethylenediamine etc.,) in order to reduce the number of silanol groups in the host matrix, which otherwise quench the luminescence of the europium ion to some extent due to the high-energy vibrations of the Si-OH groups [126] and also the silica surface is modified to improve the interactions between the organic europium complex and the silica matrix. It has already been noticed [127] that the emission intensity value observed on the lanthanide complex incorporated in some of the organically modified silicates is higher than that for the original free complex, and this implies that some modification of the lanthanide complexes takes place in their incorporation process into the silica-based matrices. Among the several methods employed for the incorporation of the complex into the organically modified mesoporous silica matrix, wet impregnation method is a widely used technique [128,129] which has also been used to prepare the composites here studied.

The lanthanide complex which is of interest for this study is tris (dibenzoylmethanido) (\( \text{o-phenanthroline} \)) europium(III) [Eu(DBM)\( _3 \)Phen] complex, that has been widely stud-
Structural and dynamic study of an organometallic complex incorporated into mesoporous silica nanoparticles

ied in the recent years [108,123,130,131]. The ligands bonded with the central lanthanide ion are dibenzoylmethane and 1,10-phenanthroline. The crystal structure of this complex is revealed by the X-ray study [132] and its molecular structure is shown in the Fig. 4.1. This complex was incorporated into mesoporous silica nanoparticles which were organically modified with different functionalizing agents such as 3-aminopropyltriethoxysilane (APTES) and ethoxytrimethoxysilane (ETMS) on their surface to improve the interactions between the organic lanthanide complex with the porous silica nanoparticles.

Figure 4.1: Molecular structure of Eu(DBM)$_3$(Phen) complex. Arrows indicate coordination bonds.

Several papers were published reporting applications of some characterization techniques like FT-IR, UV-Vis, SEM, TEM, TGA, XRD, N$_2$ absorption isotherm, photoluminescence, optical and fluorescence measurements, to the study of luminescent properties, structure and morphology of these materials, both on the free organic lanthanide com-
plexes and their composites with silica [1–17]. On the contrary, the interactions between organic and inorganic components at a nanoscale level is still not fully understood. In the last decades, the complexes formed by the lanthanide ions were used in NMR studies as the shift reagents [133–135] by exploiting their paramagnetic effect, which has been used for spectral simplification and chiral analysis both in organic and aqueous media but it is much less frequently used nowadays because of the advent of high field, pulsed multidimensional NMR techniques [136]. Indeed, in the last few years, there have been many studies performed on these kinds of lanthanide complexes using the solution state NMR techniques [106,113,137–140] whereas there were very few papers employing solid-state NMR especially concerning the characterization of europium complexes in the silica matrix [107,109,119,128]. Using $^{29}$Si and $^{13}$C high-resolution solid-state NMR techniques, the important structural information on the grafting of the organo-silanes into silica particles and the free complex ligands has been obtained [141]. Solid-state NMR could be very useful in dynamic studies: provided that suitable nuclear probes are contained in the composite materials, very detailed structural and dynamic information can be obtained at a molecular level. As far as my knowledge is concerned, there have been no publications dealt with the application of solid-state NMR for molecular dynamic investigations on composite materials containing lanthanide complexes. This is mainly due to the paramagnetic effect and quadrupolar nature of most lanthanide nuclei which broadens the NMR spectral resonances by the contribution of both quadrupolar and nucleus-electron interactions (see Subsection 1.5.4). These contributions make very difficult to extract valuable information on these organic europium complexes and their composites formed with silica nanoparticles.

In order to get insights into the structural and dynamic properties of these materials using solid-state NMR techniques, the complex with the diamagnetic mimic yttrium [142, 143] as the central metal ion was studied. Although yttrium is not formally a lanthanide element and also non-luminescent, it was chosen in order to avoid paramagnetism without altering the molecular properties: its +3 oxidation state and similar radial size (the ionic radii of eight coordinated Eu$^{3+}$ and Y$^{3+}$ are 120.6 and 115.9 pm respectively) render it a good candidate to study the structural and dynamic properties of the complex and the composites with silica in place of lanthanides using SSNMR.

4.2 Materials and aims

In this study, we applied several high and low resolution techniques on different nuclei, such as $^1$H, $^{13}$C and $^{29}$Si, in order to characterize the structural and dynamic properties of the materials just introduced. The samples were prepared and kindly provided by
the group of Prof. A. Benedetti from Department of Chemical Physics of Università Ca’ Foscari (Venice). They had used photoluminescence spectroscopy in order to verify the optical properties of the Eu(DBM)\textsubscript{3}phen/silica composites in which mesoporous silica nanoparticles (MSNs) are modified organically with different functionalizing agents. Indeed, they had seen an increase in luminescence for the organically modified mesoporous silica nanoparticles compared with the neat europium complex and the composites with unmodified silica nanoparticles. Moreover, they also observed a difference in the luminescence properties of the composites containing different functionalizing agents. This suggests that there could be some changes occurring in the interactions of the europium complex with organically modified silica nanoparticles using different functionalizing agents (APTES and ETMS).

Solid-state NMR is really a powerful tool for the characterization of structural and dynamic properties of materials at a molecular level, which can be useful for interpreting the properties showed at the macroscopic level. Specifically our focus is on the interactions occurring at the interfaces between the organometallic complex and the modified inorganic silica particles. Since the yttrium complex and the composites were prepared with the same reaction conditions as that of europium counterparts, it is possible to extend the structural and dynamic information obtained by SSNMR on yttrium/silica composites to the europium ones.

The aim of this study is to characterize the interfacial interactions between the Y(DBM)\textsubscript{3}(Phen) complex and organically modified silica nanoparticles by using several solid-state NMR techniques. High-resolution experiments were performed on \textsuperscript{13}C and \textsuperscript{1}H nuclei; in addition, \textsuperscript{1}H and \textsuperscript{13}C T\textsubscript{1} and T\textsubscript{1ρ} relaxation times were measured at variable temperature for the two composites (APTES-MSN/Y(DBM)\textsubscript{3}(Phen) & ETMS-MSN/Y(DBM)\textsubscript{3}(Phen)), the organically modified silicas (APTES-MSN & ETMS-MSN) and Y(DBM)\textsubscript{3}Phen complex. Additional detailed structural information concerning the functionalization of the silicas have been obtained from \textsuperscript{29}Si high-resolution spectra.

### 4.3 Results and discussions

This section is organized in three subsections, reporting the solid-state NMR investigations on \textsuperscript{13}C, \textsuperscript{29}Si and \textsuperscript{1}H nuclei, respectively. The detailed structural characterization of the systems investigated has been mainly obtained from \textsuperscript{13}C and \textsuperscript{29}Si CP-MAS experiments. Information on the dynamics has been obtained from the study of \textsuperscript{13}C CP dynamics, \textsuperscript{13}C selective direct excitation spectra with the \textsuperscript{13}C recycle delay of 2s and also \textsuperscript{13}C spin-lattice relaxation times (T\textsubscript{1}) measured at variable temperature. In addition to these measurements, low-resolution \textsuperscript{1}H T\textsubscript{1} and T\textsubscript{1ρ} experiments were performed.
at variable temperature in order to try to investigate more quantitatively the dynamic properties.

4.3.1 $^{13}$C

4.3.1.1 Y(DBM)$_3$(Phen) Complex

In Fig. 4.2, the structure and $^{13}$C CP-MAS spectrum of the Y(DBM)$_3$Phen complex are reported. To the best of our knowledge, in the literature there are no $^{13}$C spectra of similar complexes in the solid state with the exception of ref. [144] which dealt the dibenzoylmethane ligands coordinated with the transition metal cations. In Fig. 4.2, four main peaks can be recognized that can be tentatively assigned to dibenzoylmethane carbon a (93 ppm), to carbons of benzoyl ring and phenanthroline e, g, h carbons (127 ppm), to phenanthroline d and i carbons (140 ppm) and to phenanthroline f carbon (150 ppm). Peaks due to b and c carbons of dibenzoylmethane could not be clearly observed due to overlap with a spinning sideband. Even if the resolution of the spectrum is intrinsically quite poor, this appears well compatible with the occurrence of a single resonance structure for the three dibenzoylmethane ligands, in agreement with X-ray data reported for similar complexes [132].

In Fig. 4.3, the $^{13}$C DE-MAS spectrum of the complex is presented. This experiment was carried out in order to select the mobile part of the complex using a short recycle delay (2 s). Indeed, the signal at 127 ppm mainly due to carbons of benzoyl rings is very intense indicating that there are several aromatic carbons with a short $T_1$, and therefore a quite high mobility, while the peaks coming only from phenanthroline carbons (at 140 and 150 ppm) appear much reduced indicating a lower mobility for this ligand.

In order to further investigate the dynamics of the complex, we recorded $^{13}$C CP-MAS spectra with variable contact times between 50 µs and 15 ms (see Fig. 4.4). The peak at 127 ppm also in this case shows a peculiar behaviour: its intensity changes faster than the other signals with increasing contact times, thus indicating a shorter $T_1$ for benzoyl protons, and therefore confirming a possible faster dynamics for the benzoyl moieties. We tried to fit the intensity vs. contact time trends for the different peaks, in order to obtain CP dynamics parameters like $T_{CH}$, $^1H T_{1\rho}$, using the Eq. 1.115 described in Subsection 1.7.3. Unfortunately the presence of unusually short $T_{CH}$ values, along with the coexistence of the very big peak at 127 ppm with other much smaller peaks, rendered quite unreliable the CP dynamics parameters obtained.

In order to try to obtain further information on the dynamics of the benzoyl groups, we measured $^{13}$C $T_1$’s between 20 and 50 °C through the Torchia pulse sequence (see Sub-
Figure 4.2: $^{13}$C CP-MAS spectrum of the Y(DBM)$_3$(Phen) complex with corresponding signal assignments. The spectrum was recorded with a MAS frequency of 6 kHz; spinning sidebands are marked with asterisks.
Figure 4.3: $^{13}$C DE-MAS spectrum of the Y(DBM)$_3$(Phen) complex with the signal assignments already reported in the Fig. 4.2. The experiment was acquired with a short recycle delay (2 s) and with a MAS frequency of 6 kHz; spinning sidebands are marked with asterisks. The small signal at $\approx 110$ ppm arises from incomplete suppression of the probe and rotor background signal.
Figure 4.4: $^{13}$C CP-MAS spectrum of the Y(DBM)$_3$(Phen) complex. The experiment was acquired with the variable contact times ranging from 0.05 ms to 15 ms. The spectrum was recorded with a MAS frequency of 6 kHz.

section 2.5.6). The experimental trends, obtained after suitable spectral deconvolution were fitted with the Eq. 2.3 described in Subsection 2.5.6. Due to the long experimental times required by this experiment, reliable results could be obtained only for the peak at 127 ppm, since for the other peaks the signal to noise was too small and $T_1$’s too long. A 3-exponential decay function was necessary to fit the experimental trends at all temperatures. In Table 4.1 the values of $^{13}$C spin-lattice relaxation times in the laboratory frame $T_1$ so obtained are reported. In the fitting procedure $T_{1c}$ has been fixed to the value of 33 s, after preliminary tests, to reduce the correlation with the other fitting parameters. However, due to the complexity of the results, mainly arising from multi-exponentiality, it is hard to interpret the data obtained from $^{13}$C $T_1$ analysis. In the attempt of simplifying this interpretation, we calculated the population-weighted rate average (PWRA) quantity (see Subsubsection 2.6.2.5), thus obtaining a single average value at each temperature. The last column in Table 4.1 shows the 1/PWRA values for different temperatures: the 1/PWRA trend with temperature suggest that $^{13}$C $T_1$ of the benzoyl carbons are in the slow motion regime with respect to the $^{13}$C Larmor frequency (100 MHz).
4.3 Results and discussions

<table>
<thead>
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<th>T (°C)</th>
<th>T_{1a}</th>
<th>w_a</th>
<th>T_{1b}</th>
<th>w_b</th>
<th>T_{1c}</th>
<th>w_c</th>
<th>1/PWRA (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.42</td>
<td>0.26</td>
<td>2.4</td>
<td>0.31</td>
<td>33</td>
<td>0.43</td>
<td>1.314</td>
</tr>
<tr>
<td>30</td>
<td>0.63</td>
<td>0.45</td>
<td>3.8</td>
<td>0.21</td>
<td>33</td>
<td>0.34</td>
<td>1.282</td>
</tr>
<tr>
<td>40</td>
<td>0.30</td>
<td>0.29</td>
<td>2.03</td>
<td>0.43</td>
<td>33</td>
<td>0.28</td>
<td>0.840</td>
</tr>
<tr>
<td>50</td>
<td>0.5</td>
<td>0.48</td>
<td>3.4</td>
<td>0.27</td>
<td>33</td>
<td>0.25</td>
<td>0.955</td>
</tr>
</tbody>
</table>

Table 4.1: Spin-lattice relaxation times in the laboratory frame of the $^{13}$C nuclei of the benzoyl groups resonating at 127 ppm. The weights for the three components are given in fractional units. The estimated experimental error for $1/PWRA$ values was ± 0.1 s.

4.3.1.2 APTES-MSN

In Fig. 4.5, the CP-MAS spectrum of APTES functionalized silica nanoparticles is shown. All the characteristics peaks of the APTES organic chain were assigned [145]. Peaks at 15 and 58 ppm could arise from unhydrolysed ethoxy groups of TEOS which had been used for the preparation of silica nanoparticles as well as from the unhydrolysed ethoxy groups of APTES.

In Fig. 4.6, the $^{13}$C DE-MAS spectrum of APTES-MSN recorded with a short recycle time (2 s), is shown. All the carbon resonances of the propyl chain in APTES were present, suggesting that the propyl carbons are quite mobile. Moreover, the peaks at 15 and 58 ppm are more enhanced than those of the propyl group with respect to the CP-MAS spectrum, indicating a higher mobility for the ethoxy moieties.

4.3.1.3 ETMS-MSN

In Fig. 4.7, the CP-MAS spectrum of ETMS functionalized silica nanoparticles is presented. The signal at -2.6 ppm is due to the methyl carbons present in ETMS. Peaks at 15 and 58 ppm arise from unhydrolysed TEOS [146], and/or from small amounts of unreacted ETMS, whose presence will be shown in the following by $^{29}$Si CP-MAS spectra.

4.3.1.4 APTES-MSN/Y(DBM)$_3$(Phen) Composite

In Fig. 4.8, the CP-MAS spectrum of APTES-MSN/Y(DBM)$_3$(Phen) composite is presented along with the CP spectra of its pure components i.e. APTES-MSN and Y(DBM)$_3$(Phen). The signals of APTES organic chains resonating at 8.9, 25 and 43 ppm and benzoyl rings signal of the complex at 127 ppm can be recognized in the spectrum of the composite, suggesting that the complex has been impregnated in the functionalized
Figure 4.5: $^{13}$C CP-MAS spectrum of APTES-MSN along with the molecular structure of APTES and the signal assignments. The spectrum was recorded with a MAS frequency of 5.5 kHz.
4.3 Results and discussions

Figure 4.6: $^{13}$C DE-MAS spectrum of APTES-MSN along with the signal assignments already reported in the Fig. 4.5. The experiment was acquired with a short recycle delay of 2 s and a MAS frequency of 5.5 kHz.

Figure 4.7: $^{13}$C CP-MAS spectrum of ETMS-MSN and its molecular structure along with the signal assignments. The spectrum was recorded with a MAS frequency of 3 kHz.
silica matrix and hence indicating that the preparation process was successful. However, not all the complex signals are visible in the composite spectrum due to the quite small amount of complex sample available. In order to detect possible changes in the dynamic

![Figure 4.8: $^{13}$C CP-MAS spectra of (a) Y(DBM)$_3$(Phen)complex, (b) APTES-MSN/Y(DBM)$_3$(Phen) composite and, (c) APTES-MSN, all recorded with the same contact time of 1 ms. The spectrum of the composite was recorded with a MAS frequency of 6kHz while those of the complex and APTES-MSN were recorded with 6kHz and 5.5kHz, respectively.](image)

behaviour in passing from pure components to the composite, we recorded $^{13}$C CP-MAS spectra of the composite (not shown) at two different contact times (0.1 and 1 ms). The two spectra showed very similar intensities for both APTES and complex benzoyl signals. This was not the case for benzoyl carbon nuclei (127 ppm) in pure complex, where more intense signal were observed at 0.1 ms than at 1 ms (see Fig. 4.4). This suggests a change in the dynamics of the complex passing to the composite. However, from CP it is not possible to get quantitative or more detailed dynamic information.

In Fig. 4.9, the $^{13}$C DE-MAS spectra acquired with a short recycle delay are shown. The presence of both APTES carbon signals and complex benzoyl carbons signal suggests that both APTES chains and complex benzoyl rings are quite mobile. Moreover, though the amount of the complex is less, the intensity of complex signal in the spectrum of the composite Fig. 4.9(b) is quite comparable with the APTES chain resonances thus suggesting that complex benzoyl rings may become more mobile.
Figure 4.9: $^{13}$C DE-MAS spectra of (a) $\text{Y(DBM)}_3(\text{Phen})$ complex, (b) APTES-MSN/$\text{Y(DBM)}_3(\text{Phen})$ composite and, (c) APTES-MSN, acquired with a short recycle delay of 2 s. The spectrum of the composite was recorded with a MAS frequency of 15 kHz, while those of the complex and APTES-MSN were recorded with 6 kHz and 5.5 kHz respectively. The signal present in all the spectra at $\approx 110$ ppm arises from incomplete suppression of the probe and rotor background signal.
4.3.1.5 ETMS-MSN/\(\text{Y(DBM)}_3\text{(Phen)}\) Composite

The CP-MAS spectrum of this composite is shown in Fig. 4.10 along with the analogous spectra of complex and ETMS-MSN. The signals of ETMS methyl carbons and benzoyl groups resonances of complex can be recognized in the spectrum of the composite, indicating that the preparation was successful. Also in this composite, the other carbon resonances of the complex are not visible due to its small amount compared with the functionalized silica matrix. By looking at the spectral intensities, it seems that the amount of complex is less in this composite compared to the APTES-MSN/\(\text{Y(DBM)}_3\text{(Phen)}\) composite.

In Fig. 4.11, the selective DE-MAS spectrum of ETMS-MSN/\(\text{Y(DBM)}_3\text{(Phen)}\) composite is shown together with the spectra of complex and ETMS-MSN, all recorded with a recycle delay of 2 s. It is clear that methyl groups in ETMS and complex benzoyl rings are both quite mobile, since they both show an appreciable intensity.
4.3 Results and discussions

Figure 4.11: $^{13}$C DE-MAS spectra of (a) Y(DBM)$_3$(Phen) complex, (b) ETMS-MSN/Y(DBM)$_3$(Phen) composite and, (c) ETMS-MSN, acquired with a short recycle delay of 2 s. The spectrum of the composite was recorded with a MAS frequency of 15 kHz, while those of the complex and ETMS-MSN were recorded with 6 kHz and 5.5 kHz respectively.

4.3.2 $^{29}$Si

4.3.2.1 APTES-MSN

In Fig. 4.12, the $^{29}$Si CP-MAS spectrum of APTES-MSN is shown. Two distinct groups of signals are clearly recognizable and straightforwardly assignable; the conventional nomenclature employed for indicating silicon nuclei in different structural environments is described in Appendix A. The two peaks resonating at $-111$ and $-103$ ppm can be assigned to Q$^4$ and Q$^3$ silicons, respectively, while the two higher-frequency signals have to be ascribed to T$^3$ ($-68$ ppm) and T$^2$ ($-61$ ppm) silicon nuclei, respectively. Considering that Q and T type silicon nuclei form four and three Si-O bonds, respectively, it is straightforward that all the Q-type resonances arise from silica silicon nuclei, while the T-type signals must be assigned to the APTES silicons. Coming back to the Q signals, the presence of Q$^3$ signal shows that single silanol groups Si(OSi)$_3$(OH) are present in the silica matrix; this suggests that the TEOS used as the precursor for the preparation of silica nanoparticles is not fully condensed, while, on the other hand, the Q$^2$ signal (that should occur at $-93$ ppm), which arise from the geminal silanols Si(OSi)$_2$(OH)$_2$, is not present. However, the higher intensity of the Q$^4$ silicons suggests
that a large amount of fully condensed silicon nuclei is present. Concerning the APTES silicon signals, the presence of T<sup>3</sup> and T<sup>2</sup> peaks which arise from partially and fully condensed 29Si nuclei, can be considered an evidence that the APTES functionalization onto the silica surface has successfully taken place. Moreover, the absence of a T<sup>0</sup> signal (that usually occur at about −43 ppm) confirms that non-reacted APTES is not present. Even though CP spectra do not allow a quantitative determination of the condensation degree to be obtained, it is possible to state that, as for TEOS, the large majority of the APTES silicon nuclei is fully condensed.

![Figure 4.12: 29Si CP-MAS spectrum of APTES-MSN. The spectrum was recorded with a MAS frequency of 3.5 kHz; spinning sidebands are marked with asterisks.](image)

### 4.3.2.2 ETMS-MSN

In Fig. 4.13, the 29Si CP-MAS spectrum of ETMS-MSN is presented. In addition to Q signals that arise from silica nanoparticles, there are also signals arising from ETMS silicons present at higher frequencies, that have to be ascribed to M-type silicon nuclei (see Appendix A). Considering that the M signals come from the type of silicon nuclei which form one Si−O bond, in our case, M<sup>1</sup> (13 ppm, Si(OSi)) and M<sup>0</sup> (17 ppm, Si(OH)),
4.3 Results and discussions

single silanol) are present. Hence, the presence of M⁰ shows that there are uncondensed ethoxy groups in ETMS, though they are present in an almost negligible amount. As far as the silica silicon nuclei are concerned, the three peaks (Q⁴, Q³, Q²) come from the condensed silica bulk, single silanols and geminal silanols, respectively. The presence of the Q² silicon signal and also an intense Q³ signal show that in this mesoporous silica the condensation process was less complete compared with APTES-MSN.

Figure 4.13: $^{29}$Si CP-MAS spectrum of ETMS-MSN. The spectrum was recorded with a MAS frequency of 3.5 kHz; spinning sidebands are marked with asterisks.

4.3.3 $^1$H

Both high- and low-resolution $^1$H NMR experiments have been performed on the entire set of samples, with the aim of further investigating the structural and dynamic properties of both composites with respect to their pure components.

4.3.3.1 $^1$H-MAS NMR

In Fig. 4.14, $^1$H MAS spectra of APTES-MSN (a), APTES-MSN/Y(DBM)$_3$(Phen) (b) and complex (c) are presented. The spectrum of the composite qualitatively appears as the sum of the spectra of the two components. In particular, narrow signals present in
the composite (b) is due to APTES organic chains which resonate at around 2.3 and 5.8 ppm. The presence of the complex in the composite (b) was confirmed by the presence of an intense broad peak at ≈ 7.3 ppm which arises from the aromatic protons of complex. Even spinning at 15 kHz MAS frequency, the $^1$H-$^1$H homonuclear dipolar interactions (see Subsubsection 1.5.2.2) could not be completely removed and consequently the other signals of the complex and APTES organic chains signals cannot be distinguished due to the large residual linewidth. In APTES-MSN the narrow lines at 2.6 ppm can be ascribed to mobile groups in APTES, while the broad lines at around 7.5 ppm should arise from H-bonded silanol groups and it is possible that restricted motion of the aminopropyl side chains [147], which probably bound to the internal surface of MSN, could also contribute to this broad signal. The broad linewidth of ≈ 14 kHz at the base of the spectrum shown in Fig. 4.14 (b), suggests that there are parts of the composite which are really rigid, so that the homonuclear coupling could not be removed even by fast spinning.

Figure 4.14: $^1$H-MAS spectra of APTES-MSN (a), APTES-MSN/Y(DBM)$_3$(Phen) (b) and, the complex (c). The composite spectrum was recorded with a MAS frequency of 15 kHz, while the APTES-MSN and the complex spectra were recorded at 5.5 and 6 kHz, respectively; spinning sidebands are marked with asterisks.

In Fig. 4.15, $^1$H-MAS spectra of ETMS-MSN (a), ETMS-MSN/Y(DBM)$_3$(Phen) (b) and complex (c) are shown. In ETMS-MSN (a), the intense signal at 0.1 ppm comes from methyl groups of ETMS while the signals at 3.8 and 1.16 ppm arise from the ethoxy groups of unhydrolysed TEOS or unreacted ETMS. The peak at 2 ppm could arise from isolated silanols while the peak at 7.2 ppm arise from hydrogen-bonded silanols. In the
case of ETMS-MSN/Y(DBM)$_3$(Phen) (b) composite all the signals from ETMS-MSN are present and the resonance at 7.3 ppm comes from the complex aromatic protons. No indication about a change in mobility occurring in the composite could be obtained. The signals of ETMS remain narrow and those of the complex are broad, indicating that ETMS and complex environments remain mostly mobile and rigid, respectively, as in their pure components.

![Composite spectrum](image)

**Figure 4.15:** $^1$H-MAS spectra of ETMS-MSN (a), ETMS-MSN/Y(DBM)$_3$(Phen) (b) and, the complex (c). The composite spectrum was recorded with a MAS frequency of 15 kHz, while the ETMS-MSN and the complex spectra were recorded at 5 kHz and 6 kHz, respectively; a spinning sideband is marked with an asterisk.

### 4.3.3.2 $^1$H $T_1$ and $T_{1ρ}$

In order to achieve information on the dynamics of the systems investigated in the range of motional characteristic frequencies of kHz and MHz, proton spin-lattice relaxation times $T_{1ρ}$ and $T_1$, respectively, have been measured as a function of temperature in the range between 20 and 70 $^\circ$C for both the composites and their pure components in low-resolution, on resonance conditions, using the pulse sequences described in the Subsubsections 2.6.2.4 & 2.6.2.3. For all the samples, the recovery of the magnetization in the measurement of spin-lattice relaxation times in the laboratory frame ($T_1$) can be well fitted by means of a single exponential function (see Eq. 2.10). This indicates that spin diffusion produces a complete averaging of all the gradients of longitudinal magnetization within each sample in the $T_1$ time scale. Because of the complete averaging, a single mean spin-lattice relaxation rate in the laboratory frame (1/$T_1$) is measured, which can be interpreted in terms of molecular motions. In Table 4.2, the $T_1$ values of complex,
Structural and dynamic study of an organometallic complex incorporated into mesoporous silica nanoparticles

APTES-MSN along with their composite, at variable temperature are shown, and in Table 4.3, complex and ETMS together with their composite are also shown.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>Complex 1H T1 (s)</th>
<th>APTES-MSN 1H T1 (s)</th>
<th>Composite 1H T1 (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>23</td>
<td>1.49</td>
<td>0.59</td>
<td>0.69</td>
</tr>
<tr>
<td>30</td>
<td>1.88</td>
<td>0.59</td>
<td>0.85</td>
</tr>
<tr>
<td>40</td>
<td>2.20</td>
<td>0.63</td>
<td>0.74</td>
</tr>
<tr>
<td>50</td>
<td>2.42</td>
<td>0.64</td>
<td>0.72</td>
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<td>0.66</td>
<td>0.73</td>
</tr>
<tr>
<td>70</td>
<td>3.40</td>
<td>0.71</td>
<td>0.72</td>
</tr>
<tr>
<td>err</td>
<td>± 0.02</td>
<td>± 0.01</td>
<td>± 0.01</td>
</tr>
</tbody>
</table>

Table 4.2: 1H spin-lattice relaxation times in the laboratory frame (T1) of the complex, APTES-MSN and their composite at variable temperature. The magnetization recovery curves were always well reproduced by a mono-exponential function. In the last line, the estimated experimental error is reported.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>Complex 1H T1 (s)</th>
<th>ETMS-MSN 1H T1 (s)</th>
<th>Composite 1H T1 (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>23</td>
<td>1.49</td>
<td>0.75</td>
<td>1.09</td>
</tr>
<tr>
<td>30</td>
<td>1.88</td>
<td>0.83</td>
<td>1.08</td>
</tr>
<tr>
<td>40</td>
<td>2.20</td>
<td>0.93</td>
<td>1.24</td>
</tr>
<tr>
<td>50</td>
<td>2.42</td>
<td>1.08</td>
<td>1.29</td>
</tr>
<tr>
<td>60</td>
<td>2.66</td>
<td>1.29</td>
<td>1.32</td>
</tr>
<tr>
<td>70</td>
<td>3.40</td>
<td>1.50</td>
<td>1.33</td>
</tr>
<tr>
<td>err</td>
<td>± 0.02</td>
<td>± 0.02</td>
<td>± 0.02</td>
</tr>
</tbody>
</table>

Table 4.3: 1H spin-lattice relaxation times in the laboratory frame (T1) of the complex, ETMS-MSN and their composite at variable temperatures. The magnetization recovery curves were always well reproduced by a mono-exponential function. In the last line, the estimated experimental error is reported.

In the case of T1ρ measured at different temperatures, the trend of the magnetization could be always described by means of a bi-exponential function for the complex and ETMS-MSN/Y(DBM)3(Phen) composite, whereas, a tri-exponential function was necessary for ETMS-MSN, APTES-MSN and the APTES-MSN/ Y(DBM)3 (Phen) composite (see Eq. 2.4). This indicates that the spin-diffusion averaging effect is only partial.
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on the T<sub>1ρ</sub> time scale, which in turn results in different relaxation times for different protons; however, these are not the intrinsic ones, and therefore they do not have direct dynamic meaning. But it is possible to obtain dynamic information by calculating the corresponding T<sub>1ρ</sub> population-weighted rate average (PWRA) quantity, for all the temperatures investigated, in order to get rid of spin-diffusion effects giving a quantity directly interpretable in terms of their dynamic properties. The use of PWRA in the analysis of multi-exponential relaxation decays has already been discussed in Chapter 2 in the Subsubsection 2.6.2.5. The values of 1/PWRA as a function of temperature for the complex, APTES-MSN and their composite are presented in Table 4.4 and values of 1/PWRA as a function of temperature for the complex, ETMS-MSN and their composite are shown in Table 4.5.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>Complex</th>
<th>APTES-MSN</th>
<th>Composite</th>
</tr>
</thead>
<tbody>
<tr>
<td>22</td>
<td>1.87</td>
<td>0.78</td>
<td>0.73</td>
</tr>
<tr>
<td>30</td>
<td>1.93</td>
<td>0.84</td>
<td>0.72</td>
</tr>
<tr>
<td>40</td>
<td>1.81</td>
<td>0.82</td>
<td>0.74</td>
</tr>
<tr>
<td>50</td>
<td>1.96</td>
<td>0.87</td>
<td>0.86</td>
</tr>
<tr>
<td>60</td>
<td>2.32</td>
<td>0.96</td>
<td>0.96</td>
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<td>70</td>
<td>2.53</td>
<td>1.00</td>
<td>1.07</td>
</tr>
</tbody>
</table>

Table 4.4: <sup>1</sup>H spin-lattice relaxation times in the rotating frame (T<sub>1ρ</sub>) of the complex, APTES-MSN and their composite at variable temperature. The trends of the magnetization were always well reproduced by a multi-exponential function. In the last line, the estimated experimental error is reported.

In the following, in order to investigate and compare the dynamic properties of both the composites with respect to their pure components in MHz and kHz dynamic regimes, the comparison between the trends of T<sub>1</sub> and 1/PWRA as a function of temperature will be discussed. Despite the large complexity of the data, due to the possible occurrence of many different motions, it is however possible to draw some qualitative results.

The T<sub>1</sub> and 1/PWRA trends vs. temperature of APTES-MSN/Y(DBM)<sub>3</sub>(Phen) composite and their pure components is shown in Fig. 4.16. The increasing trend of <sup>1</sup>H T<sub>1</sub> values (see Fig. 4.16 (a)), measured at 400 MHz, of the pure complex with increasing temperature indicates that the motion responsible for this relaxation has characteristic frequencies higher than the Larmor frequency. Also considering the results obtained from <sup>13</sup>C T<sub>1</sub>’s, the motions responsible for <sup>1</sup>H T<sub>1</sub> relaxation could be probably due to the fast molecular vibrations and librations. For APTES-MSN, the trend does not
Structural and dynamic study of an organometallic complex incorporated into mesoporous silica nanoparticles

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>Complex (ms)</th>
<th>ETMS-MSN (ms)</th>
<th>Composite (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>22</td>
<td>1.87</td>
<td>2.23</td>
<td>5.37</td>
</tr>
<tr>
<td>30</td>
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<tr>
<td>70</td>
<td>2.53</td>
<td>2.29</td>
<td>6.63</td>
</tr>
</tbody>
</table>

Table 4.5: $^1$H spin-lattice relaxation times in the rotating frame ($T_{1\rho}$) of ETMS-MSN and their composite at variable temperatures. The trends of the magnetization were always well reproduced by a multi-exponential function. In the last line, the estimated experimental error is reported.

![Plot of $T_1$ (ms) vs Temperature](a)

![Plot of $T_{1\rho}$ (ms) vs Temperature](b)

Figure 4.16: $^1$H spin-lattice relaxation times in the laboratory frame ($T_1$ (s)) versus temperature (°C), measured at a Larmor frequency of 400 MHz are shown in (a) and $^1$H spin-lattice relaxation times in the rotating frame ($T_{1\rho}$ (ms)) versus temperature (°C), measured at a spin-lock frequency of 50 kHz are presented in (b) for the samples APTES-MSN/Y(DBM)$_3$(Phen) composite (red circle), Y(DBM)$_3$(Phen) complex (blue square) and APTES-MSN (green diamond) in both cases. Lines are included as a guide for the eye.
demonstrate to be significantly affected by temperature and along with the quite short $^1$H $T_1$ values, this suggests that the motions having the main impact on $T_1$ relaxation for APTES-MSN have a frequency of the same order of magnitude of the Larmor frequency (400 MHz). The motions contributing to this trend can arise from the APTES organic chains. In the case of $^1$H 1/PWRA values (see Fig. 4.16 (b)), measured at the spin-lock frequency of 50 kHz, the trend of the complex reaches a minimum at lower temperature which must arise from the motion different from that contributing to the $T_1$ trend. It is possible that the π-flip of the benzoyl ring contribute to this regime which would be compatible with $^{13}$C $T_1$ data. As far as APTES-MSN is concerned, the increasing trend of 1/PWRA with temperature indicates that the motions contributing to $T_{1\rho}$ are in the fast motional regime (faster than 50 kHz), but it is very difficult to identify them. At last, looking at the trend of APTES-MSN/Y(DBM)$_3$(Phen) composite in both $T_1$ and 1/PWRA, the composite relaxation times are clearly not the averages of those of the pure components. Therefore, strong changes probably have occurred in both fast (MHz) and intermediate (kHz) dynamics of either the complex and/or APTES-MSN. The $T_1$ and 1/PWRA values measured for the composite are smaller than those expected from the simple average of the pure components, so on average the dynamics close to 100 MHz and 50 kHz frequencies increases in passing to the composite.

![Figure 4.17](image)

Figure 4.17: $^1$H spin-lattice relaxation times in the laboratory frame ($T_1$ (s)) versus temperature ($^\circ$C), measured at a Larmor frequency of 400 MHz are shown in (a) and $^1$H spin-lattice relaxation times in the rotating frame ($T_{1\rho}$ (ms)) versus temperature ($^\circ$C), measured at a spin-lock frequency of 50 kHz are presented in (b) for the samples ETMS-MSN/Y(DBM)$_3$(Phen)composite (red circle), Y(DBM)$_3$(Phen) complex (blue square) and ETMS-MSN (green diamond) in both cases. Lines are included as a guide for the eye.
The trends of $^1H\ T_1$ and $1/PWRA$ as a function of temperature are shown in Fig. 4.17 for the ETMS-MSN/Y(DBM)$_3$(Phen) composite along with its pure components. The $T_1$ and $1/PWRA$ trends of the pure complex have been already discussed. We expect that fast methyl rotations about its ternary symmetry axis is the main cause of $T_1$ relaxation in ETMS-MSN, while other slower motions could more efficiently contribute to $T_{1\rho}$ relaxation. In passing from pure components to ETMS-MSN/Y(DBM)$_3$(Phen) composite, strong changes in the dynamic behaviour can be observed. In particular, the intrinsic $T_{1\rho}$ values of the composite are much larger than those of both pure complex and ETMS-MSN. On the other hand, the $T_1$ values measured for the composite appear much shorter than the average value that could be calculated from the pure components, especially at the highest temperatures investigated. From $T_1$ and $1/PWRA$ trends it is reasonable to hypothesize that the $\pi$-flip of the benzoyl rings of the complex becomes faster, passing from kHz to MHz regime, due to its dispersion in the silica.

In order to try to obtain more quantitative results, we attempted to analyze data obtained from ETMS-MSN/Y(DBM)$_3$(Phen) composite and their pure components with the simplest model Bloembergen-Purcell-Pound (BPP) (see Subsection 1.8.2). To relate the experimental relaxation times to the parameters of the motions, it is necessary to use expressions of the spectral density $J(\omega)$ in terms of the correlation times of motions $\tau_c$. The spectral densities have been expressed analytically according to the BPP model which is represented as follows:

$$J^{BPP}(\omega) = \frac{2\tau_c}{1 + \omega^2\tau_c^2}$$

(4.1)

As far as the dependence of correlation time ($\tau_c$) on temperature is concerned, the simplest way of describing it is given by the Arrhenius law, where this dependence is described in terms of the activation energy of the motion:

$$\tau_c = \tau_{\infty} e^{\frac{U}{kT}}$$

(4.2)

where $\tau_{\infty}$ is the correlation time in the limit of infinite temperature and $U$ is the activation energy of the motion.

The analysis could be conducted only by considering some strong assumptions that are:

1. Only the dynamics of complex changes passing from pure components to composite whereas the dynamics of ETMS-MSN remains the same in both the dynamic regimes.
2. The main motion of the complex contributing to both the $^1H\ T_1$ and $1/PWRA$ trends (i.e., in fast and intermediate regimes) of composite is the $\pi$-flip of benzoyl ring.

The contribution of the relaxation rates of both composite and ETMS-MSN used to
4.3 Results and discussions

determine the complex term is shown in the Eq. 4.3.
\[
\left( \frac{1}{T_{1\text{composite}}} \right)^* = \left( \frac{w_{\text{ETMS}}}{T_{1\text{ETMS}}} \right) + \left( \frac{1 - w_{\text{ETMS}}}{T_{1\text{complex}}} \right)
\]
where \( w_j \) are the fractions of protons involved in the \( j \)-th motion and the dependence of \( T_{1\text{complex}} \) from motional parameters can be expressed as follows:
\[
\left( \frac{1}{T_{1\text{complex}}} \right) = C \left( J(\omega_0, \tau_c) + 4J(2\omega_0, \tau_c) \right) = C \left[ \frac{2\tau_c}{1 + \frac{\omega_0^2\tau_c^2}{2}} + \frac{8\tau_c}{1 + 4\omega_0^2\tau_c^2} \right]
\]
here \( \omega_0 \) is the \(^1\text{H}\) Larmor frequency (400 MHz). Since we assumed that the same motion of the complex contributes also to the kHz regime, then we can write:
\[
\left( \frac{1}{T_{1\rho\text{composite}}} \right)^* = \left( \frac{w_{\text{ETMS}}}{T_{1\rho\text{ETMS}}} \right) + \left( \frac{1 - w_{\text{ETMS}}}{T_{1\rho\text{complex}}} \right)
\]
and similarly to \( T_1 \), \( T_{1\rho} \) complex can be expressed as:
\[
\left( \frac{1}{T_{1\rho\text{complex}}} \right) = C \left[ \frac{3}{10} J(2\omega_1, \tau_c) + \frac{1}{2} J(\omega_0, \tau_c) + \frac{1}{5} J(2\omega_0, \tau_c) \right]
\]
where \( C \) is an unknown constant depending on the homonuclear \(^1\text{H}\)–\(^1\text{H}\) dipolar interactions taking place in the sample, \( \tau_c \) is the correlation time of the motion occurring in the complex and \( \omega_1 \) is the spin-lock frequency used in \(^1\text{H}\) \( T_{1\rho} \) relaxation time measurements (50 kHz). The terms indicated with asterisks are directly taken from \( T_1 \) and \( T_{1\rho} \) measured in the composite and in pure ETMS-MSN.

Applying this model with the assumptions made, the correlation time calculated is in the ns range, indicates that the motion of benzoyl rings in the composite effectively belongs to the MHz regime, while the relaxation times suggested it to belong to the kHz regime in the pure complex. With the assumptions considered it is not possible to obtain a reliable quantitative results due to lack of information and experimental data. It would be important to know the amount of protons in ETMS-MSN compared to the complex protons in order to have fixed \( w_j \) values and also it would be important to measure \(^1\text{H}\) \( T_{1\rho} \) of the pure complex at variable spin-lock field. This could be helpful to verify the trend of \(^1\text{H}\) \( T_{1\rho} \) and could make possible a more reliable interpretation of its trend with temperature. With the availability of a larger set of data it could be possible to remove the too drastic assumption that the dynamics of ETMS-MSN does not change passing to the composite.
4.4 Conclusions

In this work several SSNMR techniques have been exploited in order characterize the structure and dynamics of the two composites prepared from two different functionalized silica nanoparticles. From $^{13}$C-CP spectra, the structures of the complex and composite were characterized. The presence of the aromatic signals from complex in both the composites indicates that the preparation process was successful and that no big structural changes occurred in passing from pure components to composites. On the other hand, qualitative dynamic information could be obtained by $^{13}$C-DE, CP-dynamics and $T_1$ measurements. The condensation degree of the mesoporous silica nanoparticles and functionalizing agent (APTES and ETMS) could be obtained by $^{29}$Si CP-MAS experiments. The $^{29}$Si-CP spectrum of APTES-MSN showed the presence of more fully condensed silica silicon nuclei ($Q^4$) than in ETMS-MSN, where a larger amount of single silanols ($Q^3$) was present. In both the composites, condensation of ETMS and APTES silica nuclei showed a large amount of fully condensed silicon ($M^1$ and $T^3$, respectively) signals.

$^1$H-MAS experiments of ETMS and its composite showed a well resolved spectrum indicating that ETMS is mobile also when it is incorporated into the silica nanoparticles, whereas APTES-MSN showed stronger $^1$H-$^1$H homonuclear interactions indicating an average less mobility of its protons giving rise to broader NMR lines, which could not be resolved even by fast spinning at 15 kHz this could suggest a larger involvement of the aminopropyl groups in intermolecular interactions. More detailed dynamic information could be obtained from $^1$H $T_1$ and $T_{1\rho}$ analysis obtained as a function of temperature. Despite the large complexity of the data, due to the possible occurrence of many different motions, it was however possible to draw some qualitative results by comparing the values of $T_1$ and $1/PWRA$ calculated from the multi-exponential $T_{1\rho}$ decay curves, obtained for the pure components and the composites. In the APTES-MSN/Y(DBM)$_3$(Phen) composite, both $T_1$ and $T_{1\rho}$ of the composite were clearly not the averages of those of the pure components suggesting that strong changes in both fast (MHz) and intermediate (kHz) dynamics of either the complex and/or APTES-MSN probably have occurred. In the ETMS-MSN/Y(DBM)$_3$(Phen) composite, strong changes occurred in both MHz and specifically in kHz dynamics, considering the big change experienced by $T_{1\rho}$ in passing from pure components to the composite. From $T_1$ and $T_{1\rho}$ curves it is reasonable to hypothesize that the $\pi$ flip of the benzoyl rings of the complex becomes faster, passing from kHz (in the complex) to the MHz regime (in the composite), due to its dispersion in the silica. In the attempt of analyzing the data of the ETMS-MSN/Y(DBM)$_3$(Phen) composite to obtain quantitative results, a simple model BPP was considered under
several assumptions. The correlation time ($\tau_c$) obtained under these assumptions for the benzoyl $\pi$-flip motion in the composite is of a few ns. However, further experiments are necessary to confirm both the nature of the motion and its characteristic parameters. For instance, $^1$H $T_{1\rho}$ could be measured at different spin-lock frequencies in order to obtain more reliable quantitative information.

4.5 Experimental

SSNMR

All the experiments were performed on a double-channel Varian Infinity Plus 400 spectrometer described in Subsection 2.4.1, equipped with a 7.5 mm CP-MAS probehead, working at 79.47 MHz for silicon-29 and at 100.59 MHz for carbon-13 and also with a 3.2 mm CP-MAS probehead, operating at 100.59 MHz for carbon-13.

High-resolution experiments on complex, APTES-MSN, ETMS-MSN were performed on 7.5 mm CP-MAS probe head, with a $^1$H 90°C pulse length of 5 $\mu$s. For the $^{29}$Si CP, 50000 scans were accumulated. For the $^{13}$C-CP of functionalized silicas 10000 scans were used while for the complex 7000 transients and contact time of 1 ms were needed. Experiments on composites were performed on a 3.2 mm CP-MAS probe head with a $^1$H 90°C pulse length of 2.5 $\mu$s, contact times of 0.1 and 1 s and 7000 transients. In the case of $^1$H MAS spectrum, 40 scans were recorded.

$^{13}$C selective direct excitation (DE) experiments were performed on 7.5 and 3.2 mm probes with a recycle delay of 2 s and $^{13}$C 90°C pulse lengths of 4.2 and 2.5 $\mu$s, respectively.

Proton $T_1$ and $T_{1\rho}$ were measured in low-resolution by using saturation recovery (delays ranging from 0.0001 to 20 s) and variable spin-lock time (delays ranging from 0.0001 to 0.05 s) pulse sequences, respectively. Usually 32 scans were used in all proton $T_1$ and $T_{1\rho}$ relaxation experiments.

$^{13}$C $T_1$ measurements were performed by Torchia cross-polarization sequence with delays ranging from 0.0001 to 30 s. The temperatures for all the relaxation times measurements were controlled to be within $\pm$ 0.4°C.

Preparation of mesoporous silica nanoparticles

TEOS was used as silica precursor for the preparation of all mesoporous silica samples with some modifications (using cetyl trimethyl ammonium bromide as surfactant), with water and ethanol as solvents, ammonia solution as base catalyst for reaction.
Functionalization of MSNs with APTES

The functionalization has been performed by addition of a cyclohexane solution containing 2 % v/v APTES and 2 % v/v n-propylamine to the powdered MSNs. The suspension was stirred at ambient temperature for 2 h, after which it was recovered and purified by repeated (3 times) centrifugation (30 min at 6 krpm), hexane washing and sonication (30 min). The obtained sample, APTES-MSN was dried under reduced pressure ($10^{-1}$ mbar for 4 h).

Functionalization of MSNs with ETMS

A typical method was carried out by which predried MSN and ethoxytrimethylsilane were added to the dry toluene and the resulting solution mixture was refluxed under the nitrogen atmosphere for 12 hours. The hydrophobically modified MSN was filtered and washed by toluene and anhydrous ethanol in turn. At last, the solid (ETMS-MSN) was air-dried overnight and then under reduced pressure ($10^{-1}$ mbar for 4 hr).

Preparation of composites

Incorporation of $Y(DBM)_3(Phen)$ complex in MSN has been carried by using wet impregnation method, where the functionalized MSN sample was stirred overnight with $Y(DBM)_3(Phen)$ complex solution in dichloromethane. Solid was subsequently dried under reduced pressure ($10^{-1}$ mbar for 4 h).
Chapter 5

Study of novel composites of isoprene rubber reinforced with in situ generated silica particles

Abstract

The synthetic isoprene rubber (IR) was reinforced with silica fillers that have been prepared by a novel method in which silica was generated in situ from tetraethoxysilane (TEOS) through sol-gel process. The applicability of these kinds of materials is strongly dependent on the filler-filler and filler-polymer interactions. Better dispersions of filler particles improve the physical and mechanical properties of these materials. Solid-state NMR is one of the most important techniques for the characterization of these materials at a molecular level.

The aim of this study was to elucidate the dependence of the preparation conditions (initial content of TEOS, sol-gel reaction time, addition of octyltriethoxysilane (OTES), as coupling agent, to the reaction mixture) on the final structural and dynamic properties of the materials using solid-state NMR techniques. The structure of the in situ generated silica was analyzed by $^{29}$Si high-resolution experiments, which highlighted for all the preparation conditions considered a high condensation degree of TEOS that decreased with increasing the reaction time. The conversion of TEOS to silica was slightly further promoted by the presence of OTES. Additional structural information was obtained from $^1$H and $^{13}$C high-resolution experiments.

The molecular dynamic properties of filled rubbers were investigated mainly through the measurement of $^1$H $T_2$ relaxation time in low resolution: three regions with different
chain mobility were detected and related with sample composition and silica-polymer interactions. Additional dynamic information was also obtained from $^1\text{H}$ $T_1$ and $T_{1\rho}$ low-resolution measurements, which indicate that the polymer is homogeneous on a 100 Å, but not on a 10 Å spatial scale.

An attempt to compare the solid-state NMR results with the mechanical, swelling and microscopy data was made. It is quite difficult to straightforwardly correlate these techniques, since the NMR timescale is much different from the rest of the techniques mentioned here, nonetheless we tried to compare the SSNMR results concerning the dimensions of the interface with SEM results giving the dimensions of silica particles.

5.1 Introduction

The incorporation of fillers, mainly carbon black and silica, as finely dispersed particles in elastomeric matrices is a process born almost simultaneously with the rubber industry and it is still a consolidated practice both in productive processes and in the development of new materials. This is due to the dramatic reinforcement effect that a suitable filler dispersion induces in the elastomeric matrix, resulting in the substantial improvement of the most important mechanical properties, such as stiffness, tear and abrasion resistance [148]. The importance of reinforcement at an applicative level is large, as demonstrated by the production of rubbers for tires, where the incorporation of suitably modified silica determines a drastic decrease of the rolling resistance, with consequent lower fuel consumption, superior wet traction and greater wear resistance. In spite of the extensive use of these materials in the industry, the molecular origins of the improvement of macroscopic properties are still largely misunderstood.

As far as the reinforcement strength is concerned, it has been observed that it is largely influenced by the particle size, and in particular it increases by decreasing the size. The theories developed to explain this behaviour assume that the presence of filler particles enhances the occurrence of dissipative phenomena, which relieve local stress [149, 150]. Such dissipative phenomena are supposed to be primarily based on slipping of adsorbed chains over filler surfaces, but there could also be a contribution from the slipping of unabsorbed chains, which are entangled with the adsorbed ones. In both molecular mechanisms, the extent of energy dissipation increases with increased filler surface area, i.e., with smaller particles. Chain slipping leads to develop little, sub-critical damages spread over a larger volume, rather than quickly developing severe damages in a smaller volume, a circumstance which would result in facile cracking and reduced strength. Moreover, in heavily filled systems composed of small particles (size of the order of 10-100 nm), once a crack begins to grow, it quickly encounters a rigid filler particle, and its “progress” is arrested [149]. The enhancement of elastic modulus due
to the presence of fillers in rubber compounds has been widely investigated [151,152].

It is generally accepted that the modulus of a filled rubber is the result of the addition of various contributions [153]: elastomer’s stiffness, hydrodynamic effect (which measures the modulus increase due to the presence of rigid, virtually un deformable, particles embedded in the soft rubber matrix [154]), polymer-filler and filler-filler interactions. It is generally accepted that interfacial interactions between filler and rubber play a very important role for a successful reinforcement, but the direct experimental investigation of the phenomena occurring at molecular and nanometric levels is not straightforward.

The experimental investigation of the phenomena occurring at a molecular level in rubber/filler composites is not an easy task; solid-state NMR (SSNMR) appears as one of the most powerful techniques for tackling this issue. In particular, properties such as structural and dynamic properties of both the fillers and the rubber, as well as of their interfaces, can be effectively characterized through the combination of different suitable SSNMR techniques.

In the field of elastomer (rubber)/filler composites, important studies based on SSNMR are present in the literature, especially on natural rubber (NR), polyisoprene (IR), styrene-butadiene rubber (SBR), polydimethylsiloxane (PDMS), EPDM (ethylene propylene diene monomer rubber) reinforced by inclusion of carbon black or silica [155–168]. The most successful approach turned out to be that based on the measurement of the residual $^1\text{H}^1\text{H}$ homonuclear dipolar interaction, that is the extent of the interaction not averaged out by molecular motions, which can be considered as an indirect measurement of the average degree of molecular mobility of the system. One of the most used experimental approaches has been the measurement of proton spin-spin relaxation times ($T_2$). Indeed, at least at relatively small values of $T_2$ (from tens of $\mu$s to tens of ms), this is mainly related to the inverse of the proton static linewidth, which is in turn mainly due to residual dipolar couplings. Increasing $T_2$ values are measured for increasingly mobile sample regions. Proton $T_2$ measurements, performed through the analysis of the decay of proton transverse magnetization, have been quite largely exploited in the study of rubber/filler composites [156–158, 165, 167, 168], on systems at different compositions subjected, for instance, to vulcanization, solvent swelling and extraction of the so-called bound rubber, i.e. of the polymeric fraction more strongly interacting with the filler. It appears quite well established that the presence of the filler determines a distribution of motionally different rubber domains: in particular a clear mobility reduction is generally observed for a fraction of rubber chains directly interacting with the filler surface. A more quantitatively reliable and precise measurement of the residual dipolar interaction, which has also been directly related to quantities like rubber cross-link density, can be achieved through Multiple Quantum experiments, in
which multiple quantum coherences that comprise two or more coupled spins are excited [159, 161–163, 166, 167]. This is especially important when $T_2$’s are quite large (approximatively hundreds of ms), since in that case they can be also affected by non-dynamic factors, as magnetic field gradients occurring in the samples. In composite materials such gradients have been observed since the materials heterogeneity can cause magnetic susceptibility differences within the samples [169].

At present, the knowledge of the possible relationships between the properties observed at “molecular” and “macroscopic” level is still quite scarce, due to intrinsic difficulties in relating the corresponding very different spatial and time scales, as well as to the relatively small number of combined studies including the characterization of both types of properties (see for instance ref. [166, 167]).

5.2 Materials, aims and methods

In this chapter I present a quite extensive SSNMR study focused on novel composites of isoprene rubber with silica generated in situ from tetraethoxysilane through sol-gel process. This study was carried out in collaboration with the group of Prof. M. Messori (Dipartimento di Ingegneria dei Materiali e dell’Ambiente dell’Università degli Studi di Modena e Reggio Emilia), who synthesized the composites under investigation and performed TGA and SEM characterizations, and with the group of Prof. F. Bignotti (Dipartimento di Ingegneria Meccanica e Industriale, Università degli Studi di Brescia), who carried out swelling and mechanical measurements.

A drawback of silica, when used as filler, is that the presence of polar hydroxyl groups on its surface induces, in conventional non-polar elastomers, particle aggregation and poor dispersion, which results in a decrement of the mechanical properties. Furthermore, the incorporation of silica into elastomers by mechanical mixing requires long mixing times at elevated temperatures and therefore high power consumption. Among the various strategies devised to circumvent the above problems, the most popular is the reduction of silica surface polarity by treatment with silane coupling agents, which, however, are expensive and can interfere with the vulcanization process [170].

In this study silica reinforced polyisoprene rubber samples were prepared by exploiting the sol-gel process, a strategy that has been recently applied in this field for obtaining good silica dispersions [171–173]. In fact with this approach silica is generated in situ, i.e. directly in the rubber matrix, from a liquid precursor, typically tetraethoxysilane (TEOS), previously incorporated in the rubber. During the sol-gel process, as a result of the hydrolysis of TEOS ethoxysilane (-Si-OC$_2$H$_5$) groups, silanol (-Si-OH) groups are first formed, which then react with other ethoxysilane or silanol groups and form
siloxane (Si-O-Si) linkages through condensation reactions, in which water or ethanol are eliminated [171–173]. The use of TEOS to prepare silica filled elastomers has been reported for several polymers (see for instance ref. [174–178]). A major potential of the sol-gel technique stems from the possibility to control the amount of silica generated in-situ and its morphological characteristics by a proper selection of the reaction conditions (e.g. amount of TEOS, type and amount of catalyst, temperature and reaction time). Furthermore, it is possible to tailor filler-filler and filler-rubber interactions through the incorporation of silane coupling agents in the reaction mixture. These compounds carry in their molecule functional groups suitable to improve filler-matrix interactions, thus allowing to obtain a better silica dispersion and a higher mechanical reinforcement [179, 180].

In this work isoprene rubber (IR) was dissolved in toluene at the refluxing temperature and, after cooling at room temperature, a given amount of TEOS, water and ethanol were added, together with dibutyltin dilaurate as catalyst for the sol-gel process and a vulcanizing agent. In some cases octyltriethoxysilane (OTES) was added as coupling agent between silica and IR. The mixtures were stirred and heated for different times to activate the hydrolysis of TEOS, and then toluene, ethanol and water were eliminated by evaporation. All samples were eventually vulcanized. All the experimental details of samples preparation can be found in the experimental section at the end of this chapter, as well as in a recent publication by us [181].

The aim of the SSNMR study has been a detailed characterization of several molecular properties of these novel composites. In particular we have focussed on the structural properties of the in-situ generated silica, which have been investigated through high-resolution $^{29}\text{Si}$, $^{13}\text{C}$ and $^1\text{H}$ spectra, and on the dynamic properties of the hybrid systems, for which we exploited measurements of proton spin-spin ($T_2$) and spin-lattice relaxation times in the laboratory ($T_1$) and rotating frame ($T_{1\rho}$), as well as 2D $^1\text{H}$-$^{29}\text{Si}$ WISE experiment. Especially valuable has been the availability of a large number of different IR/SiO$_2$ vulcanizates, which allowed us to study the influence of several variables on the structural and dynamic properties investigated through SSNMR. In particular, the following variables have been considered:

a) initial content of TEOS,

b) sol-gel reaction time, and

c) addition to the reaction mixture of octyltriethoxysilane (OTES), a silane coupling agent.

More specifically, three initial TEOS contents were considered and, for each content,
the sol-gel reaction was stopped at different times and the resulting compound was vulcanized. Thus, three series of vulcanizates were obtained, which were coded IRV\(_{30z}\), IRV\(_{50z}\) and IRV\(_{70z}\), where \(z\) is the reaction time (in minutes), while 30, 50 and 70 represent the nominal silica contents, i.e. the phr (parts per hundred of rubber) of silica expected on the basis of the initial TEOS content, assuming a complete conversion of TEOS. For the composition corresponding to 30 phr of silica, two further samples were considered, namely IRV\(_{30 \_0 \_180}\) and IRV\(_{30 \_30 \_180}\), which differed for the time of addition of OTES (at 0 min and at 30 min of the sol-gel reaction time, respectively). Finally, the unfilled IR vulcanizate (IRV) was used as a reference material. The complete list of the materials investigated in this work is reported in Table 5.1, together with compositional data as obtained from TGA.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Silica content</th>
<th>(C_{\text{TEOS}})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>phr</td>
<td>wt%</td>
</tr>
<tr>
<td>IRV(_{30_0})</td>
<td>10.9</td>
<td>9.8</td>
</tr>
<tr>
<td>IRV(_{30_30})</td>
<td>16.1</td>
<td>13.9</td>
</tr>
<tr>
<td>IRV(_{30_60})</td>
<td>17.9</td>
<td>15.2</td>
</tr>
<tr>
<td>IRV(_{30_180})</td>
<td>23.9</td>
<td>19.3</td>
</tr>
<tr>
<td>IRV(_{50_0})</td>
<td>9.6</td>
<td>8.7</td>
</tr>
<tr>
<td>IRV(_{50_30})</td>
<td>34.5</td>
<td>25.6</td>
</tr>
<tr>
<td>IRV(_{50_60})</td>
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<td>28.0</td>
</tr>
<tr>
<td>IRV(_{50_180})</td>
<td>43.0</td>
<td>30.1</td>
</tr>
<tr>
<td>IRV(_{70_0})</td>
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<td>12.5</td>
</tr>
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<td>49.5</td>
<td>33.1</td>
</tr>
<tr>
<td>IRV(_{30_0_180})</td>
<td>29.9</td>
<td>23.0</td>
</tr>
<tr>
<td>IRV(_{30_30_180})</td>
<td>27.7</td>
<td>21.7</td>
</tr>
</tbody>
</table>

Table 5.1: Silica content as determined by TGA and conversion of TEOS to silica \((C_{\text{TEOS}})\) of the prepared filled rubber samples.

The SSNMR results were also compared with the results of other important characterization techniques such as TGA, SEM and mechanical measurements, performed by the Modena and Brescia groups.

The results of this work are presented in the following section, in which structural and dynamic properties of the samples are separately considered.
5.3 Results and discussions

5.3.1 Structural Properties

5.3.1.1 $^{29}$Si

The structure of the in situ generated silica (and of OTES when added) has been characterized in detail by means of $^{29}$Si high-resolution spectra. This is quite important considering that the preparation of this kind of systems was performed for the first time and thus it appears of interest to get insights into the structural features of the obtained silica and the kinetics of the sol-gel process, both in dependence of several experimental variables.

With the aim of characterizing the structural dependence of the in situ generated silica on the TEOS content as well as its evolution with the sol-gel reaction time, we recorded $^{29}$Si CP-MAS spectra of all the filled rubbers (Fig. 5.1). In all the spectra three signals can be clearly recognized at -112, -103 and -94 ppm and assigned to fully condensed silicon nuclei ($Q^4$ : (Si(OSi)$_4$)), single silanols ($Q^3$ : (Si(OSi)$_3$OH)), and geminal silanols ($Q^2$ : (Si(OSi)$_2$(OH)$_2$)), respectively (see Appendix A). Indeed, the same signals could also arise from non- or partially hydrolyzed TEOS; however, the presence of ethoxy groups could be ruled out from the $^{13}$C CP-MAS spectrum at least for IRV$_{30}$.180 (reported in the following). Given the dependence of CP signal integrals on contact time, different for silicon nuclei experiencing different $^1$H-$^{29}$Si dipolar couplings, CP spectra are intrinsically non-quantitative, being generally favoured, in decreasing order, $Q^2$, $Q^3$, $Q^4$ signals [90].

Nonetheless, since we verified a similar CP dynamics for all samples, the spectra, recorded in the same experimental conditions, can be compared and commented in terms of structural differences among the samples. The first observation concerns the overall integral of the spectra, which is related to the content of silica. It is evident that for IRV$_{50}$z and IRV$_{70}$z there is a strong increase of the integral in passing from 0 to 30 minutes of sol-gel reaction time, while for longer times the increase is less pronounced. On the contrary, for IRV$_{30}$z the increase between 0 and 60 minutes is quite small and the maximum increase is observed in passing from 60 to 180 minutes of sol-gel reaction, in qualitative agreement with composition data reported in Table 5.1, indicating that the kinetics of the reaction is quite strongly related to the TEOS content. Qualitative information on the condensation degree of the formed silica can be obtained by looking at the intensity of $Q^3$ and $Q^2$ silicon signals with respect to that of $Q^4$: the most evident result is the increase of the $Q^3/Q^4$ ratio with increasing the reaction time, which indicates a corresponding decrease of the condensation degree of the silica formed. In order
Study of novel composites of isoprene rubber reinforced with in situ generated silica particles

Figure 5.1: $^{29}$Si CP-MAS spectra, acquired at a MAS frequency of 3.5 kHz, of (a) IRV$_{30\,x}$; (b) IRV$_{50\,x}$; (c) IRV$_{70\,x}$; small peaks visible at about -60, -70 ppm are spinning sidebands. The signal assignments are reported on the peaks.
to obtain a quantitative estimate of the silica condensation degree, a DE (see Subsec-
tion 2.5.1) $^{29}\text{Si}$ spectrum was recorded on one vulcanizate (IRV$_{30\_180}$), using a recycle
delay between two consecutive transients long enough (300 s) to ensure the quantification
of the signal integrals.

\[
\text{c.d.} = \frac{4Q_4 + 3Q_3 + 2Q_2}{4(Q_4 + Q_3 + Q_2)} \quad (5.1)
\]

where $Q_i$ is the integral, in arbitrary units, of the corresponding $Q^i$ signal. The silica
condensation degree values obtained for the various rubbers analyzed are reported in
Table 5.2 and plotted vs. the sol-gel reaction time in Fig. 5.4. It can be observed that
the condensation degree is always high (0.915 ÷ 0.946); at almost all the reaction times
it decreases in passing from IRV$_{50\_z}$ to IRV$_{30\_z}$ to IRV$_{70\_z}$, and, for all the three
series, it tends to decrease with increasing the reaction time.

Figure 5.2: Comparison between $^{29}\text{Si}$ CP- and DE-MAS spectra of IRV$_{30\_180}$, acquired at a MAS
frequency of 3.5 kHz. The small peaks visible at about -20 ppm (marked with asterisk) in DE-MAS
spectrum is probably due to impurities of silicone rubber. The signal assignments are reported on the
peaks.

The DE spectrum clearly shows that fully condensed ($Q^4$) silicon nuclei are the
most abundant species, contrary to what appears from the CP spectrum of the same
sample Fig. 5.2. By comparing $Q^2$, $Q^3$ and $Q^4$ signal integrals in the DE spectrum
with the corresponding ones in the CP spectrum, both obtained by suitable spectral
deconvolutions (see Fig. 5.3) we could obtain scaling factors that, applied to the signal
integrals of the CP spectra of all the samples, allowed us to estimate their corresponding
quantitative values (see Table 5.2). Then, by using these values, we could estimate the
condensation degree (c.d.) of silica in all materials, defined by the following equation as
the ratio between condensed Si-O-Si groups and total number of Si-O groups:
Figure 5.3: Deconvolution of the $^{29}$Si CP-MAS spectrum of IRV$_{30,180}$ composite. The spectrum was well deconvolved with the 85, 100 and 87 % of Gaussian lineshape and the corresponding linewidths were 590, 490 and 670 Hz for $Q^2$, $Q^3$ and $Q^4$ signals, respectively.

Figure 5.4: Plot of silica condensation degree vs. sol-gel reaction time, as obtained from $^{29}$Si SSNMR spectra. Symbols: open circle: IRV$_{30,x}$; full diamond: IRV$_{30,0,x}$; open diamond: IRV$_{30,30,x}$; full triangle: IRV$_{50,x}$; open triangle: IRV$_{70,x}$. 
<table>
<thead>
<tr>
<th>Sample</th>
<th>Cross-Polarization</th>
<th>Direct-Excitation</th>
<th>Condensation degree</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$Q^2$ %</td>
<td>$Q^3$ %</td>
<td>$Q^4$ %</td>
</tr>
<tr>
<td>IRV_30_0</td>
<td>5.0</td>
<td>45.2</td>
<td>49.8</td>
</tr>
<tr>
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<td>49.7</td>
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<td>40.6</td>
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<td>IRV_30_30_180</td>
<td>5.5</td>
<td>45.9</td>
<td>48.6</td>
</tr>
</tbody>
</table>

Table 5.2: Integrals of the signals of the different silica silicon species ($Q_i$) obtained from deconvolutions of $^{29}$Si CP-MAS spectra (“Cross-Polarization” columns). In the “Direct Excitation” column the signal integrals of the quantitative DE-MAS spectrum of IRV\_30\_180, representing the actual $Q_i$ silicon percentages, are reported. As described in the text, the “Direct Excitation” $Q_i$ values for all the other samples have been calculated by multiplying the $Q_i$ integrals measured in their CP spectra for the corresponding scaling factors $Q_i$(DE)/$Q_i$(CP) experimentally obtained for IRV\_30\_180. In the last column of the table, silica condensation degree values, calculated as defined in Eq. 5.1, have been reported. The experimental uncertainties on $Q_i$ integrals and condensation degree values are ± 0.05 and ± 0.002, respectively.
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These results empirically suggest that, as a consequence of the complex interplay of the many kinetic and thermodynamic factors involved in the sol-gel processes, the hydrolysis and condensation reactions tend to become more and less favored, respectively, as the reaction time increases. From an alternative standpoint, a larger fraction of silanols becomes sterically unaccessible for condensation. Moreover, the compositions of the IRV.50_z are the ones ensuring the most efficient condensation degree at almost all the reaction times, even though the differences with the other compositions are quite small.

![Figure 5.5: 29Si CP-MAS spectra, acquired at a MAS frequency of 6 kHz, of IRV.30.0.180 and IRV.30.30.180; in the inset an expansion of the T silicon signals is shown. The signal assignments are reported on the peaks.](image)

29Si CP-MAS spectra were also recorded for the samples containing OTES (IRV.30.0.180 and IRV.30.30.180) and they are shown in Fig. 5.5. Signals ascribable to T3 \((\text{Si(OSi)}_3 \text{R})\) and T2 \((\text{Si(OSi)}_2 \text{(OX)} \text{R, with X=H or CH}_2 \text{CH}_3)\) OTES silicon nuclei can be observed at -67 and -58 ppm, respectively. Their presence indicates a noticeable degree of condensation for the SiO groups of OTES reacted with silica, which must be probably ascribed also to a partial self-condensation among OTES molecules. The spectra clearly show that OTES condensation is higher when it is added at the beginning of the reaction. By comparing the silica condensation degree in these two materials (obtained by applying the above described scaling factors to the \(Q_i\) signal integrals in their CP spectra recorded in the same experimental conditions as used for all the rubbers without OTES) with that of the corresponding vulcanizate without OTES i.e. IRV.30.180 (see Table 5.2), it can be observed that the presence of OTES, especially if added after 30 minutes of the sol-gel reaction, seems to favor the condensation of silica.
5.3.1.2 $^{13}$C

In Fig. 5.6, $^{13}$C CP-MAS spectra of pure polymer (IRV) and IRV$_{30,180}$ is presented. All the characteristic signals of the cis-isoprene are visible (shown in Fig. 5.6 (a)), in addition, some trans-isoprene signals can be seen whose methyl and methylene carbons resonate at 15 and 39 ppm respectively. There are no significant changes between polymer and IRV$_{30,180}$ composite. The absence of ethoxy signals (which usually resonate at 17 and 59 ppm) suggests that there is no unhydrolyzed TEOS present in the composite.

![Figure 5.6: $^{13}$C CP-MAS spectra, acquired at a MAS frequency of 4 kHz, of IRV (a) and IRV$_{30,180}$ (b). The signal assignments are reported on the peaks along with the molecular structure of cis-polyisoprene. The small peaks marked with asterisks arise from the impurities.](image)

The $^{13}$C CP-MAS experiment was also performed on a composite containing OTES (IRV$_{30,30,180}$), but the presence of OTES could not be confirmed due to its very small amount compared to the polymer. The significant evidence of the presence of OTES has been given by $^{29}$Si spectra discussed before. The selective direct excitation experiment was also performed on carbon with a short recycle delay of 2 s, in order to select only...
the mobile components of the system (see Subsection 2.5.1). On the whole, the direct excitation spectra of polymer and composites didn’t show significant differences from that of their corresponding CP spectra. However, the signal to noise ratios obtained for all the carbons signals were quite high compared to their CP counterparts which implies that the most of the polymer is quite mobile.

5.3.1.3 $^1$H

In Fig. 5.7, the $^1$H MAS spectrum of the pure polymer is reported. All the proton resonances of the polyisoprene are present. The $^1$H spectra of polymer (IRV) (see Fig. 5.7) and of the composites (not shown) were similar. The narrow protons peaks confirm that the bulk of the polymer is mobile. Due to the very small amount of silanol protons present in the composite (maximum 2 % of silanol protons) the silanol proton signal is not clearly visible in the proton MAS spectrum.

Figure 5.7: $^1$H MAS spectra of IRV, acquired at a MAS frequency of 6.5 kHz. The signal assignements are reported on the peaks.

The $^1$H spectra of polymer and composites acquired at static conditions (not shown),
show that, in addition to the narrow proton linewidth of $\approx 1$ kHz, there is a broader peak in all the samples studied. This suggests the presence of quite rigid domains together with the mobile polymer bulk. In order to get better insights about the dynamic properties of these systems, it is better to move on to the relaxation times measurements which will be discussed in the following together with the 2D WISE experiment.

5.3 Dynamic Properties

In order to investigate the dynamic properties of IR in the composites, and in particular their possible relations with chemical composition, preparation conditions and mechanical properties, we measured $^1$H spin-spin ($T_2$) and spin-lattice in the laboratory ($T_1$) and rotating ($T_{1\rho}$) frames relaxation times.

$T_2$ were measured at a magnetic field of 25 MHz, working with the FID in on-resonance conditions (see Subsection 2.6.2). Since from preliminary measurements it was quite clear that the FID had different components, decaying with quite different $T_2$, both solid-echo (SEPS) and Hahn echo (HEPS) pulse sequences (described in Subsubsection 2.6.2.1), which are suitable for fast and slow decaying components, respectively, were used. In particular, transverse magnetization decay curves were built by matching the first 160 $\mu$S of the FIDs as obtained from SEPS with the decay curves obtained from HEPS (magnetization vs. $2\tau$) [156] (all the experimental details will be reported in Section 5.5). Transverse magnetization decay curves were obtained for all samples reported in Table 5.1. $T_2$ values could be obtained by fitting the experimental curves to a linear combination of the minimum number of suitable analytical functions as described in Subsubsection 2.6.2.1. For all the samples the curves resulted to be well fitted by a combination of two exponentials and a Weibullian function has shown in Fig. 5.8. The analytical expression of the fitting function was the following:

$$M(t) = M_a(0)\left[e^{-\frac{t}{T_{2a}}}\right] + M_b(0)\left[e^{-\left(\frac{t}{T_{2b}}\right)^\alpha}\right] + M_c(0)\left[e^{-\left(\frac{t}{T_{2c}}\right)}\right]$$

where $M_i(0)$ is the amplitude of the relaxation components, which suitably normalized corresponds to the percentage of protons in the sample having $T_2 = T_{2i}$, $T_{2i}$ is the spin-spin relaxation time, and $\alpha$ is the Weibullian decay shape parameter (ranging from 1 to 2). Since in all cases $T_{2a}$ and $\alpha$ were approximatively the same, we fixed their values in order to reduce the correlation among the fitting parameters and facilitate the physical interpretation of the results. The fitting results for all samples are reported in Table 5.3. In all samples three motionally different proton fractions can be identified. The one characterized by a $T_2$ of 70 $\mu$s is the most rigid and can be assigned to the IR chains closest to the silica domains, whose mobility is strongly restricted by the interfacial interactions with the filler. The most abundant protons fraction shows a $T_2$
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Figure 5.8: Fitting curve of a sample together with the experimental points is shown; (a) $^1$H Transverse magnetization decay curve of a composite: Experimental (dots) and fitting function (line), (b) Experimental (dots) and individual components of the fitting function (red line - 1st component, blue line - 2nd component, green line - 3rd component; in the inset an expansion of the initial part of the magnetization decay curve is shown.
Sample & $1^{st}$ component, $f = E$ & $2^{nd}$ component, $f = W$ & $3^{rd}$ component, $f = E$ & T$_{2a}$ [ms] (fixed) & wt % & T$_{2b}$ [ms], $\alpha = 1.5$ & wt % & T$_{2c}$ [ms] & wt % \\
IRV & 0.07 & 2 & 1.33 & 91 & 10 & 7 \\
IRV_{30,0} & 0.07 & 7 & 1.65 & 78 & 5 & 15 \\
IRV_{30,30} & 0.07 & 7 & 1.67 & 81 & 5 & 12 \\
IRV_{30,60} & 0.07 & 5 & 1.38 & 89 & 10 & 6 \\
IRV_{30,180} & 0.07 & 16 & 1.56 & 79 & 10 & 5 \\
IRV_{50,0} & 0.07 & 4 & 1.37 & 83 & 5 & 13 \\
IRV_{50,30} & 0.07 & 7 & 1.35 & 90 & 10 & 3 \\
IRV_{50,60} & 0.07 & 7 & 1.34 & 89 & 10 & 4 \\
IRV_{50,180} & 0.07 & 7 & 1.36 & 87 & 10 & 6 \\
IRV_{70,0} & 0.07 & 5 & 1.35 & 86 & 10 & 9 \\
IRV_{70,30} & 0.07 & 8 & 1.44 & 90 & 10 & 2 \\
IRV_{70,60} & 0.07 & 7 & 1.35 & 87 & 10 & 6 \\
IRV_{70,180} & 0.07 & 8 & 1.38 & 88 & 10 & 4 \\
IRV_{30,0,180} & 0.07 & 7 & 1.35 & 89 & 10 & 4 \\
IRV_{30,30,180} & 0.07 & 6 & 1.31 & 89 & 10 & 5 \\
error & - & 3 % & 1 % & 1 % & - & 10 % \\

Table 5.3: Results of the $^1$H-FID analysis performed on all samples. For each function ($f$) proton transverse relaxation time ($T_2$) and weight percentage (wt %) are reported. In the last line, standard error of the fitting procedures is reported. $E$ and $W$ indicate exponential and Weibullian functions, respectively.
of about 1.4 ms and must be assigned to the bulk of the rubber, while that with the longest $T_2$ can be ascribed to “free” chains of the polymer, as end chains or chains free from entanglements, experiencing the largest mobility. This assignment is coherent with the results previously reported in the literature. Indeed, in particular an increased rigidity induced on rubber chains interfacially interacting with inorganic filler particles, corresponding to a $T_2$ of the order of tens of µs has been reported in several studies, for instance in natural rubber filled with Stöber silica [157] and EPDM filled with carbon black [156], and confirmed by $^1$H multiple quantum measurements [167]. It must be mentioned that a contribution of silica silanol protons to the fast decaying component cannot be ruled out. Indeed it is known that silanol protons in silica samples have a $T_2$ of the order of hundreds of µs [90, 157], which can be strongly affected by the extent of hydrogen bonds that they are able to form. However, from quantitative $^{29}$Si spectra we could estimate a maximum amount of silanol protons of about 2 % of the total amount of protons in the samples. The higher value of $M_a(0)$ obtained by $T_2$ measurement in all the samples confirms that a significant fraction of polymer protons is responsible for the short $T_{2a}$.

Moreover, in order to further confirm this interpretation we recorded a 2D $^1$H-$^{29}$Si

Figure 5.9: 2D $^1$H-$^{29}$Si WISE map of IRV$_{30,180}$ acquired at a MAS frequency of 3.5 kHz. On the left hand side, $^1$H static spectrum corresponds to the Q$^3$ silicons is presented.
WISE spectrum (described in Subsubsection 2.5.8.2) which has been reported in Fig. 5.9: for each $^{29}$Si isotropic signal resolved in the first dimension, the broad-line signal of the dipolarly coupled $^1$H nuclei is observed in the second dimension. The experiment is carried out under slow magic-angle spinning (3.5 kHz) in order to achieve resolution in the $^{29}$Si dimension. For all the $^{29}$Si signals an intense 13 kHz wide proton signal was observed. Considering the relation between $T_2$ and $\Delta \nu$ ($\Delta \nu = 1/\pi T_2$, at least in the case of an exponential FID), this value is larger than that corresponding to a proton $T_2$ of 70 $\mu$s ($\approx$ 4 kHz) but such a difference can be ascribed to the higher magnetic field strength (corresponding to a $^1$H Larmor frequency of 400 MHz) at which the WISE experiment was carried out compared to that used for proton $T_2$ measurements (24 MHz), which can sensibly increase the extent of proton chemical shift anisotropy and chemical shift distribution. However the result of this experiment confirms that there is a noticeable fraction of protons with restricted mobility in close proximity to $^{29}$Si nuclei.

It is interesting to look at the trend of the weight of shortest $T_2$ component, which can be related to the amount of rubber-silica interface, as a function of samples composition, which is reported in Fig. 5.10. This component is almost absent in the pure polymer (IRV), while it immediately appears in the composites, even at the beginning of the sol-gel reaction, in agreement with the early formation of some silica, as indicated by TGA (see Table 5.1). Then the amount of interface remains approximatively the same (6 ± 2 %) up to 180 minutes of sol-gel reaction, except for the IRV 30 z sample in
which it shows a remarkable increase (up to 16 %) after 180 minutes of reaction. This peculiar increase is in agreement with the peculiar kinetics of silica formation of this sample highlighted by $^{29}$Si spectra and also TGA, but the very high value of the weight of this fraction cannot be explained with a correspondingly high silica content. Indeed it is clear from TGA that, after 180 minutes of reaction, the sample IRV$_{30}$ is the one containing the lowest amount of silica. Therefore the large amount of interface highlighted by T$_2$ measurements suggests that IRV$_{30,180}$ has a very good silica dispersion which maximizes the interface with the rubber.

![Figure 5.11: Plot of the T$_2$ of the Weibullian component of the FID for the pure polymer and the composites IRV$_{30,z}$, IRV$_{50,z}$ and IRV$_{70,z}$ obtained at different sol-gel reaction times.](image)

In Fig. 5.11, the trend of the T$_2$ of the Weibullian component is reported: it shows that the dynamics of the polymer chains seems to not substantially change from pure polymer to IRV$_{50}$ and IRV$_{70}$ and it is not very much affected by the reaction times. On the contrary, IRV$_{30}$ shows again a different behaviour. In particular, it always show a clearly longer T$_2$, suggesting that the peculiar amount and dispersion of silica improves the mobility of the polymeric chains, may be reducing the cross links or entanglements of the polymer network.

As far as the very mobile component is concerned, its T$_2$ is always very long, indicating a high mobility while its weight tends to decrease with increasing reaction time, which can be ascribed to the increasing amount of silica, which can induce a partial reduction of the free end chain mobility. The trend of the weight of this longest T$_2$
component as a function of samples composition is shown in Fig. 5.12.

![Graph showing weight of longest T₂ component as a function of reaction time for pure polymer and composites IRV₃₀, IRV₅₀, and IRV₇₀](image)

Figure 5.12: Plot of the weight of longest $T_2$ component of the FID for the pure polymer and the composites IRV₃₀, IRV₅₀, and IRV₇₀ obtained at different sol-gel reaction times.

The effect of the presence of OTES was investigated on samples IRV₃₀₀₁₈₀ and IRV₃₀₃₀₁₈₀ and the results are reported in Table 5.3. The results show that there is 10% of protons which is “transferred” from the fastest decaying exponential component to the Weibullian one. The amount of protons ascribable to OTES is less than 2%, therefore these results indicate an average increased mobility of the samples and a decrease of the rigid interface. This can be ascribed to the presence of the silane alkyl chains which could reduce the direct interfacial interactions between silica and the rubber, so decreasing the amount of chains with restricted mobility [157]. The time at which OTES is added does not seem to affect the result.

In order to investigate the dynamic properties of the polymer on the composites in the motional frequency regimes of tens of kHz and tens-hundreds of MHz proton $T_1$ and $T_1\rho$ were also measured for all the composites at 180 minutes of sol-gel reaction. In all samples a single and two different values were measured for $T_1$ (see Table 5.4) and $T_1\rho$ (see Table 5.5), respectively. This must be ascribed to a different spin-diffusion behavior and indicates that the polymeric fractions of the samples are homogeneous on, approximately, a 100 Å spatial scale, while they are not fully homogeneous on a 10 Å scale. By comparing the results obtained for the different samples it is possible to conclude that no significant differences exist among them, indicating that, on the whole,
the dynamic behavior of the polymer in the kHz-MHz regime is not detectably affected by the presence of the filler.

<table>
<thead>
<tr>
<th>Sample</th>
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<tr>
<td>IRV_{70_180}</td>
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Table 5.4: $^1$H spin-lattice relaxation times in the laboratory frame ($T_1$) measured at a Larmor frequency of 400 MHz for the polymer and its composites with different initial silica content obtained at 180 min of reaction time. The magnetization recovery curves were well reproduced by a mono-exponential function for all the samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_{1p}^\rho$ (ms)</th>
<th>$T_{1p}^\rho$ (ms)</th>
<th>1/PWRA (ms)</th>
</tr>
</thead>
<tbody>
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<td>$T_{1p}$ (wt %)</td>
<td>$T_{1p}$ (wt %)</td>
<td></td>
</tr>
<tr>
<td>IRV</td>
<td>4.5 15 13.2 85</td>
<td>10.3</td>
<td></td>
</tr>
<tr>
<td>IRV_{30_180}</td>
<td>3.4 14 13.2 86</td>
<td>9.4</td>
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<tr>
<td>IRV_{50_180}</td>
<td>3.3 15 13.0 85</td>
<td>9.0</td>
<td></td>
</tr>
<tr>
<td>IRV_{70_180}</td>
<td>4.5 19 14.2 81</td>
<td>10.1</td>
<td></td>
</tr>
</tbody>
</table>

Table 5.5: $^1$H spin-lattice relaxation times in the rotating frame ($T_{1p}^\rho$) measured at a Larmor frequency of 400 MHz and at a spin-lock frequency of 35 kHz for the polymer and its composites with different initial silica content obtained at 180 min of reaction time. The trends magnetization were well reproduced by bi-exponential function for all the samples.

5.3.2.1 Comparison with results of morphological analysis, swelling and mechanical measurements

Even if, considering the very different spatial and time scales investigated by the different techniques, a direct comparison is not straightforward, it is worth reporting the most significant results of SEM, swelling and mechanical analyses that were carried out by the groups of Modena and Brescia on the samples investigated [181] and compare them with the NMR results.

In Fig. 5.13–5.17 SEM images of samples at 60 and 180 minutes of reactions are shown. IRV_{30\_z} were characterized by a homogeneous distribution of silica particles within the rubber matrix. The average dimensions increased with the reaction time (diameter values of 1 µm or less for IRV_{30\_60} and of 3 µm or less for IRV_{30\_180}) presumably due to both the increased amount of silica formed and to coalescence phenomena of
5.3 Results and discussions

Figure 5.13: SEM micrographs of a cross-section of IRV\(_{30,60}\) (a, b) and IRV\(_{30,180}\) (c, d).

Figure 5.14: SEM micrographs of a cross-section of IRV\(_{50,60}\) (a, b) and IRV\(_{50,180}\) (c, d).
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Figure 5.15: SEM micrographs of a cross-section of IRV\textsubscript{70,60} (a, b) and IRV\textsubscript{70,180} (c, d).

Figure 5.16: SEM micrographs of a cross-section of IRV\textsubscript{30,0,60} (a-c) and IRV\textsubscript{30,0,180} (d-f).
the growing particles. The distribution of silica particles was quite homogeneous also in the case of the intermediate initial TEOS content and sol-gel reaction time (IRV$_{30,60}$, Fig. 5.14) while a significantly increased inhomogeneity was observed for IRV$_{50,180}$, IRV$_{70,60}$ and IRV$_{70,180}$ (Fig. 5.14–5.15). Apart from a worse distribution, some big particles (diameter of 10-30 µm) were observed in IRV$_{50,180}$ and IRV$_{70,180}$, presumably due to coalescence phenomena, even if the typical diameter of silica particles was actually maintained in the range 1-3 µm or less.

SEM micrographs reported in Fig. 5.16–5.17 show that the delayed addition of OTES (IRV$_{30,30,z}$ with respect to IRV$_{30,0,z}$) led to a markedly improved homogeneity with particular concern to the highest sol-gel reaction time. Indeed, the average size and distribution of silica particles were more or less the same for IRV$_{30,0,60}$ and IRV$_{30,30,60}$, while after 180 min of sol-gel reaction time a very good distribution uniformity was obtained only in the case of IRV$_{30,30,180}$.

It is worth noticing that the sample showing the highest amount of interface from T$_2$ measurements, IRV$_{30,180}$, is the one showing the best silica dispersion within the polymer matrix, which indeed should maximize the interface between the rubber and the filler.

In Fig. 5.18, the swelling ratio, i.e. the solvent absorbed per unit mass of material, is plotted as a function of reaction time for the different sets of samples. This quantity decreases with time and substantially follows the increase of silica concentration (see
Figure 5.18: Swelling ratio as a function of the sol-gel reaction time for rubbers prepared in the absence (a) and in the presence (b) of OTES. Symbols: full circle: IRV; open circle: IRV_{30,z}; full diamond: IRV_{30,0,z}; open diamond: IRV_{30,30,z}; full triangle: IRV_{50,z}; open triangle: IRV_{70,z}.
Table 5.1), not showing particular correlation with $T_2$ results. The swelling behavior is dominated by the concentration of the filler and indicates good whole adhesion between rubber and silica at their interface. Silica does not absorb the solvent used for swelling, that is toluene, and when good adhesion exists at the rubber-filler interface, non-absorbing silica particles restrict swelling of the IR network located in proximity of the interface. The differences in the amount of interface detected by NMR probably occur on a scale that is too small for swelling measurements sensitivity.

At last several mechanical measurements were carried out on the samples. In Fig. 5.19 variation of the initial modulus\(^1\) (black symbols) and of the secant modulus\(^2\) at $e = 1$ (grey symbols) is shown vs. the silica volume fraction\(^3\) ($\Phi$) in the unswollen state. Even if some scattering of the experimental data can be noticed, the values of $E_{in}$ for the various systems can be described at least approximately by a single curve and the same occurs for $E_{sec,e=1}$. The curves calculated from the Guth equation [154]:

$$E = E_o(1 + 2.5\Phi + 14.1\Phi^2)$$

are shown for comparison. In Eq. 5.3, $E$ and $E_o$ are the moduli (initial or secant) of

---

\(^1\)The initial slope of the stress-strain curve.

\(^2\)The slope of the line connecting the origin and a given point on the stress-strain curve.

\(^3\)The volume fraction ($\Phi$) is defined as the volume of a constituent of a mixture divided by the sum of volumes of all constituents prior to mixing.
the filled and unfilled rubber, respectively. The Guth equation is useful to predict the modulus of rubbers containing rigid spherical particles. Its validity is limited to low contents, where the filler particles are either isolated or interact pair-wise. At higher concentrations, large deviations from the Guth equation are observed because, above a critical concentration (percolation threshold), the filler particles form a physical network [152] within the matrix, which causes a considerable raise of modulus in comparison with predictions of Eq. 5.3.

As regards the initial modulus, the Guth equation can fit the experimental data only for \( \Phi < 0.16 \) (corresponding to approximately 25 wt\% of silica), which therefore represents at least approximately the percolation threshold for the systems investigated in this work. In contrast, the secant modulus data follow the prediction of Eq. 5.3 in the whole range of silica contents explored \((0 < \Phi < 0.22)\). In addition, it is evident from Fig. 5.19 that for \( \Phi > 0.16 \) a drastic stiffness reduction occurs passing from low to large strain levels. This behavior resembles the non-linear dynamic-mechanical behavior typical of filled rubbers, for which the dynamic storage modulus decreases with increasing the strain amplitude (Payne effect) [182]. The Payne effect is generally considered as a consequence of the disruption of the filler network under cyclic strain [183]. Therefore data of Fig. 5.19 suggest that, when the materials with the highest silica contents \((\text{IRV}_{50\,60}, \text{IRV}_{50\,180}, \text{IRV}_{70\,30}, \text{IRV}_{70\,60} \text{and IRV}_{70\,180})\) are in the un-deformed state, the filler forms a network that strongly increases the stiffness of these rubbers. When they are stretched to a sufficiently high elongation, the silica network is disrupted and a remarkable modulus drop takes place. The good fitting of \( E_{sec,e=1} \) data obtained with the Guth equation suggests that, for \( e = 1 \), mainly isolated or pair-wise interacting particles are dispersed within the stretched IR matrix.

It is therefore quite evident that also the mechanical behaviour is mainly determined by silica content and a direct comparison with dynamic properties investigated through NMR is made difficult certainly by very different frequency ranges involved in mechanical and in NMR measurements. Nonetheless, it is worth noticing that samples \( \text{IRV}_{30\,X} \) are always in the range predicted by the Guth equation, in agreement with the particularly good silica dispersion and interfacial interactions highlighted by SEM and NMR \( T_2 \) measurements.

5.4 Conclusions

The combination of high-resolution \(^{29}\text{Si}, ^{13}\text{C} \) and \(^{1}\text{H} \) spectra with low-resolution proton relaxation time measurements, carried out on a very extensive set of samples, allowed the characterization of the main molecular structural and dynamic properties of novel
composites of isoprene rubber filled with silica generated in situ through sol-gel process. In particular, from $^{29}$Si CP and DE spectra it was possible to monitor the evolution of the structure of the in situ generated silica with the time of the sol-gel reaction for different TEOS content and quantify its condensation degree. Silica resulted to be always well condensed, with a quite small but significant dependence on TEOS content and a condensation degree decreasing with increasing the time of the sol-gel reaction.

From the $^{13}$C CP-MAS spectra of polymer and composite no significant differences were found and the presence of OTES signals is not clearly visible due to its very less amount. The $^1$H MAS spectrum of polymer has quite narrow signals highlighting that they arise from the bulk of the polymer which seems quite mobile.

Proton relaxation times measurement gave a quite complete view of the homogeneity of the samples and of the dynamic properties of the polymer over a wide range of motional frequencies. In the composites the polymeric fractions resulted to be homogeneous on a 100 Å spatial scale, but not on a 10 Å spatial scale. No significant differences could be detected among the dynamic properties of different samples in the motional frequencies range of kHz-GHz, while interesting differences were detected in the slow motional processes (characteristic frequency of the order of Hz-kHz). In particular, three motionally different polymer fractions could be identified: a fraction interacting at the interface with silica, showing a restricted mobility, the more mobile polymer bulk, and the very much mobile “free” polymer chains. The rubber fraction ascribed to the interface with silica showed an interesting behaviour with samples composition. In particular, T$_2$ measurements highlighted an especially large amount of interface in the sample with the lowest TEOS content and reacted for the longest time (IRV$_{30\text{,180}}$).

The comparison with SEM, swelling and mechanical measurements, even if quite difficult, due to the very different spatial and time scales explored with respect to NMR, gave interesting results. Even if it was quite clear that swelling and mechanical properties are strongly influenced by silica content, the quality of the silica dispersion and the amount of interface also play an important role. The sample with the largest amount of interface as detected from proton T$_2$ measurements also showed the best silica dispersion and mechanical properties always in agreement with a model of isolated or pairwise interacting filler particles.
5.5 Experimental

Samples

Tetraethoxysilane, octyltriethoxysilane, dibutyltin dilaurate (DL), dicumyl peroxide (DCP), ethanol (EtOH) and toluene were purchased from Sigma-Aldrich and were used without further purification. Isoprene rubber with a 97% content of cis units, a viscosity-average molecular mass of $2.3 \times 10^6$ g/mol, a glass transition temperature of -67°C and a density of 0.91 g/cm$^3$ was purchased from Sigma-Aldrich.

IR polymer (4 g) was dissolved in toluene (100 ml) at the refluxing temperature and, after cooling at room temperature, a given amount of TEOS, H$_2$O and EtOH (TEOS:H$_2$O:EtOH = 1:4:4 molar ratio), DL (2 wt% relative to TEOS as catalyst for the sol-process) and DCP (1 wt% relative to IR as vulcanizing agent) were added. In some cases, OTES (4 wt% relative to IR) was added to mixtures corresponding to a nominal content of silica of 30 phr at the established reaction time, as surfactant/coupling agent. The mixtures usually assumed the aspect of an emulsion because of the presence of a significant amount of water in an organic medium. The mixtures were magnetically stirred and heated at 80 °C for different times (up to 3 hours) to activate the hydrolytic condensation of TEOS to silica. After the given reaction time, toluene and other volatile products such as H$_2$O and EtOH were eliminated by using a rotary evaporator operating at reduced pressure and room temperature, in order to avoid any significant further progress of the sol-gel reaction in solution.

All the samples were moulded into rectangular sheets (100×50×1.5 mm$^3$) and vulcanized at 150 °C for 20 min under a pressure of 150 bar by using a hot-plate hydraulic press (Carver Ltd).

SSNMR

$^{13}$C and $^{29}$Si high-resolution measurements were performed on a two-channel Varian Infinity Plus 400 spectrometer described in Chapter 2 in the Subsection 2.4.1, operating at 100.59 MHz for carbon-13 and at 79.47 MHz for silicon-29 nuclei, and equipped with a 7.5 mm CP-MAS (Cross Polarization-Magic Angle Spinning) probe, using a $^1$H 90° pulse length of 5 µs.

The $^{29}$Si CP and Direct Excitation (DE) MAS spectra were recorded under high-power $^1$H decoupling conditions and at a MAS frequency of 3.5 kHz. For samples with OTES the spectra were recorded at MAS frequencies of 3.5 and 6 kHz. For CP-MAS spectra, a contact time of 5 ms and a recycle delay of 3.5 s were used and 18000 transients were recorded. In the case of DE, the $^{29}$Si 90° pulse length was 6 µs, a recycle delay of 300 s
was used and 2000 scans were accumulated. $^1$H - $^{29}$Si 2D WISE experiment was carried out at a MAS frequency of 3.5 kHz under high power $^1$H decoupling conditions, using a recycle delay of 2 s. The proton evolution time ($t_1$) was incremented from 2 - 256 $\mu$s with steps of 2 $\mu$s and a contact pulse of 7 ms was used. 950 transients were recorded. The $^{13}$C CP- and DE-MAS spectra were acquired under high-power $^1$H decoupling conditions and at a MAS frequency of 4 kHz. For CP-MAS spectra, a contact time of 10 ms was used. In the case of selective DE-MAS spectra, a $^{13}$C 90$^\circ$ pulse length of 4.2 $\mu$s and a recycle delay of 2 s were used. In both the experiments, 22000 transients were recorded for all the samples investigated.

The $^1$H MAS spectra were recorded with 16 scans, a recycle delay of 3.5 s and at a spinning rate of 6.5 kHz.

Proton $T_1$ and $T_{1\rho}$ were measured in low-resolution (at static condition) by using saturation recovery and variable spin-lock time pulse sequences (see Subsection 2.6.2), respectively. For $^1$H $T_1$ the magnetization curve was obtained (Eq. 2.10) with $\tau$ values ranging from 0.001 to 5 s. In the case of $^1$H $T_{1\rho}$ the magnetization decay curve was obtained (Eq. 2.4) from the array of different spin lock (sl) times ranging from 0.1 to 50 ms. The pulse delay used for measuring the proton $T_{1\rho}$ was 3.5 s. Both the proton relaxation times measurements were recorded with 4 scans.

$^1$H $T_2$’s were measured in low-resolution on the Varian XL-100 interfaced with Stelar DS- NMR acquisition system described in Subsection 2.4.2 equipped with 5 mm probe head working at a $^1$H frequency of 25 MHz. $^1$H $T_2$’s were measured by combining Solid echo (SEPS) and Hahn echo (HEPS) sequences as described in the Subsection 5.3.2. Both Solid and Hahn echo were recorded with $^1$H 90$^\circ$ pulse length of 4 $\mu$s and with the recycle delay of 0.1 s. In the case of solid echo the delay $\tau$ between the 90$^\circ$ pulses (see Subsubsection 2.6.2.1 & Fig. 2.15) was always 14 $\mu$s for all the samples studied and 1000 scans were recorded. For Hahn echo (see Fig. 2.16 from Chapter 2), 500 scans were recorded and variable echo delays were employed ranging from 40 $\mu$s to 25 ms (112 delays were recorded). Since the experiment was carried on an on-resonance conditions, the intensity of the signal was obtained from the average of the intensities of first three points of the FID and the magnetization $vs. 2\tau$ decay curve was obtained for HEPS.

All the experiments were acquired at room temperature.

**TGA**

The actual silica content in the filled rubber was determined by measuring the weight loss of a sample when combusted to oxidize all organic matter according to ASTM D 5630 Technical Standard (Procedure A. Muffle-Furnace Technique). At least two specimens were tested for each material.
The morphological investigation was carried out by scanning electron microscopy using a Quanta 200 FEI microscope under an accelerating voltage of 15 kV. The sample surfaces (cross section) were coated with gold by an electro-deposition method to impart electrical conduction before recording SEM micrographs.

The density of neat silica, purposely prepared according to the above reported synthetic conditions from TEOS and DL only, was determined by a pycnometer (AccuPyc 1330 apparatus, Micromeritics, Norcross, GA, USA).

Swelling experiments

Samples 5×5×1.5 mm³ in size were immersed in toluene, which was replaced daily with fresh solvent, and after 96 hrs their swollen mass mₘ was recorded. Toluene was eliminated to determine the dry mass mₖ of the samples. The swelling ratio qₘ was evaluated from an average of at least three measurements according to Eq. 5.4:

\[ qₘ = \frac{mₘ}{mₖ} \]  

(5.4)

Mechanical measurements

Uniaxial tensile tests were performed by an Instron dynamometer (model 3366). The experiments were run at room temperature, on strips 50×5×1.5 mm³ in size, using a gage length of 25 mm and a crosshead speed of 10 mm/min. Tensile test data were obtained as nominal stress \( \sigmaₙ = F/A₀ \) versus elongation \( e=Δl/l₀ \) curves, where \( F \) is the applied force and \( A₀ \) is the initial cross-section area of the specimen, while \( Δl \) and \( l₀ \) are the change in length and the gage length, respectively. The initial modulus \( Eᵢn \) was calculated as the slope of the initial portion of the \( \sigmaₙ - e \) curves. The secant modulus at a given elongation \( Eₖₑc,e \) was calculated as \( Eₖₑc,e = \sigmaₙ(e)/e \), where \( \sigmaₙ(e) \) is the nominal stress at the elongation (e) considered. All mechanical properties were determined on an average of at least four specimens.
Chapter 6

Study of modified bentonite clays and LDPE-clay nanocomposites

Abstract

Nowadays, clay minerals have attracted a great interest in designing and preparing nanocomposites with a wide variety of polymer systems, since these materials show remarkably improved properties (mechanical properties, as well as decreased gas permeability and flammability, etc.) with respect to their micro counterparts and pristine polymers. Due to the substantially apolar character of most of the organic polymers, natural occurring hydrophilic clays are modified into organophilic, and consequently increases the polymer/clay compatibility. Different strategies have been developed for the preparation of nanocomposites with the improved properties which can be achieved by the complete dispersion of clay platelets in the polymer matrix.

In this chapter I will report the study of a natural clay, montmorillonite-containing bentonite, in two different forms: an organophilic one obtained by ion-exchanging with 2C\textsubscript{18}-dimethyldioctadecylammonium cations and a doubly organically modified (or functionalized) form, obtained by performing a grafting reaction of an alkoxy silane containing a polymerizable group (TMSPM) onto 2C\textsubscript{18}-dimethyldioctadecylammonium cation exchanged clay. The study was carried out also on low-density polyethylene (LDPE)/clay nanocomposites which were prepared from these two different clay forms.

The basic structural characterization of the organophilic clays was carried out by \textsuperscript{13}C and \textsuperscript{29}Si DE-MAS spectra, which allowed to investigate the results of clay modifications. Useful information about polymer-clay interfacial interactions and morphology of nanocomposites could be obtained from \textsuperscript{1}H T\textsubscript{1}’s by exploiting the presence of Fe\textsuperscript{3+}
paramagnetic centers in the clay.

6.1 Introduction

Clay minerals

Clay is a naturally occurring material primarily composed of fine-grained minerals, with particle size of less than 2 µm. Clay deposits are mostly composed of clay minerals (phyllosilicate minerals) which usually contain other materials, as small quartz particles and variable amounts of water trapped in the mineral structure by polar attraction. Fig. 6.1 shows the naturally occurring clay.

Clay minerals include the following groups:

- Kaolin group which includes the minerals kaolinite, dickite, halloysite and nacrite.
- Smectite group which includes dioctahedral smectites such as montmorillonite and nontronite and trioctahedral smectites, for example saponite.
- Illite group which includes the clay-micas. Illite is the only common mineral.
- Chlorite group which includes a wide variety of similar minerals with considerable chemical variation.

Clay minerals are characterized by: two-dimensional sheets of corner sharing SiO₄ tetrahedra. Each tetrahedron shares 3 of its vertex oxygen atoms with other tetrahedra forming a hexagonal array in two-dimensions as shown in Fig. 6.2. The fourth vertex is not shared with tetrahedron and all of the tetrahedra “point” in the same direction. In clays, the tetrahedral sheets are always bonded to octahedral sheets formed by cations, such as aluminium or magnesium, coordinated by oxygen atoms and hydroxyl groups as shown in Fig. 6.2. The unshared vertex of the tetrahedral sheet also forms part of
one side of the octahedral sheet. Clays can be categorized depending on the way that tetrahedral and octahedral sheets are packed into layers. If there is only one tetrahedral and one octahedral sheet in each layer the clay is known as a 1:1 clay. The alternative, known as a 2:1 clay, has two tetrahedral sheets with an octahedral sheet in between (see Fig. 6.2). Depending on the composition of the tetrahedral and octahedral sheets, the layer will have no charge, or will have a net negative charge. If the layers are charged the charge is balanced by absorbed interlayer cations such as Na\(^+\) or K\(^+\). In both cases the interlayer can also contain water and the crystal structure is formed from a stack of layers which is presented in Fig. 6.3.

**Montmorillonite-containing bentonite clay**

Bentonite which is of interest to this study is a clay mineral whose name was derived from the location of the first commercial deposits mined at Fort Benton, Wyoming, U.S.A. Geologically bentonites are mainly of volcanic origin and the majority of commercial deposits were formed by the hydrolysis of volcanic rock or ash. Mineralogically, bentonite principally consists of montmorillonite in combination with 10 to 20 percent various mineral impurities such as feldspars, calcite, silica, gypsum, etc. Montmorillonite belongs to the smectite family, is a 2:1 clay, meaning that it has two tetrahedral sheets sandwiching a central octahedral sheet as shown in Fig. 6.3. The particles are plate-shaped with an average diameter of approximately 1 \(\mu\)m.
Montmorillonite’s water content is variable and it increases greatly in volume when it absorbs water. Chemically it is hydrated sodium calcium aluminium silicate hydroxide \( \text{Na}_0.2\text{Ca}_0.1\text{Al}_2(\text{Si}_4\text{O}_{10})(\text{OH})_2 \cdot n\text{H}_2\text{O} \). Potassium, iron and other cations are common substitutes of Al and Mg and their exact ratio of cations varies with source. This isomorphic substitution within the layers (for example, \( \text{Al}^{3+} \) is replaced by \( \text{Fe}^{2+} \) or \( \text{Mg}^{2+} \)) generates negative charges at the surface that are counterbalanced by alkali and alkaline earth cations. These counterions can be shared by two neighboring platelets, resulting in stacks of platelets that are tightly held together (see Fig. 6.4).

Montmorillonite swells with the addition of water. However, some montmorillonites expand considerably more than other clays due to water penetrating inside the interlayer molecular spaces and concomitant adsorption. The amount of expansion is largely due to the type of exchangeable cations contained in the material. The presence of sodium as the predominant exchangeable cation can result in the clay swelling to several times
its original volume. Hence, sodium montmorillonite has come to be used as the major constituent in non-explosive agents for splitting rock in natural stone quarries in order to limit the amount of waste. This swelling property makes montmorillonite-containing bentonite useful also as an annular seal or plug for water wells and as a protective liner for landfills.

The natural hydrophilicity of montmorillonite and other layered silicates can be modified by ion-exchange using long alkyl chain cations that can quite easily replace the cations present in the clay. By exchanging them with various organic cations, montmorillonite-containing bentonite clay can be used in a wide variety of applications. These organo-clay systems are employed in many industrial and scientific applications such as adsorbents for organic pollutants, pharmaceutical and cosmetic additives, water treatment, catalysts, reinforcing fillers for plastics, rheological control agents, electric and nanocomposite materials [37].

Polymer-clay nanocomposites

In recent years intensive research on polymer-clay nanocomposites has been carried out because clay nanocomposites have a high modulus, dimensional stability, low gas permeability, and reduced flammability [184–187]. Especially composites of polymers with montmorillonite, have received significant attention because of improvements in mechanical, thermal, electrical and barrier properties [188–190]. The interaction between the filler and the polymer matrix can be physical as well as chemical: it is well known, for example, that in polyolefin elastomers mixed with silica or carbon black, an insoluble gel called bound rubber [191] is formed, which plays an important role in the strengthening effect [192]. The use of functionalized elastomers can help the interfacial interaction between the two phases, for instance due to the formation of hydrogen bonds among organic and inorganic functional groups [193]. It is also a common practice to soak silica surface with functionalized siloxanes which can act as coupling agents: the siloxane portion can interact with the filler, while the organic groups can react with proper matrices [194,195].

Layered silicates can be similarly modified in order to favor the formation of polymer-layered silicates nanocomposite materials which can be intercalated or exfoliated (Fig.6.5). The intercalated polymer-clay nanocomposites are formed by the infiltration of one or more layers of polymer into the clay platelets whereas the exfoliated nanocomposites are formed by the complete dispersion or separation of clay tactoids in a polymer matrix (see Fig.6.5). Exfoliation with homogeneous dispersion of clay layers within polymer matrix is particularly desirable, since exfoliated nanocomposites generally provide best properties enhancement due to the large aspect ratio and surface area of the clay. Usually, it is
necessary to functionalize both the silicate (usually with organically modified quaternary ammonium salts) and the matrix, in order to obtain a composite with exfoliated morphology [196]. For instance, maleic anhydride grafted Linear low-density polyethylene, LLDPE (LLDPE-g-MAH) with a 0.1 wt% functionalization degree (FD) needs a quaternary ammonium salt substituted with aliphatic chains containing at least 18 carbon atoms, in order to assure the formation of the exfoliated nanocomposite [197]; shorter aliphatic chains require higher FDs and with unfunctionalized LLDPE only intercalated morphology can be obtained [198]. Differently from silica, only a few examples are known of nanocomposites in which the filler is chemically bonded to the matrix. Biasci et al. [199] realized the copolymerization of methylmethacrylate (MMA) with a montmorillonite containing quaternary ammonium salts with acrylic groups [2-(N-methyl-N,N-diethylammonium iodide) ethylacrylate and 2-(N-butyl-N,N-diethylammonium bromide) ethylacrylate].

The reactive extrusion of epoxypropyl methacrylate intercalated montmorillonite and polypropylene with a peroxy-initiator has been also reported [200].

6.2 Materials, methods and aims

The solid-state NMR study reported in this chapter was aimed at the characterization of an organically modified bentonite and nanocomposites obtained by a suitable dispersion of this filler clay in Low Density Polyethylene (LDPE). This study arises from the collaboration with Prof. Ruggeri and coworkers (Dipartimento di Chimica e Chim-
ica Industriale, Università di Pisa), who performed the synthesis and X-ray Diffraction, Fourier Transform Infrared Spectroscopy and Thermo-gravimetric Analysis characterizations of these systems\(^1\).

This study is part of a more general work concerning the preparation and characterization of polyolefin-inorganic composites where the compatibility between organic and inorganic components is enhanced by directly grafting the fillers to the polymer matrix, in the perspective of obtaining materials with improved mechanical and barrier properties with respect to the pristine polymer. In particular, it was attempted to develop a synthetic route for functionalizing micro and nano-sized inorganic fillers (bentonite) with polymerizable groups, then to disperse such modified fillers into polyolefins by melt mixing and finally to promote their grafting onto the matrix by UV irradiation. We wanted to deeply characterize both the organically-modified fillers and the final composites in order to get information about their structural properties and the nature of interactions and interfaces between organic and inorganic components. To this aim, along with traditional characterization techniques, like IR, TGA, XRD, etc. we used solid-state NMR spectroscopy methods. From a NMR standpoint, we also took advantage from the comparison of organically-modified bentonites with equivalent systems where laponite was present in the place of bentonite. A complete characterization of modified laponite has been already reported in [91].

Inorganic filler bentonite has been subjected to a double organic modification treatment, consisting first in a ion exchange leading to the intercalation of an alkylammonium cation surfactant (in the following this modified bentonite will be denoted as N\(_{15}\)), then in a grafting reaction onto the clay platelets of an alkoxysilane (TMSPM) containing a polymerizable group (this doubly modified bentonite will be denoted as N\(_{15}\)-TMSPM\)), subsequently employable in nanocomposites preparation\(^2\). The complete list of samples studied is reported in Table 6.1.

In Fig. 6.6 the chemical formulae of the employed double chain surfactant dimethyl- dioctyldecylammonium chloride (2C\(_{18}\)) and of the alkoxysilane (3-(trimethoxysilyl)propyl methacrylate - TMSPM), are reported.

The employed alkoxysilane TMSPM was hydrolyzed in an EtOH/H\(_2\)O solvent mixture under neutral conditions: it is known [201] that in these conditions the hydrolysis of the alkoxysilane (converting the SiOR groups in SiOH ones) is known to proceed slowly but it should be favored with respect to the oligomerization of TMSPM (occurring

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\(^1\)The detailed experimental results of the preparation and characterization is reported at the end of this chapter (Section 6.5).

\(^2\)To our best knowledge, the possibility of such a double organic modification is still quite unexplored in the case of bentonite.
Table 6.1: List of samples referred to in the discussion of this chapter.

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(^a) N15</td>
</tr>
<tr>
<td>2</td>
<td>(^b) N15-TMSPM</td>
</tr>
<tr>
<td>3</td>
<td>(^c) LDPE</td>
</tr>
<tr>
<td>4</td>
<td>(^d) B15</td>
</tr>
<tr>
<td>5</td>
<td>(^e) B16</td>
</tr>
<tr>
<td>6</td>
<td>(^f) Laponite-2C(_{18})</td>
</tr>
<tr>
<td>7</td>
<td>(^g) Laponite-TMSPM</td>
</tr>
</tbody>
</table>

\(^a\) Modified organophilic bentonite.
\(^b\) Doubly modified organophilic bentonite with TMSPM.
\(^c\) Low density polyethylene.
\(^d\) This sample was obtained by blending both sample 1 and 3.
\(^e\) This sample was obtained by blending sample 2 and 3.
\(^f\) This sample was prepared with the same conditions and it is equivalent to sample 1 except that bentonite is replaced with laponite, which is free from paramagnetic impurities.
\(^g\) This sample was prepared with the same conditions and it is equivalent to sample 2 except that laponite is used in this case.

Figure 6.6: Chemical structures and atom labeling of 2C\(_{18}\) (top) and TMSPM (bottom).
through the formation of Si-O-Si bonds). This self-aggregation of TMSPM molecules forming TMSPM oligomers with a large molecular size, compared with the bentonite interlayer distance, inhibits the process of intercalation. After adding organophilic bentonite (N15), the reaction between silanol groups on the clay surface and hydrolyzed TMSPM occur, and is expected to proceed in competition with the TMSPM oligomerization. Indications on the occurrence of filler functionalization were obtained by FT-IR and TGA.

From IR spectra of N15 and N15-TMSPM, the presence of TMSPM was identified in N15-TMSPM. Also the presence of non hydrogen-bonded and hydrogen-bonded bentonite OH groups was suggested by IR spectrum of N15 while the spectrum of N15-TMSPM suggested the involvement of a fraction of hydrogen-bonded bentonite hydroxyl groups in the reaction with TMSPM. From TGA data, we could calculate a TMSPM content of 14.8 wt%. The experimental TGA, XRD and IR data will be discussed in detail in Subsection 6.5.3.

XRD analysis of N15 and N15-TMSPM showed that in the case of N15-TMSPM the interlayer distance between the platelets was 22.6 Å, shorter than that of the unfunctionalized bentonite (N15) for which the interlayer distance was 28.5 Å. This contraction passing from N15 to N15-TMSPM could be ascribed to the establishment of bonds between the silanol groups of TMSPM and the bentonite surface groups, inducing a volume decrease of the clay platelets.

LDPE/N15 composite (B15) was prepared by blending the melt of LDPE, LDPE-g-MAH and N15, in weight ratios of 85:10:5. LDPE/N15-TMSPM composite (B16) was prepared from a melt-mixture of LDPE, LDPE with grafted maleic anhydride groups (LDPE-g-MAH), N15-TMSPM and a photoinitiator (P1), in weight ratios of 84:10:5:1. The blend compositions of the composites are summarized in Table 6.2. The polar groups present in LDPE-g-MAH are known to favor the filler-LDPE mixing; the photoinitiator employed was a mixture of alkyl substituted α-hydroxy ketones, with an average chain of twelve. In Table 6.1, the samples list is reported.

Finally, the B16 nanocomposite was subject to UV irradiation: by forming R-C· radicals, the photoinitiator can promote the reaction among the methacrylic double bonds of N15-TMSPM and LDPE. Evidences of the occurrence of a chemical reaction between N15-TMSPM and LDPE were obtained by FT-IR, which showed that the conversion degree of both photoinitiator and methacrylate results quite low, and in particular lower than that previously observed for similar silica/LDPE blends [90].

Thin films (100-150 µm thickness) were prepared by compression moulding at 180 °C and 20-25 bar.

B15 and B16 nanocomposites, despite the low percentage of inorganic component,
184 Study of modified bentonite clays and LDPE-clay nanocomposites

<table>
<thead>
<tr>
<th>Blend</th>
<th>LDPE</th>
<th>P1</th>
<th>N15</th>
<th>N15-TMSPM</th>
<th>LDPE-g-MAH</th>
</tr>
</thead>
<tbody>
<tr>
<td>B15</td>
<td>85</td>
<td>-</td>
<td>5</td>
<td>-</td>
<td>10</td>
</tr>
<tr>
<td>B16</td>
<td>84</td>
<td>1</td>
<td>-</td>
<td>5</td>
<td>10</td>
</tr>
</tbody>
</table>

Table 6.2: Blends composition (wt %).

exhibited higher Young’s modulus with respect to the pristine polymer containing only LDPE and LDPE-g-MAH (90:10), shown in Table 6.3. Extraction experiments detected 10 wt% insoluble residue in B15 and 28 wt% in B16, suggesting in both cases the occurrence of interactions between polymer chains and bentonite platelets. In the case of B16, the much larger residue fraction could further be in agreement with the establishment of chemical bonds between functionalized filler (N15-TMSPM) and polymer (LDPE).

<table>
<thead>
<tr>
<th>Blend</th>
<th>UV</th>
<th>Young’s modulus (MPa)</th>
<th>Insoluble residue (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDPE/</td>
<td>NO</td>
<td>188.4</td>
<td>0</td>
</tr>
<tr>
<td>LDPE-g-MAH</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B15</td>
<td>NO</td>
<td>239.6</td>
<td>10</td>
</tr>
<tr>
<td>B16</td>
<td>YES</td>
<td>213.8</td>
<td>28</td>
</tr>
</tbody>
</table>

Table 6.3: Properties of bentonite-filled blends.

The aim of the solid-state NMR study was to carry out a structural characterization of the organically modified bentonites (N15 and N15-TMSPM) and to get insights into the structural properties and interactions of the polymer/filler nanocomposites. $^{13}$C and $^{29}$Si high-resolution techniques have been used together with the measurement of $^1$H $T_1$ by exploiting the presence of Fe$^{3+}$ paramagnetic species in bentonite and their effects on $T_1$’s of the nearby protons of the organic fractions, as it will be discussed in Subsection 6.3.3.

6.3 Results and discussions

A structural characterization of N15 and N15-TMSPM has been carried out by recording $^{29}$Si and $^{13}$C high-resolution spectra. In this case, due to the presence of Fe$^{3+}$ paramagnetic ions in the clay, the usually employed cross-polarization technique is not convenient. Indeed the paramagnetic interaction with the Fe$^{3+}$ electron spins affects the nuclear relaxation times, in particular strongly shortening the $^1$H spin-lattice relaxation
times (ref. Subsection 1.5.4). By recording $^{29}\text{Si}$ and $^{13}\text{C}$ cross Polarization spectra of N15 and N15-TMSPM (here not reported), we could observe a large loss in sensitivity ascribable to the shortening of the $^1\text{H}$ spin-lattice relaxation times in the rotating frame. Therefore $^{29}\text{Si}$ and $^{13}\text{C}$ spectra have been acquired through direct excitation.

### 6.3.1 $^{29}\text{Si}$ DE-MAS on N15 and N15-TMSPM

![Figure 6.7: $^{29}\text{Si}$ DE-MAS spectra recorded with a recycle delay of 5 s and a MAS frequency of 6 kHz of (a) N15 and (b) N15-TMSPM. Spinning sidebands are marked with asterisks.](image-url)

In Fig. 6.7, the $^{29}\text{Si}$ DE-MAS spectra of N15 and N15-TMSPM are reported; in both of them two intense signals are present at about -110 and -95 ppm, which must be ascribed to fully condensed $Q^4\text{Si(OAl)(OSi)}_3$ and $Q^3\text{Si(OAl)(OSi)}_2\text{OH}$ silicon nuclei, respectively (see Appendix A), both present in the tetrahedral silica layers of the clay. In the spectrum of N15-TMSPM a weak and broad signal centered at about -64 ppm can also be recognized and assigned to condensed T silicon nuclei of TMSPM, which seem to be mainly $T^3\text{Si(OSi)}_3\text{R}$, $\delta \approx -65$ ppm) and, in part, $T^2\text{Si(OSi)}_2\text{(OX)}\text{R}$ with X=H or CH$_3$, $\delta \approx -56$ ppm) [91], so confirming the occurred condensation reaction between TMSPM and N15 silanols. Even if these spectra are not quantitative due to the short recycle delay used (5 s), by assuming that $^{29}\text{Si} T_1$’s do not change much in passing from N15 to N15-TMSPM, the comparison between the two spectra clearly shows...
an increased $Q^4/Q^3$ ratio in \textbf{N15-TMSPM}, again confirming the reaction between TMSPM and clay silanols.

![Figure 6.8: $^{29}$Si quantitative DE-MAS spectrum of N15-TMSPM, acquired with a recycle delay of 120 s and at a MAS frequency of 6 kHz. In the inset the region of T silicon signals is highlighted. Spinning sidebands are marked with asterisks.](image)

In the case of \textbf{N15-TMSPM} we also recorded a quantitative $^{29}$Si DE-MAS spectrum, which is reported in Fig. 6.8. The relative intensities of the peaks are quite different from those observed in the previously shown non quantitative spectrum, suggesting that especially $Q^4$ silicon nuclei have a quite long $T_1$, as it is expected considering the lack of close protons. By measuring the signal areas, through a proper spectral deconvolution procedure, also taking into account the quite intense spinning sidebands, we could estimate the relative amounts of the different silicon nuclei that resulted to be: 38\% $Q^4$, 60\% $Q^3$ and 2\% T. Calculating a sort of scaling factor for the $Q^4/Q^3$ ratio in passing from the DE spectrum acquired with a short recycle delay to the quantitative spectrum of \textbf{N15-TMSPM}, and applying the same factor to the $Q^4/Q^3$ ratio measured from the
6.3 Results and discussions

non quantitative spectrum of $\text{N}_{15}$, it has been possible to estimate the relative amounts of $Q^1$ and $Q^3$ in $\text{N}_{15}$, finding 33 % and 67 % respectively. By comparing these data with those of $\text{N}_{15}-\text{TMSPM}$ it is possible to estimate that about 6 % of the silicon nuclei of $\text{N}_{15}$, all of $Q^3$ type were transformed into $Q^4$ sites. Since the amount of TMSPM condensed silicons is about 2 % this means that either each TMSPM silicon condensed with two or three clay silanols, which is in agreement with the absence of $T^1$ signals, or that some clay silanols underwent a self condensation process, as it was previously observed for the same process applied on a different clay (ref. [91]).

6.3.2 $^{13}$C DE-MAS on $\text{N}_{15}$ and $\text{N}_{15}$-TMSPM

Figure 6.9: $^{13}$C DE-MAS spectra of (a) $\text{N}_{15}$ and (b) $\text{N}_{15}$-TMSPM, acquired at a MAS frequency of 6 kHz. Spinning sidebands are marked with asterisks and the signal at about 110 ppm is due to incomplete probe background signal suppression.

In Fig. 6.9, the $^{13}$C DE-MAS spectra of $\text{N}_{15}$ and $\text{N}_{15}$-TMSPM are shown. The two spectra are almost coincident, the most intense signals being those of the quaternary
ammonium cations. In particular, signals are observed at 15, 24, 31 and 52 ppm, which can be assigned to C19, C18, C3-C17 and C1 (see Fig. 6.6 (top) for atom labelling) of $2\text{C}_{18}$; the signal of C2, expected at about 65-70 ppm (ref. [91]) could not be resolved because of its scarce intensity and line-broadening due to the proximity of nitrogen.

The spectral resolution is relatively scarce, which can be ascribed to a distribution of different situations experienced by the cations and/or to a shortening of $^{13}\text{C} T_2$ due to the presence of the paramagnetic centers. In particular, the signal ascribed to C3-C17 appears quite large and, even if it is centered at 31 ppm, the presence of a signal at 33 ppm, due to the alkyl chains in the all-trans conformation, is quite likely. Even if TMSPM signals are quite small and mostly overlapped with the cation signals, some peaks can be recognized in the spectrum of N15-TMSPM, in particular at about 18 ppm (C7), 137 ppm (C6) and 168 ppm (C5) (see Fig. 6.6 (bottom) for atom labeling).

6.3.3 $^1\text{H} T_1$ measurement

It is well known that $^1\text{H}$ spin-lattice relaxation times in the laboratory frame ($^1\text{H} T_1$) can be exploited, in solid heterogeneous systems, either for investigating the miscibility among the heterodomains on a scale of about 100 Å, and/or to get information about the dynamics in the MHz-GHz frequency range. However, when paramagnetic centers are present, $^1\text{H} T_1$’s can be peculiarly used to obtain information about the morphology of the material: VanderHart et al. have shown how, when the paramagnetic centers are contained, as in our case, within clay layers, information such as the degree of exfoliation of the clay and its homogeneity can be derived from a very accurate and complex analysis of experimental relaxation times, combined with detailed data, available from other sources, concerning the compositional and structural properties of the material [202].

The analysis of $^1\text{H} T_1$’s to derive morphological information can be very complex, since the experimental relaxation time values may be determined by a combination of many processes and properties, including motions in the fast regime, proton spin diffusion, distribution and concentration of paramagnetic centers, and so on. In our case the detailed analysis proposed by VanderHart et al. is prevented from the lack of detailed non-NMR data and the unavailability of samples with variable and known clay content, but some less quantitative considerations can still be drawn from the experimental relaxation times.

For all of our samples the measured $^1\text{H} T_1$’s exhibited a mono-exponential behavior, and their values are reported in Table 6.4.

We can attempt a qualitative explanation of the measured values. In N15 $^1\text{H} T_1$ is very short, since all the protons (silanols, hydroxyls and protons of the organic modifier) are very close to the clay layers surface or within the layers themselves, and therefore they
Table 6.4: $^1$H spin-lattice relaxation times in the laboratory frame ($T_1$) of the samples. The magnetization recovery curves were always well reproduced by a mono-exponential function for all the samples. Samples 6 and 7 listed here, are equivalent to samples 1 and 2, respectively, with the difference that bentonite is replaced with laponite, that is free from paramagnetic centers.

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Sample</th>
<th>$T_1$ (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>N15</td>
<td>11</td>
</tr>
<tr>
<td>2</td>
<td>N15-TMSPM</td>
<td>6</td>
</tr>
<tr>
<td>3</td>
<td>LDPE</td>
<td>735</td>
</tr>
<tr>
<td>4</td>
<td>B15</td>
<td>694</td>
</tr>
<tr>
<td>5</td>
<td>B16</td>
<td>692</td>
</tr>
<tr>
<td>6</td>
<td>Laponite-2C$_{18}$</td>
<td>164</td>
</tr>
<tr>
<td>7</td>
<td>Laponite-TMSPM</td>
<td>209</td>
</tr>
</tbody>
</table>

are strongly affected by the interaction with the unpaired electron of Fe$^{3+}$ species (ref. Subsection 1.5.4). The measured value is slightly higher than that (2.5 ms) predicted by Bourbigot et al. for the “intrinsic” relaxation time assigned to a 4 Å-thick interfacial region [203], in agreement with an interlayer distance of 28.5 Å obtained by XRD. The shortening in the relaxation time observed in passing from N15 to N15-TMSPM is indeed in agreement with the reduction of the interlayer distance (from 28.5 to 22.6 Å) observed by XRD. The much higher relaxation time values measured for similar laponite systems confirms that the interaction with unpaired electron of Fe$^{3+}$ centers, present within bentonite layers, is the dominant relaxation mechanism. The relaxation time measured for LDPE is almost two orders of magnitude higher than that of N15 and N15-TMSPM, and it only arises from the polymer dynamic behavior. A contribution from both polymer dynamics and paramagnetic centers is expected in B15 and B16, where the measured $T_1$ is slightly shorter than in LDPE.

In the composite systems, the measured relaxation rate ($1/T_1$ meas) can be indeed written as the sum of the relaxation rate due to the dynamics of the polymer ($1/T_1$ dyn) and that due to the effect of paramagnetic centers ($1/T_1$ para) [204, 205]:

$$\frac{1}{T_1 \text{ meas}} = \frac{1}{T_1 \text{ dyn}} + \frac{1}{T_1 \text{ para}}$$

(6.1)

If we assume that the fast dynamics of the polymer is not affected by the presence of the clay [204, 205] the $1/T_1$ dyn term corresponds with the value of $^1$H $T_1$ measured for the pure polymer, and the $1/T_1$ para term can be therefore calculated. This is important since $1/T_1$ para is proportional to the surface (of the interface)-to-volume (of the polymer)
ratio, and therefore it can be related to the interfacial area with the clay [204]:

\[
\frac{1}{T_1_{\text{para}}} \propto \frac{S_{\text{clay}}}{V_{\text{LDPE}}}
\]  

(6.2)

No quantitative estimations about the average number of stuck platelets present in the composite can be given in our case, due to the lack of a series of samples at variable and known clay concentration. Nevertheless, we can compare the results obtained for the two composites B15 and B16, having the same clay content and, therefore, the same \(V_{\text{LDPE}}\) value. Indeed, the two composites exhibit an equal relaxation time within the experimental error, indicating that they have approximately the same interfacial area. This is in apparent contradiction with the results obtained by XRD, which showed an almost complete clay exfoliation for B16, and the intercalation of the polymer in B15 (Fig. 6.10). However, as long as the intercalation of the polymer takes place regularly, i.e. without sticking of different clay platelets, the interfacial area in the two cases is the same, and it corresponds to the total clay surface. It is reasonable that the measured \(T_1\) is sensitive to the total interfacial area but not to the different morphology of the composites because of the role played by spin diffusion, which tends to average the different “intrinsic” relaxation times throughout the sample to a single value. Similar results were also reported by Grandjean et al. [206], who found equal \(^1\text{H} T_1\) values for two poly(ε-caprolactone)/clay composites having the same composition but different morphology (one intercalated and the other exfoliated).

6.4 Conclusions

In this work it has been shown that it is possible to functionalize inorganic bentonite fillers with polymerizable groups by a one pot and very simple procedure and with high
6.5 Experimental 191

modification rates. Such functionalized inorganic fillers can be photo-grafted onto LPDE, enhancing the compatibility between the inorganic and the polymer matrix. Data support the hypothesis of chemical bonds establishment between the two phases and the obtainment of clay exfoliation. Composite materials obtained with this procedure present improved mechanical properties.

The SSNMR study allowed us to confirm and characterize the bentonite modifications as well as to investigate the morphologies of different composites by means of $^1$H $T_1$ relaxation behavior by exploiting the interaction of polymer nuclei with unpaired electrons of paramagnetic impurities present within clay layers.

6.5 Experimental

Materials

Organophilic bentonite (Nanofil 15, N15, from Sud-Chemie) was dried overnight at 180 °C to remove absorbed water. 3-(Trimethoxysilyl)propyl methacrylate (TMSPM, 98 %, Aldrich) was used as received, without any further purification. Photoinitiator (P1) was a mixture of alkyl-substituted $\alpha$-hydroxy ketones with an average chain length of twelve, supplied by Lamberti S. p. A. Low density polyethylene (LDPE, LD 158 JD from Exxon Chemical, with $M_w$ 70.6 $\times 10^3$; $M_n$ 19.0 $\times 10^3$; antioxidant: Irganox 1076, 500 pm 150 ppm) was used as received, without removing the antioxidant. Maleic anhydride-functionalized low density polyethylene (LDPE-g-MAH, Bynel 42E703 from Du Pont) was used as received.

6.5.1 Preparation of functionalized N15 (N15-TMSPM)

3 ml of 3-(trimethoxysilyl)propyl methacrylate (TMSPM) and 20 mL of an EtOH-H$_2$O (95 : 5, v/v) mixture was stirred for 0.5 h at room temperature; then 2 g of N15 were added. The resulting mixture was stirred at room temperature for 2 days then filtered and washed with ethanol. The obtained solid was then extracted with CHCl$_3$ in Soxhlet for 8 h and then dried under vacuum for 16 h. The obtained solid was pulverized by means of a ball mill.

6.5.2 Blends preparation

Blends were prepared in a Brabender Plastograph® (model OHG 47055, with 30 ml mixing chamber) at 170 °C, 50 rpm, for 10 minutes. Polymers pellets were previously mixed together with the filler; the photoinitiator, when present, was added to the melt.
mixture. UV irradiation was carried out on B16 thin films, inside a dry box chamber (O₂ < 1 ppm; H₂O < 2 ppm). The UV source was a conventional medium pressure mercury lamp (model HG100, 125 W) with an energy output of 5000 ± 10 µW/cm² at 365 nm and of 3800 ± 10 µW/cm² at 254 nm. After the irradiation, films were kept in the dark inside the dry box for 72 hours in order to let radicals decay, then they were drawn from the chamber still keeping them in the dark and in inert atmosphere using a desiccator.

6.5.3 Samples characterization

Characterization methods

FT-IR spectra were recorded with a Perkin Elmer Spectrum One spectrometer; inorganic fillers were finely grounded together with KBr and pressed; polymer blends were examined as thin films. X-ray diffraction analysis (XRD) was made with a Siemens Diffractometer D 500/501, model Kristalloflex 810, with X-ray source CuKα (λ = 1.5406 Å), 2θ scanning from 1.5° to 30°, both on bentonite powder and on polymer films. Thermo-gravimetric analysis on inorganic fillers (TGA) was made with a Mettler Toledo TGA/SDTA 851 calorimeter from 30 to 600 °C at a scanning rate of 10 °C/min. Polymer blends were extracted with boiling xylene for 14 hours in a Kumagawa extractor. Stress/strain measurements were made with an Instron dynamometer, model 5564, with 2 kN load cell, at 30 mm/min strain speed, according to method ASTM D 882-91; Young’s modulus value was calculated as average among at least five measurements for each sample.

6.5.3.1 Inorganic fillers characterization (N15 and N15-TMSPM)

A comparison between the IR spectra of N15 and N15-TMSPM is reported in Fig. 6.11 and 6.12. The presence of TMSPM was verified by the occurrence of the signal at 1709 cm⁻¹ in the spectrum of N15-TMSPM, due to the C=O stretching of the TMSPM acrylic group. In pure TMSPM this stretching is observed at 1720 cm⁻¹ and this shift can be explained with the formation of hydrogen-bonds between TMSPM and clay OH groups. Moreover, this band can also be interpreted as a sign of the absence of TMSPM oligomers, for which the C=O stretching would be expected at 1735 cm⁻¹. By analyzing the hydroxyl spectral region (see Fig. 6.12), it is possible to identify three distinct O-H stretching bands: those at 3633 and 3432 cm⁻¹ (the sole present in the spectrum of N15) are ascribable to non hydrogen-bonded and hydrogen-bonded bentonite OH groups, respectively; the shoulder at 3199 cm⁻¹, detectable only in the spectrum of N15-TMSPM, is due to the stretching of hydrogen-bonded TMSPM hydroxyl groups.
Figure 6.11: FT-IR spectra of N15 (straight line) and N15-TMSPM (dashed line).

Figure 6.12: FT-IR spectra of N15 (straight line) and N15-TMSPM (dashed line) with the expansion in the area of OH stretching.
It must be noticed that, in passing from N15 to N15-TMSPM, the intensity of the band at 3432 cm$^{-1}$ strongly decreases, in agreement with the involvement of a fraction of hydrogen-bonded bentonite hydroxyl groups in the reaction with TMSPM.

The TGA analysis of the functionalized bentonite (Fig. 6.13) shows a first degradation step with onset temperature at 210 °C, due to the quaternary ammonium salt decomposition, and a second degradation step at 364 °C attributed to the loss of the intercalated TMSPM. It is important to notice the rise in temperature of TMSPM degradation after intercalation from 99 to 364 °C, which indicates molecular stabilization due to the intercalation process. By a deconvolution process on the derivative curve of N15-TMSPM thermogram, we could calculate a TMSPM content of 14.8 wt%.

![Figure 6.13: TGA analysis of N15 (dots) and N15-TMSPM (line).](image)

XRD analysis (Fig. 6.14) indicates an interlayer distance in N15-TMSPM of 22.6 Å, shorter than that of the pristine bentonite (N15, 28.5 Å). This contraction can be ascribed to the establishment of bonds between the silanol groups of TMSPM and the bentonite surface groups, inducing a volume decrease of the silicate channels.

### 6.5.4 SSNMR

All the experiments were performed on a double-channel Varian Infinity Plus 400 spectrometer (see Subsection 2.4.1) working at 399.88, 79.44 and 100.56 MHz for $^1$H, $^{29}$Si and $^{13}$C respectively. The $^{13}$C and $^{29}$Si high resolution measurements were carried out on a 7.5 mm CP-MAS probehead. The 90° pulse length was 4.5 µs for $^1$H and $^{29}$Si, respectively and 4 µs for $^{13}$C. In order to acquire a quantitative $^{29}$Si DE-MAS spectrum,
the recycle delay of 120 s and 2000 transients were used while non-quantitative DE-MAS spectra were acquired with 5 s recycle delay and accumulating 8000 transients. $^{13}$C DE-MAS spectra were acquired using the depth pulse sequence (see Subsection 2.5.1) and a recycle delay of 2 s was used. 27000 transients were accumulated. A MAS frequency of 6 kHz was used for all the spectra.

The proton $T_1$ relaxation times experiments were performed on a goniometric probe-head (described in Subsection 2.4.1). The 90° pulse length of $^1$H in this case was 3.3 $\mu$s. The $^1$H $T_1$ relaxation times measurements were carried out in low-resolution (in static conditions) by using saturation recovery pulse sequence (described in Subsubsection 2.6.2.3 in Chapter 2) with the delays ranging from 0.01 ms to 8 s and the recycle delay of 0.01 s. Usually 32 scans were enough for all the samples. Due to the presence of the paramagnetic species in the material, which shorten the $^1$H $T_2$ and thereby cause the fast decay of the FID. We combined the saturation recovery sequence with the solid-echo pulse sequence (see Subsubsection 2.6.2.1), in order to avoid the loss of signal at the initial part of the FID. The proton 90° pulse length was 3.3 $\mu$s. The first echo delay $\tau$ between the last pulse of saturation recovery and the first 90° pulse of solid-echo was 10 $\mu$s while the second echo delay was 6 $\mu$s.

It is necessary to state at this point that the $^1$H $T_1$ values obtained by the combination of the saturation recovery and solid-echo were biased by the background signal. Indeed in some of the samples investigated the amount of protons was unusually low, and therefore the background contribution to the signal could not be neglected. This was found by the occurrence of biexponentiality of the $T_1$ values obtained for N15 and N15-TMSPM in which the long exponential component was present in equiva-
lent percentage as the short $T_1$ component. This was controversial to the fact that in the pure clay systems (without polymers) most of the protons were expected to have a very short $T_1$ because of the presence of paramagnetic species. Moreover, when we tried to acquire the same measurement with empty tube and without tube, indeed a signal was detected, corresponding to a long $T_1$. So we concluded that it could arise from the probehead background signal. In order to eliminate this background signal, we applied the model proposed by Schmidt et al. which is described in the following to the measurement of $T_1$, including either a $90^\circ$ or $180^\circ$ pulse between the saturation recovery and solid-echo sequence. In this way, the background signal could be suppressed and the magnetization recovery curves were well reproduced by monoexponential function using Eq. 2.10. Especially for N15 and N15-TMSPM the very long component was no longer present, as expected.

6.5.4.1 Suppression of the probe background signal

The background signal arising from the probe was suppressed by using a model proposed by Schmidt et al. [207]. Subtraction of the signal of the empty probehead from the spectrum of interest is often not a reasonable solution to this problem, since it requires arbitrary scaling and phasing of the two spectra and, moreover, the presence of the sample in the coil changes the electronic properties of the resonance circuit. This is either a very simple model for reducing probehead background signal which involves only a single, relatively short excitation pulse.

![Figure 6.15: (a) Schematic representation of the one-pulse sequence with signals from inside and outside the coil (b) Same as (a), except with an $L$-times longer excitation pulse. The background signal from outside the coil is increased close to $L$-fold.](image)

The proton signal of a one-pulse sequence as indicated in Fig. 6.15 can be represented as:

$$I_{tot}(\omega) = \langle I(\omega; t_p) \rangle$$

where $t_p$ is the pulse length. The pointed brackets indicate the ensemble averaged over all the protons present inside and outside the coil.
6.5 Experimental

In the scheme, two one-pulse spectra were recorded, the first spectrum with pulse length $t_{p1}$, and the second with pulse length $t_{p2} = Lt_{p1}$, with $L$ typically between 1.5 and 2.5. The second spectrum, scaled by $1/L$, is subtracted from the first:

$$I_{corr}(\omega; t_p; L) = \langle I(\omega; t_p) \rangle - 1/L \langle I(\omega; Lt_p) \rangle$$ (6.4)

The protons signals arising from inside and outside the coil can be distinguished by the $B_1$ field strength effectively felt by these two. The $B_1$ field inside the coil is stronger than the $B_1$ field outside the coil, i.e. $B_{1,\text{outside}}$ is weaker by a factor $b > 4$ ($B_{1,\text{outside}} = B_{1,\text{inside}}/b$). It has to be noted that inside the coil, the flip angle is $\beta_{\text{inside}} = \gamma B_{1,\text{inside}} t_p$, while in the outside of the coil it is, $\beta_{\text{outside}} = \beta_{\text{inside}}/b$.

In our case, since the $90^\circ$ pulse length needed for the sample is approximately 4 times lesser than the empty tube and coil\(^3\) ($b \approx 4$), we have applied 90 and 180\(^\circ\) pulses ($L = 2$) in place of the last $90^\circ$ pulse of the saturation recovery pulse sequence and acquired two different spectra, one containing the contribution of the sample as well as of the background (inside and outside the coil) and an other only that from the background (outside the coil), respectively. The intensity of the signal from inside the coil is represented as:

$$I_i(\omega; 90^\circ) = I_i(\omega) \sin(90^\circ) = I_i(\omega)$$ (6.5)
$$I_i(\omega; 180^\circ) = I_i(\omega) \sin(180^\circ) = 0$$ (6.6)

and the background signal from outside the coil is:

$$I_o(\omega; 22.5^\circ) = I_o(\omega) \sin(22.5^\circ) = 0.38 \times I_o(\omega)$$ (6.7)
$$I_o(\omega; 45^\circ) = I_o(\omega) \sin(45^\circ) = 0.71 \times I_o(\omega)$$ (6.8)

Here, $I_i(\omega)$ and $I_o(\omega)$ are the maximum-intensity spectra from inside and outside the coil respectively. By scaling the intensities obtained from Eqs. 6.5 and 6.7 by the factor $L = 2$ and then subtracting it with spectral intensities obtained from Eqs. 6.6 and 6.8 almost nullifies the background contribution only leaving the sample proton signal.

$$I_{iscale}(\omega) = 2 \times (I_i(\omega) + 0.38 \times I_o(\omega))$$ (6.9)
$$I_{corr}(\omega) = I_{iscale}(\omega) - 0.71 \times I_o(\omega)$$ (6.10)

\(^3\)Pulse length is inversely proportional to the $B_1$ field strength.
Conclusions

The extensive application of solid-state NMR techniques allowed the characterization of several sets of multi-component solid materials, having an hybrid organic-inorganic nature (OIMMs, Organic-Inorganic Multi-component Materials), and in particular: (a) encapsulated particles of silica with PMMA; (b) mesoporous silica nanoparticles impregnated with Yttrium complexes; (c) polyisoprene rubbers filled with silica particles formed by sol-gel process; (d) polyethylenes filled with natural clay platelets. These studies concerned in particular the interfacial properties that, in such kinds of complex materials, are thought being strictly related to their applicative macroscopic properties. Several aspects of the interfaces were dealt with, which can be roughly divided into: (i) structural, (ii) dynamic, and (iii) morphological properties, even though all these aspects are somehow strongly correlated among each other. In particular, the structural aspects substantially concerned all the four sets of samples: in most cases they involved the degree of condensation (i.e. the fractional amount of Si-O-Si bondings) and the distribution of silanol groups in silicate networks, modified or not by different types of organic silanes. When the latter were present, a crucial finding was the condensation of the organic silanes groups and among them and the “bulk” silicate, constituted either by pre-formed silica, silica particles formed in situ or a clay.

The dynamic aspects of the interface were the main focus of the studies of systems (b) and (c): in these cases the interactions between different components [the organometallic complex and organically modified silicas in (b), and the polymer and silica particles in (c)] did not occur through the formation of chemical bonds. Therefore, the occurrence of interactions at the interfaces could more efficiently tackled with the observation of changes in the dynamic behavior of the single components in passing from their pure state to the composite. A change in the dynamic behavior of the organometallic complex was observed when this was impregnated onto different organically-modified systems in (b); on the other hand, the formation of interfacial polymeric layers around silica particles, showing a strongly reduced mobility with respect to the bulk was clearly detected in (c) systems, which could also be quantified to assess the fractional amount of the
interface with respect to the bulk.

The “morphological” aspects were mostly investigated in systems (d), where the study of the interface between the polymeric matrix and the dispersed clay was mainly related to the degree of exfoliation of the clay itself.

The interfacial properties, determined through the three different aspects described above, were typically investigated as a function of some parameters concerning the materials. For instance, the effects of the presence or the absence of organic silanes as modifiers of the silica particles or clay layers were detected for all the sets of materials. Moreover, other parameters taken into account were, for instance, the dimension of the silica particles in (a), the type of organic silane used as silica-modifier in (b), as well as the relative amount of organic and inorganic components and the synthetic conditions employed in (c).

Summarizing, it can be stated that the use of solid-state NMR techniques to investigate the interfacial properties of OIMMs revealed to be at the same time very complex and very powerful. The main reasons of complexity mainly rely on the non-standard experimental approach, which must be devised and tested from case to case, depending not only on the type of material investigated, but also on the peculiar nuclear properties of the different nuclei “observed” by NMR, which of course cannot be known before undertaking the experiments. Indeed, in this thesis, very different approaches were necessary for the four sets of materials studied. Moreover, the extraction of physical results often resulted not straightforward, and in some cases it required the use of elaborate theoretical models. On the other hand, the powerfulness of solid-state NMR is mainly due to its capability of achieving very detailed results over a very broad range of spatial (from the sub- to supra-molecular) and time (as much as 14 decades) scales, when structural and dynamic properties are concerned, respectively. As it was quite clear from this thesis, this can be achieved by resorting to the observation of both different nuclei (in our case $^1$H, $^{13}$C, $^{29}$Si) and different nuclear properties (isotropic chemical shifts, linewidths, various relaxation times: spin-spin, spin-lattice in the laboratory and rotating frames, etc.), which could give different and complementary pieces of information. This implied the use of a large variety of experimental methods, including both low- and high-resolution techniques, which also required the use of different instrumental apparatuses. The extraction of detailed physical information by solid-state NMR often required the complementary support of other spectroscopic, microscopic, and calorimetric techniques.

As a final conclusion of this thesis, it can be stated that, in spite of its complexity, and in several cases the very long experimental times it requires, solid-state NMR confirmed to be extremely powerful for investigating the interfacial properties in complex multi-component materials. Nonetheless, further big progresses should be expected in
the future, since the potential of the large variety of solid-state NMR techniques already available has not been fully exploited yet, and, moreover, further technological developments are expected, as higher MAS spinning speeds and/or improved homonuclear decoupling schemes, which should open very interesting new perspectives, especially for the observation of $^1\text{H}$ nuclei.
Appendix A

Conventional nomenclature for silicon structural constituents

As already stated, one of the X nuclei investigated was $^{29}\text{Si}$: one-dimensional experiments such as SPE (see Subsection 2.5.1) with the aim of obtaining quantitative information and CP (see Subsection 1.7.3) for obtaining the structural information on silicon sites have been employed. As far as the systems investigated in this thesis are concerned, spinning at MAS frequencies of $5 - 7$ kHz resulted to be sufficient to completely or mostly average out the $^{29}\text{Si}$ nuclei chemical shift anisotropy and, due to the presence of silanol protons, the employment of high-power decoupling has been almost always indispensable to the obtainment of high-resolution spectra (Subsection 1.7.2).

Due to the importance of $^{29}\text{Si}$ observation in the thesis, I report here the conventional terminology by which silicon atoms in different structural units are usually denoted. Due to the occurrence of silicon-oxygen bonds in most of the inorganic as well as silyl terminated organic compounds, this terminology aims at easily providing the number of Si-O and Si-O-Si bonds involving the silicon of interest; a silicon atom bonded to one, two, three or four oxygen atoms is therefore referred to as M$^n$, D$^n$, T$^n$, Q$^n$, respectively, where the superscript $n$ is the number of the oxygen atoms further bonded to another silicon nucleus. Since an oxygen atom already involved in a Si-O bond can form only another covalent bond, it is clear that $n$ can assume values in the range 0-1, 0-2, 0-3, 0-4 for M, D, T, Q silicons, respectively. As an example, in Fig. A.1 the structures of T$^3$, T$^2$ and M$^1$ silicons are shown: in all the systems investigated in this thesis and, in general, in most of the cases, R is either an alkylic group or an hydrogen.

Concerning the chemical or geometrical structure of the components, as well as the interfaces of the materials, the isotropic chemical shifts of the resolved $^{29}\text{Si}$ signals allow
to obtain chemical structure of the components that constitute the materials. More interestingly, the interfaces among them can also be elucidated, especially by looking at the signals arising from M, D and T silicon atoms originated by the different types of organo-silanes mostly present at the interfaces between organic and inorganic components. This types of investigations, based on $^{29}\text{Si}$ observation, were applied to almost all the systems studied in this thesis (see chapters 3, 4, 5 and 6).
Bibliography


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