Scientific report

Project implementation ***Structure-dynamics-properties relationships and aging effects in nanocomposite elastomers and proton exchange membranes***

October – December 2011

The following objective for year 2011, research project PN II Idea 307/2011 is:

O1. The development of a new tool based on DQ Fourier spectra and DQ filtered spin-diffusion NMR experiments and Laplace distributions for the determination of morphology of reinforced EPDM samples at the changes of the filler type and content.

A new procedure based on Fourier transforms to analyze the DQ curves

The typical radiofrequency pulse sequence which contains 5 pluses to generate double quantum build-up curves is presented in Fig 1. For this type of pulse sequence the double quantum NMR signal may be expressed in function of residual dipolar interaction constant $\overline{\omega}_D$ and the effective relaxation time as,

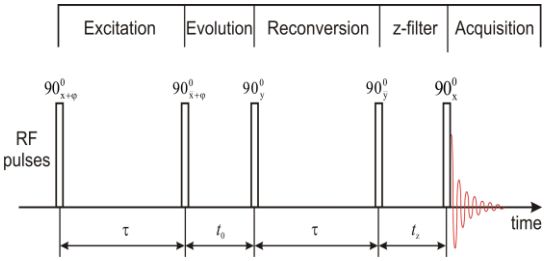

Fig. 1 The double quantum pulse sequence used for measurement of DQ buildup curves.

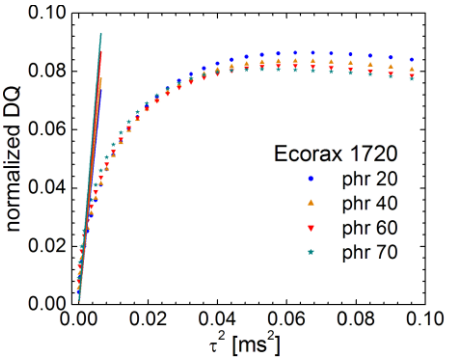

Fig. 2. DQ curves represented in function of square excitation/reconversion time τ^2, for EPDM reinforced sample with Ecorax® 1720 at different concentrations.

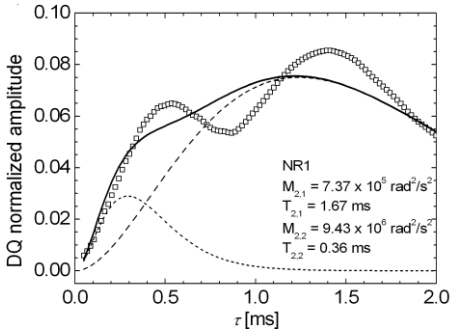

Fig. 3 Fitting with equation (2) of DQ curves for natural rubber naturally aged shows a bimodal distribution for which are choosing two components described by van Vleck moments and relaxation times.

$$S_{DQ}(2\tau)=\left\langle \sin^2\left(\overline{\omega}_D\tau\right)\exp\left(-\frac{2\tau}{T_2^*}\right)\right\rangle, \qquad (1)$$

where $\langle\ldots\rangle$ is the mediation over the statistically ensemble. The analysis of double quantum filtered is realized in ordinary way: i) by fitting the DQ curves in the initial domain of excitation/reconversion time τ^2 (Fig. 2) or ii) fitting with an expression which contains the second order residual van Vleck moment,

$$S(\tau)=\left[1-\exp\left(-\frac{M_2\tau^2}{2}\right)\right]\times\exp\left(-\frac{2\tau}{T_2^*}\right). \qquad (2)$$

Both approaches have advantages and disadvantages but the major inconvenience is that they fail to describe DQ build-up curves for complex systems characterized by bimodal distributions of macroscopic parameter such as the filled EPDM samples and aged natural rubber, see Fig.3. To characterize the DQ curves measured on such complex systems is necessary to implement a different approach, which should use the entire DQ curves to be analyzed using the Fourier transform. The DQ curve can't be used as it is obtained from NMR measurements because the information of residual dipolar couplings distribution $\overline{\omega}_D$ is hidden by a wide line which appears at zero frequency. So that, in order that such a DQ curves to be analyzed by Fourier transform, we need a new procedure which uses an exponential correction term with a prefactor that depends on the type of functional groups located in the polymer chains and determination of the best value of the correction relaxation time,

$$\mathcal{FT}\left\{S_{DQ}(2\tau)\right\}=$$
$$\mathcal{FT}\left\{\begin{array}{l}-\frac{4}{7}\left\langle \sin^2\left(\overline{\omega}_D^{(CH_2)}\tau\right)\exp\left(-\frac{2\tau}{T_2^{(CH_2)}}\right)\right\rangle\\ -\frac{9}{35}\left\langle \sin^2\left(\overline{\omega}_D^{(CH_3)}\tau\right)\exp\left(-\frac{2\tau}{T_2^{(CH_3)}}\right)\right\rangle\\ +\frac{29}{70}\exp\left(-\frac{2\tau}{T_2^*}\right)\end{array}\right\}\cong\frac{1}{14}\mathcal{FT}\left\{\begin{array}{l}\left\langle 4\cos\left(2\overline{\omega}_D^{(CH_2)}\tau\right)\exp\left(-\frac{2\tau}{T_2^{(CH_2)}}\right)\right\rangle\\ +\left\langle\frac{9}{5}\cos\left(2\overline{\omega}_D^{(CH_3)}\tau\right)\exp\left(-\frac{2\tau}{T_2^{(CH_3)}}\right)\right\rangle\end{array}\right\}. \qquad (3)$$

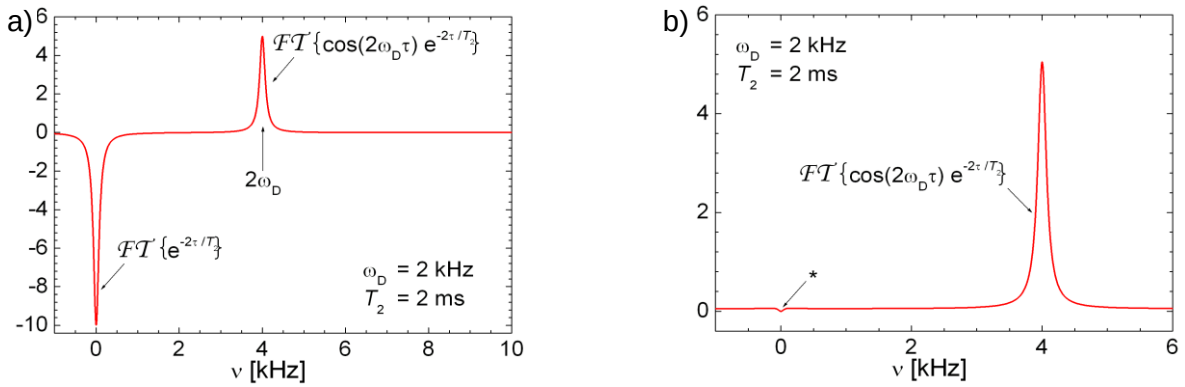

Fig. 4 a) Fourier spectra of DQ signal simulated with equation (1) for residual dipolar coupling constant value $\overline{\omega}_D$ = 2 kHz and the effective relaxation time T_2^* = 2 ms without correction; b) Fourier spectra of DQ after the application of correction procedure. The symbol"*" represent the minim error in the spectra which appear after correction procedure.

DQ Fourier spectra for EPDM samples reinforced with fillers based on carbon black, silane and $CaCO_3$ precipitate

For the entire series of EPDM samples reinforced with 8 types of different fillers, based on carbon black, silane, and $CaCO_3$ precipitate at 20, 40, 60 and 70 phr concentration the DQ Fourier spectra were obtained. Some representative examples are shown below for each type of filler. The DQ curves and the correspondent Fourier spectra are extremely similar for all the samples with the exception of Precarb 400 at 40-70 phr.

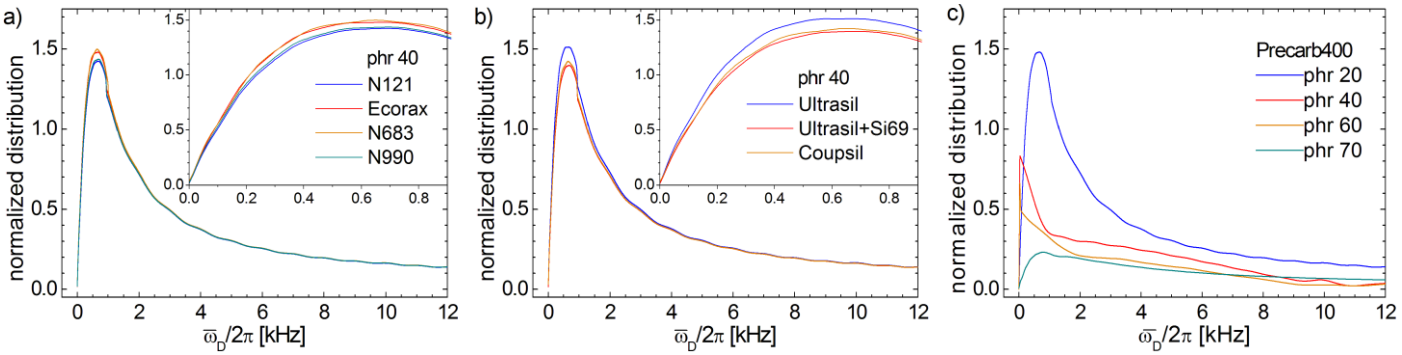

Fig.5 DQ Fourier spectra for EPDM elastomers reinforced with filers based on a) carbon-black and b) silane at 40 phr concentration and c) based on $CaCO_3$ function of filler concentartion from 20 phr to 70 phr.

The specific parameter value, distributions and dependency on the topological constraints (filer's cluster and cross-link density)

The parameter specific to DQ curves which result from the NMR signal (see eq.1) based on the irreducible algebra operators using statistical density matrix formalism is the residual dipolar coupling constant $\overline{\omega}_D$, which describes the dipolar interaction between nuclear spins in premeditate rapid movement localized in functional groups along the polymer chain described by the end-to-end vector, $\vec{R}$:

$$\overline{\omega}_D(R) = -\frac{1}{2}\sqrt{6}DS_s P_2(\cos\beta)\left(\vec{R}\right)^2 \Big/ \left\langle R^2 \right\rangle \cdot \tag{4}$$

The residual dipolar coupling constant value determined from DQ build-up curves (Fig. 5) grow with the growing of filer content in the domain 0-60 phr for all filler types based by carbon-black (Fig. 6a), silane and calcium carbonate precipitate (not presented here). Another parameter which describes the behavior of polymer chain mobile segment, correlated with residual dipolar coupling, is the second order van Vleck moment M_2^b, which present the same behavior in the entire domain of 0 – 70 phr. For entire series of natural rubber with different cross-link density

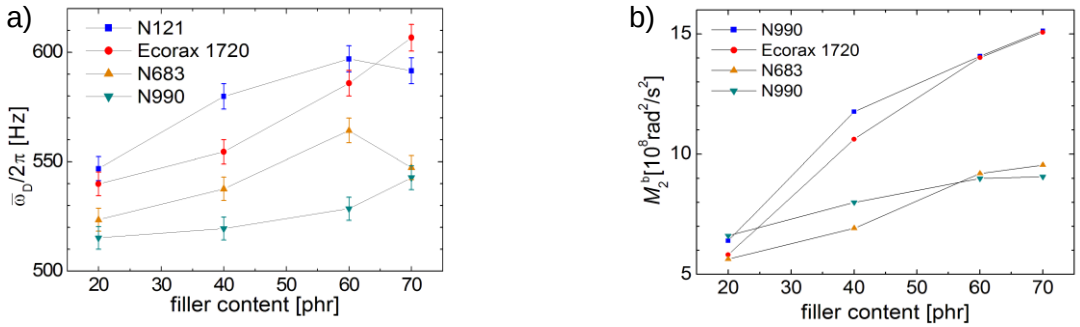

Fig. 6 a) The residual dipolar coupling and b) Van Vleck second order residual moment in function of the concentration of the filler for EPDM samples reinforced with fillers from category of carbon-black (N121, Ecorax® 1720, N683, N990).

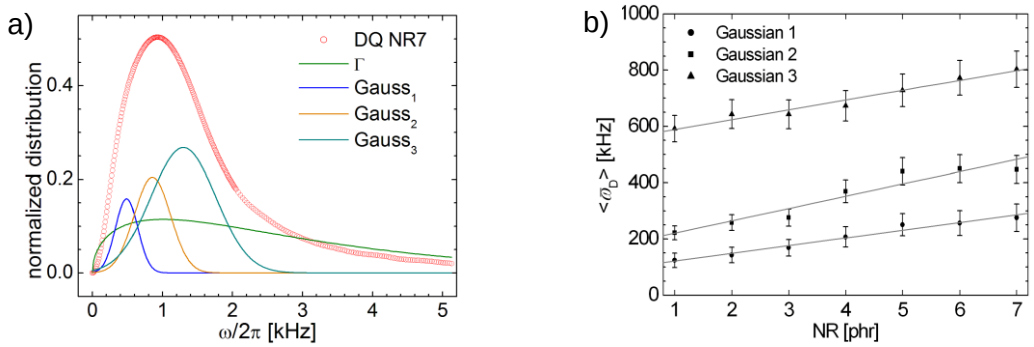

Fig. 7 a) Fourier spectra of DQ for NR7, the Γ and $Gauss_{1,2,3}$ distributions which compose this spectra; b) Linear dependence of half-height bandwidth for $Gauss_{1,2,3}$ distributions function of crosslink density.

the dipolar coupling constant distribution was measured by Fourier-DQ spectra deconvolution.

A new Laplace procedure based on theoretical and numerical solutions of one-dimensional spin diffusion equations

The concentration or Z-magnetization density of nuclear spins $m(\vec{r},t)$ in position $\vec{r}$ at an arbitrary time moment is,

$$m(\vec{r},t)=\frac{1}{\rho(\vec{r})}\frac{dM(\vec{r},t)}{dV(\vec{r})}, \tag{5}$$

Fig. 8 a) The representation of One-dimensional morphology, b) The relevant half of the 1D spin-diffusion problem.

where $dM(\vec{r},t)$ is the total z-magnetization of an infinitesimal volume element $dV(\vec{r})$ found on position $\vec{r}$ at a moment of time *t*. The numerical density of spins $\rho(\vec{r})$ from the volume element depends only on the position $\vec{r}$ and is independent of time. Diffusion equations for the spin-diffusion constants, with D_1 and D_2 coefficients, describing the bounded and mobile polymeric chains and the initial conditions for spin diffusion experiment immediately after applying the filter are,

$$\begin{cases}\dfrac{\partial m_1}{\partial t}=D_1\dfrac{\partial^2 m_1}{\partial x^2}\\[2ex] \dfrac{\partial m_2}{\partial t}=D_2\dfrac{\partial^2 m_2}{\partial x^2}\end{cases}. \quad \text{and conditions} \begin{cases} m_1(x,0)=m_1^0 & pt \quad 0\le x\le l_1\\ m_2(x,0)=0 & pt \quad l_1\le x\le l_1+l_2\end{cases} \tag{6}$$

Where after solving the problem of experimental data, these are integral fitted with integral quantities for source,

$$I_1(t_d)=\int_0^{l_1} m_1(x,t_d)\rho(x)dx=\frac{\rho l_1 l_2 m_1^0}{l_1+l_2}-\sum_{m=1}^{\infty}\frac{\dfrac{2\rho m_1^0}{\beta_m^2}\sqrt{\dfrac{D_2}{D_1}}\sin\left(l_2\beta_m\sqrt{\dfrac{D_1}{D_2}}\right)\sin(\beta_m l_1)e^{-D_1\beta_m^2 t_d}}{l\cos(l_1\beta_m)\cos\left(l_2\beta_m\sqrt{\dfrac{D_1}{D_2}}\right)-\left[l_2\sqrt{\dfrac{D_1}{D_2}}+l_1\sqrt{\dfrac{D_2}{D_1}}\right]\sin(l_1\beta_m)\sin\left(l_2\beta_m\sqrt{\dfrac{D_1}{D_2}}\right)}, \tag{7}$$

and for diffuse media,

$$I_2(t)=I_1(0)-I_1(t), \tag{8}$$

where the values $\pm\beta_m$ with m = 1, 2, 3, ... are calculated like the roots of the hyperbolic equation,

$$\sqrt{\frac{D_1}{D_2}}\sin(\beta_m l_1)\cos\left(\beta_m\sqrt{\frac{D_1}{D_2}}l_2\right)+\cos(\beta_m l_1)\sin\left(\beta_m\sqrt{\frac{D_1}{D_2}}l_2\right)=0. \tag{9}$$

The equations (7) and (8) are describing the NMR signal intensity for source (polymeric chain bounded to filler cluster) and for the diffuse media (polymeric chain connected to mobile EPDM). As is shown in equation (7) the signal decay for source is described by an equation which must be calculated as an infinite sum which, in addition, contains the roots of trigonometric equations (9). For the first time we wrote a new type of Laplace transform procedure whose kernel is no longer described by a function but is read as a 2D matrix dependent on the experimental diffusion time value t_d and domains length l_1 of EPDM polymeric chains linked to filler clusters and the mobile EPDM polymer chains l_2. The results of algorithm will not be the distributions of relaxation times but will be the distributions of mobile chain length for different fillers and filler concentrations (see the last section).

The results of multiple DQ filter applications. The Laplace and Fourier spectra for spin diffusion experiments

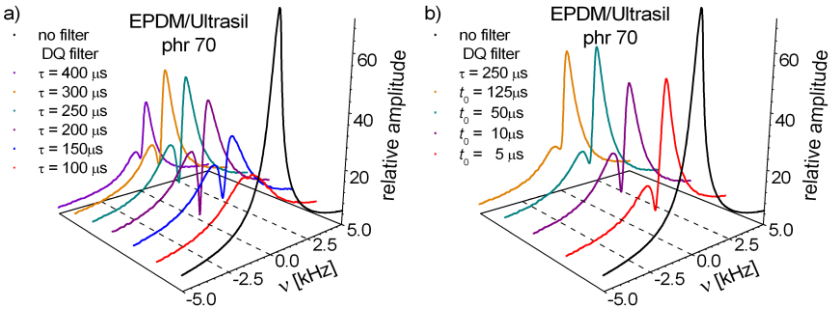

Fig. 9 Fourier spectra obtained after applying different DQ filters for which have been modified a) excitation/reconversion time τ and b) evolution time t_0 (see Fig. 1).

The spin-diffusion experiments assume the selection of magnetization for a component (usually the rigid) and magnetization "destruction" in the other component (usually mobile) by applying a NMR filter. In Fig. 9 are presented some Fourier spectra obtained for EPDM sample reinforced with Ultrasil 7000 at phr 70 and which were used to test the effectiveness of the DQ filter.

In Fig. 10a are presented the Fourier spectra filtered by DQ coherences measured for the reinforced EPDM samples N683 with a filler content of phr 60 for some particular values of spin diffusion time t_d = 10.7 μs ÷ 1020 μs. The T_2 distribution of Laplace spectra (Fig. 9b) were obtained by Laplace inversion of FID curves for which for the first time was used a function which consists of one Abragamian function and one exponential function,

$$FID(t)=\int_0^{\infty} f_A(T_2)\frac{\sin(a\cdot t)}{a\cdot t}\exp\left(-\frac{t}{T_2}\right)dT_2+\int_0^{\infty} f_E(T_2)\exp\left(-\frac{t}{T_2}\right)dT_2\,, \qquad (10)$$

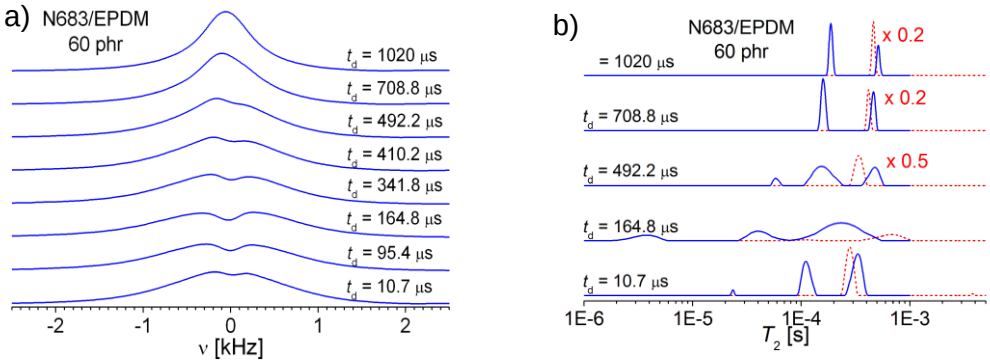

Fig. 10 Fourier spectra as overlapping Abragamian and Lorentzian distributions (a) and Laplace-like an overlapping of Abragamian and Gauss distributions presented in logarithmic scale (b) provided by DQ filtered NMR measurements for EPDM samples reinforced with N683 at 60phr content, for some particular value of spin diffusion time.

Spin diffusion curves in functions of diffusion times. Spin diffusion coefficients.

Both components of the nuclear magnetization which corresponds to polymeric chain bounded to the filler cluster and mobile unbound, are calculated like integral areas of all Gaussian spectral peaks in logarithmic scale from the Abragamian regime (for bound segments) and Gaussian regime (for mobile segments) like in Fig.10b. In fig. 11a are presented the ordinary spin-diffusion curves function of square roots of diffusion time for EPDM samples reinforced with carbon-black N683 at phr 60, to extract the lengths of bounded polymer chains segments (ℓ_b) and mobile (ℓ_m) and spin diffusion coefficients corresponding to these chains D_b and D_m respectively. The fitting of the experimental data is good but is not describing perfectly their dependence. This fact is due to the use for the lengths of EPDM chains of the average values.

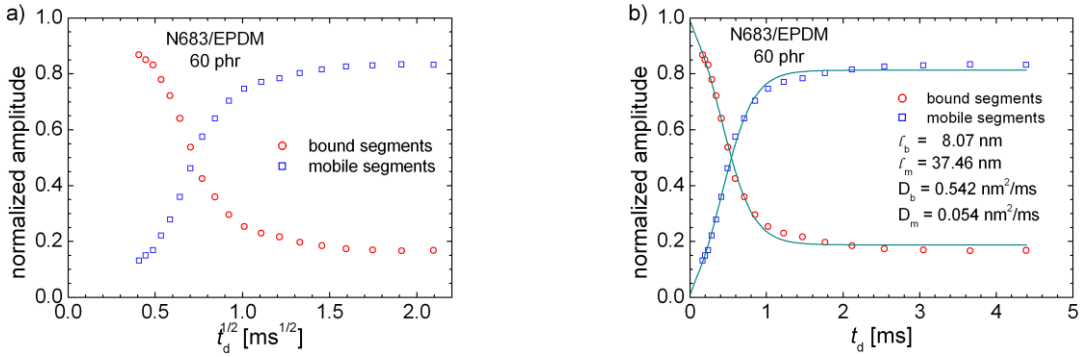

Fig. 11 a) Normalized probability of bound and mobile EPDM polymer segments represented in function of square root of spin diffusion time t_d and b) The fitting of experimental data function of spin diffusion time with the equations (7) and (8).

The distribution of EPDM polymer chains domains in the presence of fillers. Anisotropy. Results interpretation

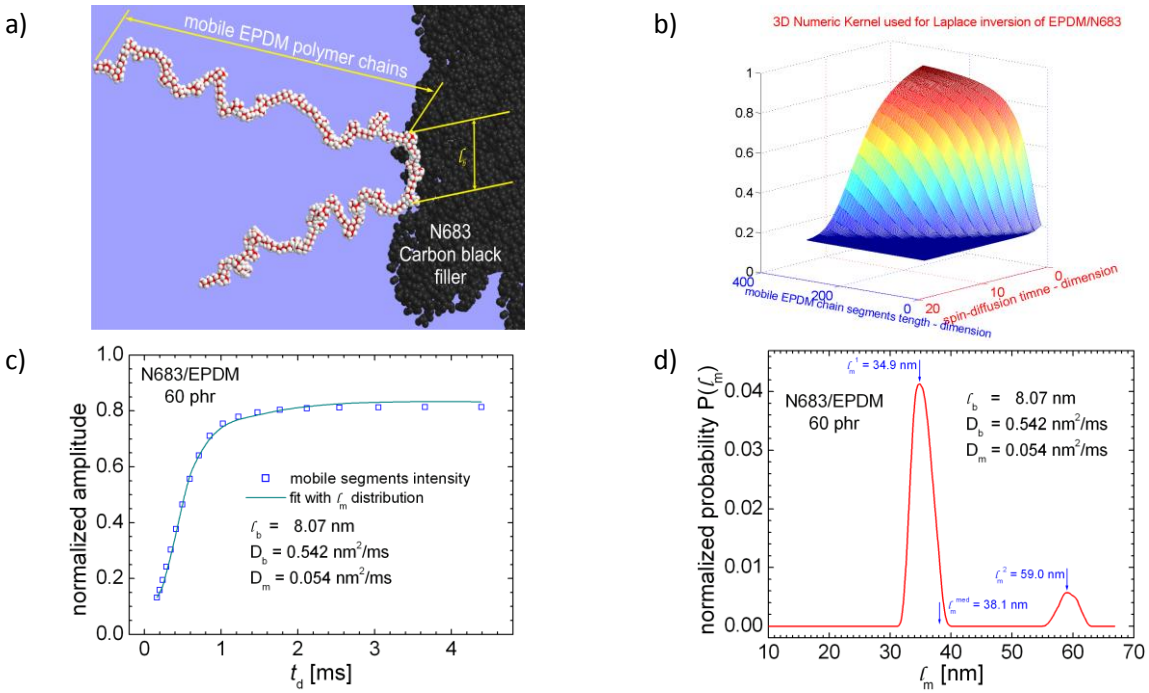

Fig. 12 a) ChemOffice® modeling of an EPDM chain interacting with a filler cluster; b) representation of a numeric kernel generated by equation (6) for inverse Laplace transform of some spin-difusion data; c) The fit of the build-up magnetization curve of mobile EPDM/N683 polymer chains segments function of spin-diffusion time t_d by Laplace inversion method; d) the distribution of EPDM mobile polymer chains lengths interacting with 60 phr N683 as obtained from the Laplace transform.

In the previous section was shown that the mean values of spin diffusion parameter, cannot describe perfectly the dependence of magnetization intensity corresponding to the mobile and bound EPDM chains segments. A more realistic model would assume that the mobile segment length of the polymer chains will not have a fixed value but a distribution of values. In Fig. 12 is presented a modeling of the interaction between the EPDM chains interacting with a cluster of carbon black fillers. One can observe that the lengths of both mobile ends are different. We wrote a C++ program to fit the spin-diffusion experimental data and the average values are presented in medallion of Fig 11b for EPDM/N683. With these obtained average values for the lengths of bound segments l_b and spin-diffusion coefficients D_b and D_m, we generate (with a new program written in C + +) new spin diffusion curves dependent on the length of mobile segments l_m. In this way we built a new tool which for the first time performs a numerical Laplace inversion using a numeric kernel (Fig. 12b) to obtain the distributions of lengths l_m (Fig. 12d). Anisotropy can be defined in function of the maxima values of both distributions and the average value:

$$\eta = \frac{l_m^2 - l_m^1}{l_m^{med}}, \tag{11}$$

where using the values shown in Fig. 12d, for this sample is obtained for a value of $\eta_{EPDM/N683}$ = 63.25 %. It was observed that the anisotropy increases with increasing filler content.

For the first time it was used a new tool based on spin diffusion NMR experiments combined with Laplace distributions for the determination of morphology (size rigid and mobile domains of polymer chains) of some elastomers like the EPDM reinforced with different fillers at various contents. Multimodal distributions were obtained for the lengths of mobile EPDM polymer chains segments which connects the filler clusters.

Publications:

1. C. Filipoi, D. E. Demco, X. Zhu, R. Vinokur, O. Conradi, R. Fechete, M. Möller, Channel orientation anisotropy in perfluorosulfonic acid/SiO_2 composite proton exchange membranes: Water self-diffusion study using NMR, Chem. Phys. Lett., 513, 251–255 (2011).
2. D. Moldovan, M. Pop, R. Fechete, A. Baudouine, M. Todica, Investigate the Effects of Degradation of High Density Polyethylene by ^{13}C NMR Spectroscopy and ^{1}H Relaxometry, (Accepted Studia Chemica Babes-Bolyai, 2011).

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12.12.2011

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