Summary

In the Habilitation Thesis entitled *Nanocomposite materials and biomaterials characterized by modern NMR techniques* I present in seven chapters NMR studies of different classes of nano-composite materials like filled EPDM rubber, cross-linked natural rubber, grafted PDMS rubber, proton exchange membranes (PEMs) for fuel cells applications, instable and porous media and bio-materials like the sheep Achilles tendon and wool and hair hard α-keratin fibers. In the second section I present my scientiffic and academic achievements and some of my future directions of research where I show how the present research can be extendet to other types of materials like human brain, micro-gels systems or other types of biomaterials.

In chapter 1 a series of filled EPDM elastomers were studied from NMR and mechanical point of view. A broad variety of filler types like carbon black, silane, and calcium-carbonate were chosen. The heterogeneity was characterized by ^{1}H transverse T_2, longitudinal T_1 and longitudinal in rotating frame $T_{1\rho}$ relaxation times. The data were analyzed using a Laplace inversion algorithm. Another type of NMR measurement was based on the Hahn echo decays with a dipolar filter and the distributions of residual second moment $\widetilde{M}_2$ and correlation time were obtained. First, the Hahn-echo decays were fitted to obtain the average values of residual second moment and correlation time. Then a log-Gauss distribution for the correlation time was assumed. Finally, using an averaged value of the correlation time, the distributions of $\widetilde{M}_2$ were determined. The correlation with the mechanical properties was obtained from the Payne effect which was used to obtain the distribution of filler-filler interactions of week, medium and strong character.

In chapter 2 the single-sided NMR-MOUSE sensor with a butterfly coil operating in inhomogeneous magnetic fields is described. In the first part the NMR-MOUSE® sensor is numerically characterized and the slice selection and sensitive volume were simulated. Then the ^{1}H CPMG decays for a series of cross-linked natural rubber samples is presented and the effective relaxation rates $1/T_{2,\text{short}}$ and $1/T_{2,\text{long}}$ were determined. The dynamics of soft polymer network was analyzed in terms of multi-exponential decays. The effect of T_1/T_2 ratio in

inhomogeneous magnetic fields on the CPMG decays was numerically studied. A correction factor $T_2/T_{2,\text{eff}}$ is derived function of the T_1/T_2 ratio. Finally, corrected 2D T_1-T_2 correlations maps are obtained. In the last part, for the series of NR samples aged naturally the ^{1}H DQ Fourier and Laplace-like spectra are characterized. The DQ build-up curves of natural aged samples presents two peaks. The Fourier spectra of DQ curves can be obtained using a correction procedure. The DQ Fourier spectra were described as distributions of RDCs and the $\overline{M}_2$ and $\overline{M}_4$ are calculated. More resolved Laplace-like spectra were used to discuss the effect of six years natural aging for cross-linked NR.

In chapter 3 the segmental dynamic heterogeneity of short-chain grafted PDMS on pyrogenic silica was investigated using ^{1}H NMR spin-diffusion. A double-quantum dipolar filter was employed for selection of the interface (rigid) region. 1D spin-diffusion equations were resolved numerically for a space distribution of spin diffusivity $D(x)$ of the mobile PDMS chains. The degree of heterogeneity was quantified by the parameters of Gaussian and exponential diffusivity distribution functions. The rigid and mobile domain sizes were correlated with the PDMS chain length, the temperature and ^{1}H residual dipolar couplings.

In chapter 4 some proton exchange membranes for fuel cell applications are introduced and discussed. In this sense the diffusion-exchange model in the assumption of two water pools was applied to describe the water transport in perfluorinated sulfonic acid (PFSA)/SiO_2 nancomposites. The water diffusivity in-plane and through-plane in solution cast films was measured by NMR. The anisotropy of the PFSA channels orientation was determined function of the nanofiller content. Gaussian displacement distribution for water diffusion was detected in PFSA membrane independent of the direction of gradients for small concentration in silica.

In chapter 5 2D T_2-T_2 molecular exchange NMR experiments are presented. The two-dimensional time maps were analyzed by the 2D Laplace algorithm. The 2D ^{1}H NMR correlation maps of air bubbles in water and foams, oil and water in sand, molecular exchange of liquid/foam and liquid/saturated vapors of chloroform are presented and discussed. Uni– and bi–directional exchange processes were observed in several cases. The effects of molecular exchange processes on the 2D T_2-T_2 maps were studied by Monte–Carlo numerical simulations. Systematic simulations were performed function of various parameters like the molecular self-diffusion coefficient, storage time τ_{store} and T_1/τ_{store} ratio. The influence of pores connectivity and interface and pore geometry was also studied.

In chapter 6 the problem of free water diffusion in a sheep Achilles tendon was studied. For this purpose the azimuthally angular dependence of the self-diffusion coefficient was measured using the PGSE in combination with CPMG pulse sequences. The diffusion tensor reveals a fast and a slow diffusion process. A model, which describes the stimulated-echo amplitude encoded by the water diffusion and magnetization transfer was used for evaluation of the fast diffusion coefficients which characterize the water molecules in pores surrounding the collagen fibrils. An orientation distribution function of pores that follows the collagen fibrils orientation was considered. The average aspect ratio of pores was estimated from the principal values of water diffusion tensor.

In chapter 7 the wool hard α-keratin and hair hard α-keratin was investigated. In particular the focus is i) on the thermal denaturation of keratin in wool investigated by ^{1}H spin-diffusion NMR and ii) on the effect of hard α-keratin hydration from Caucasian hair fibers investigated by ^{1}H solid-state NMR. The rigid, semi-rigid and an amorphous phase were obtained from ^{1}H wide line NMR spectra. The detected change in the phase composition was associated with the denaturation process. The morphological domain sizes were measured using ^{1}H spin-diffusion NMR. 2D square and 2D cylindrical morphologies were compared in order to give the best description of the spin-diffusion data. A qualitative model describing the denaturation process of keratin protein was developed. ^{1}H spin-diffusion NMR experiments using a DQ filter were employed on hydrated Caucasian hair fibers to obtain the domain sizes from the solution of the spin-diffusion equation for cylindrical morphologies in the initial rate approximation in combination with the quasi-equilibrium signal intensities. A qualitative model describing the water-keratin protein interaction was developed.

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