Scientific report

related to the implementation of project: ***Structure-dynamics-properties relationships and aging effects in nanocomposite elastomers and proton exchange membranes***

in the period January – December 2012

The objectives of year 2012

O2 The development of new tools based on 1D and 2D Laplace distributions for the quantitative study of the dynamic and morphological modification and diffusion anisotropy of filled elastomers while swelling various spherical and linear solvent molecules.

The absorption degree of several solvents in filled EPDM rubber was tested. Table 1 present the degree of absorption of the solvents: toluene (spherical molecule) n-hexane and octane (linear molecules) at filler content of 60 phr.

Table 1 Types of solvents with spherical and linear molecules absorbed in EPDM and the mass uptake Q_w.

Solvent	EPDM rubber with various solvents (60 phr)							
	N121	Ecorax® 1720	N683	N990	Ultrasil® 7000 GR	Ultrasil® 7000 GR + Si69	Coupsil® 8113	Precarb® 400
Toluene (C_7H_8)	1.40	1.15	1.31	0.10	1.11	2.38	1.96	0.79
n-Hexane (C_6H_{14})	1.01	0.86	0.83	0.56	0.72	1.76	1.28	0.34
Octane (C_8H_{18})	1.08	0.89	0.90	0.06	1.70	0.75	1.53	0.23

A new pulse sequence which filters the solvent NMR signal was implemented. This is based on the implementation of a new double quantum dipolar filter in front of the CPMG pulse sequence (see Fig. 1a), moreover the magnetization time was set at 0.2 s so that additionally a partial T_1 filter was used. The CPMG echoes train decay curve of n-hexane absorbed in EPDM rubber filled with Ultrasil is presented with red in 1b.

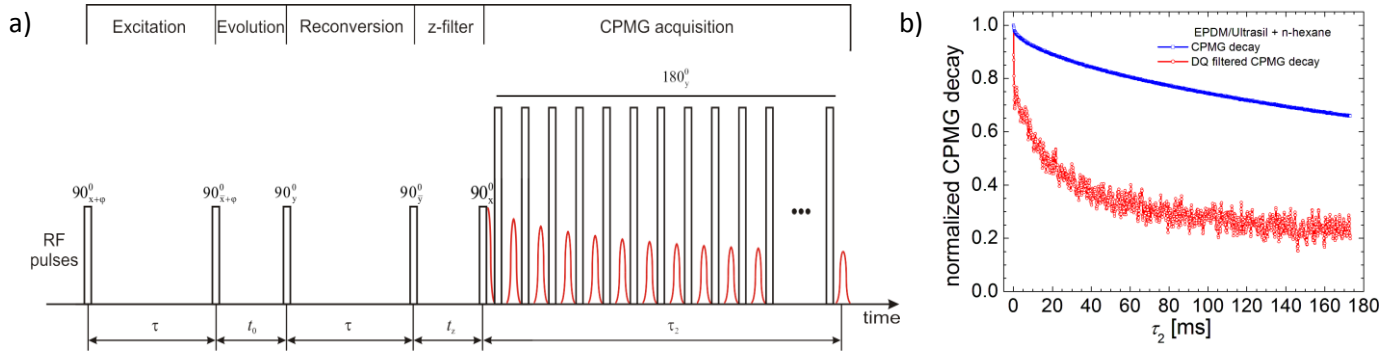

Fig. 1 a) The CPMG pulse sequence with a double quantum dipolar filter; b) The CPMG decays without dipolar filter (blue curve) and with dipolar filter (red curve).

In order to filter out the polymer signal the CPMG pulse sequence with 10 s remagnetization time and 4 ms echo time was used, and the first echoes were neglected. The 1D T_2 distributions for absorbed n-hexane in EPDM with Ultrasil+ Si69 and Coupsil presented in Fig. 2 have 4 peaks. The firs peak (T_2 ~10-30 ms) belongs to ultra-mobile

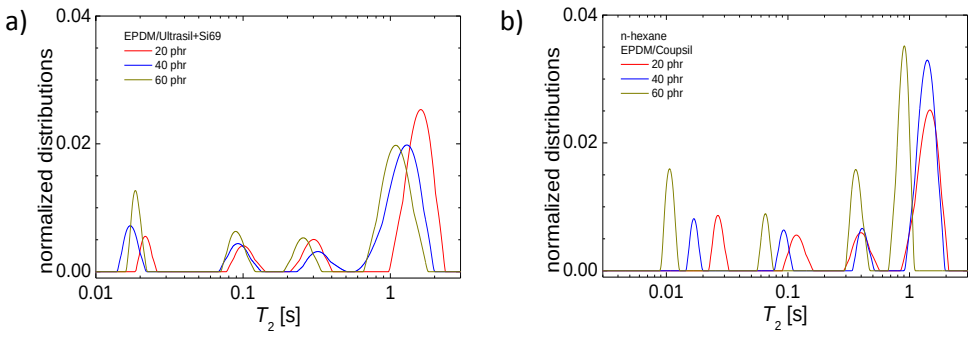

Fig. 2 The T_2 transverse relaxation times distributions of n-hexane absorbed in EPDM rubber with a) Ultrasil+Si69 and b) Coupsil.

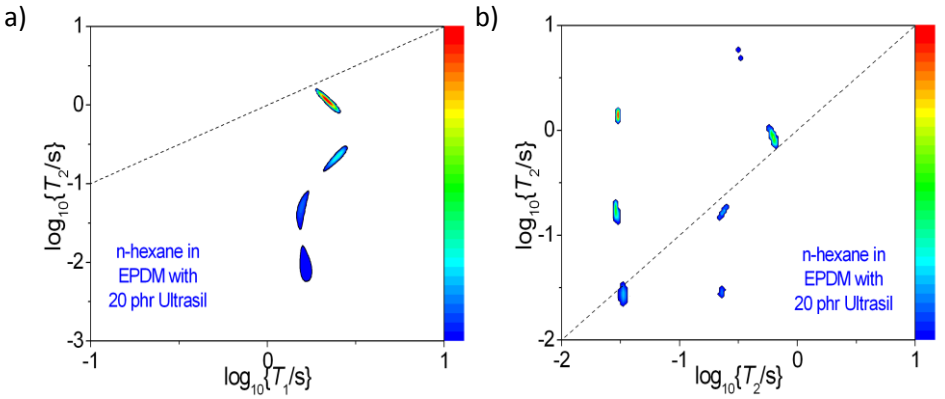

Fig. 3 The a) T_1–T_2 si b) T_2–T_2 correlation maps of n-hexane molecules absorbed in EPDM with 20 phr Ultrasil filler.

polymer chains, while the peaks observed in the range T_2 ~ 60 ms - 2 s) are associated with the n-hexan solvent which explore the pores and canals between the EPDM polymer chains which connect the fillers. This interpretation was correlated with the analysis of 2D T_1–T_2 and T_2–T_2 correlation maps of absorbed solvents in filled EPDM rubber. In Fig. 3a the T_1–T_2 correlation maps show four peaks widely distributed along T_2 and narrowed distributed in T_1. In Fig. 3b the T_2–T_2 exchange map present three diagonal peaks associated with three types of environments where n-hexane solvent can be found and between which the exchange is possible as one can observe from the apparition of extra-diagonal peaks.

The dynamics of solvent molecules located in the filled EPDM polymeric network pores and canals was evidenced from the measurement of the distribution of self-diffusion D. For that, the curves registered (see Fig. 4a as example of absorbed toluene in EPDM with Ultrasil) by PGSE (pulsed gradient stimulated echo) were analyzed using the Laplace transform. The distribution of self-diffusion coefficient for pure toluene sows a main peak and another small peak located at large values of D (the black curve in Fig. 4b). The last peak can be associated with the superficial shell from which the toluene molecules evaporated fast. For the absorbed toluene in rubber, additionally to those two peaks we may observe the third peak located at much lower D values which indicates a restriction in the toluene molecular mobility due to the interaction with the EPDM polymeric network bonded to filler clusters. The anisotropy of D was measured and we report sensitivity to filler type and content (see the legend in Fig. 4b).

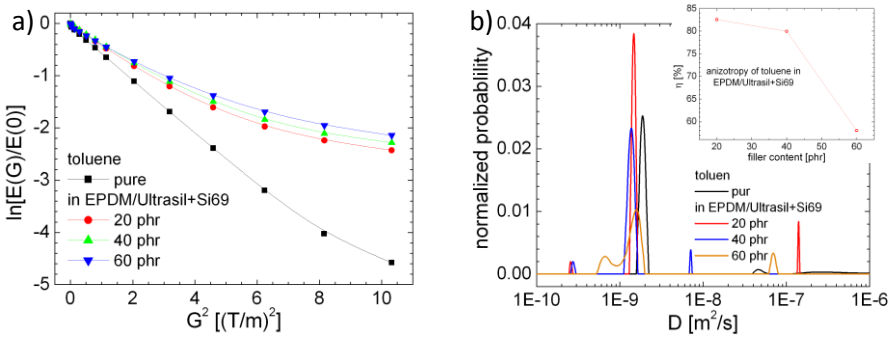

Fig. 4 a) The stimulated echo decay curves in PGSE NMR experiments for pure toluene absorbed in EPDM rubber with 20, 40 and 60 phr Ultrasil+Si69 content; b) The distribution of self-diffusion coefficient D, of toluene obtained from curves shown in a) and the anisotropy.

O3 **Characterization of the effect of temperature variations on the global structural and dynamical properties of filled elastomers and cross-linked natural rubber.**

The residual dipolar coupling curves (Fig. 5a) are obtained function of cross-link density of natural rubber samples natural aged over six years. These were obtained also by Laplace inversion of DQ NMR curves described by,

$$S_{DQ}\left(2\tau,T_2^*\right)= \exp\left(-\frac{2\tau}{T_2^*}\right)\int_0^{\infty} f\left(\overline{\omega}_D\right)\sin^2\left(\overline{\omega}_D\tau\right)d\overline{\omega}_D \quad ,(1)$$

Registered for all samples from NR1-NR7 (Fig. 5b).

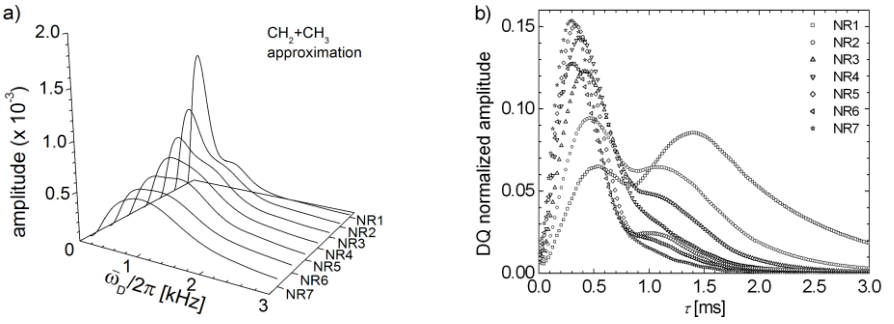

Fig. 5 a) The distribution of rsidual dipolar coupling constant for a series of six years natural agad natural rubber samples obtained from b) the bimodal double quantum build-up curves of the serie NR1-NR7.

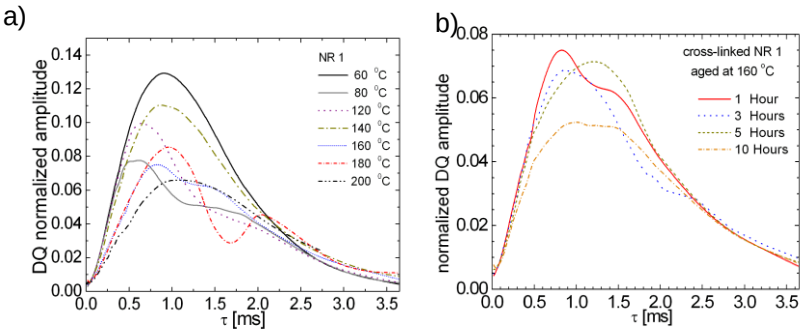

Fig. 6 The DQ curves for aged NR1 a) for one hour at various temperatures 60 – 200 °C and b) at 160 °C function of ageing time.

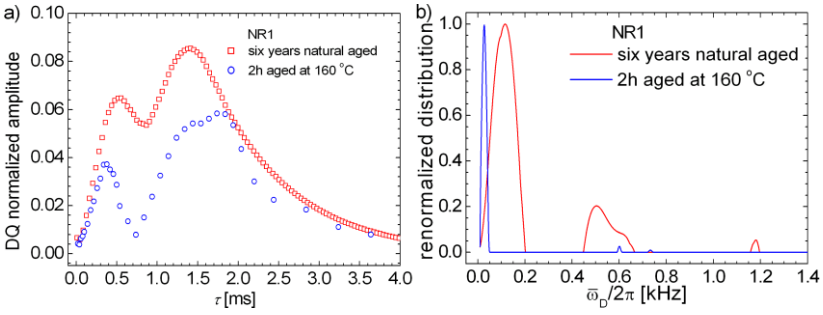

Fig. 7 a) The DQ curves for NR1 six years natural ages and artificial aged for 2h at 160 °C and b) comparison of distribution of residual dipolar couplings obtained for data presented in Fig. a).

The DQ NMR curves of artificial agent at different temperatures NR samples were recorded. In Fig. 6a are presented a selection of such DQ curves for NR1 measured after one hour, aged at 60 °C to 200 °C. The dramatic changes in DQ curves suggest a deep effect of temperature on the residual dipolar couplings characteristic to polymer network. The aging time effect on the DQ curves was investigated. In Fig. 6b are presented some DQ curves for NR1 aged at 160 °C for 1h up to 10 h. The aging under the effect of temperature presents a bimodal character observed also for natural aged (Fig. 7a). From Laplace analysis one can establish correlation between residual dipolar couplings affected by both artificial and natural age (Fig. 7b).

O4 The development of specific NMR, FTIR, DSC and AFM techniques for the study of changes at elastomers surface subjected to thermal, UV, chemical and mechanical accelerated aging.

The T_2 relaxation time distributions obtained for a series of nano-composite non-aged elastomers, measured at the rubber surface are presented in Fig. 8a. From the measurement of peaks maximum or from spectra deconvolution two components, the short and the long ones are obtained, which can be correlated with the rigid and mobile segments of the polymer chains. Just the short component can be correlated with the second residual van Vleck moment,

$$\frac{1}{T_{2,s}} = \sqrt{\frac{\overline{M}_2}{2}}\,, \qquad (2)$$

which is represented in Fig. 8b.

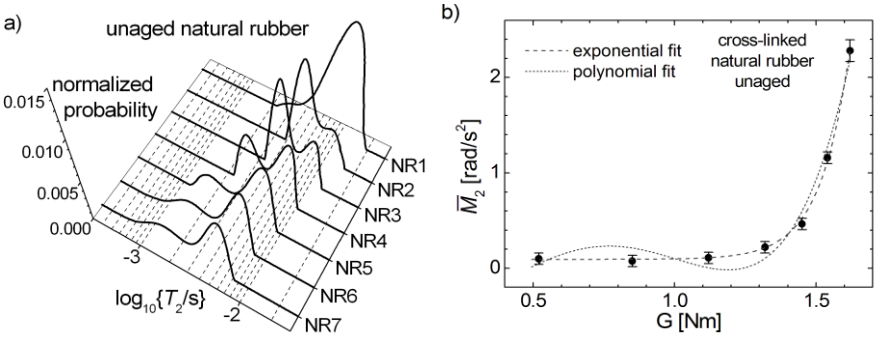

Fig. 8 a) The T_2 distribution curves for NR serie measured at surface with NMR-MOUSE®; b) the variation of rsidual second van Vleck moment function of share modulus for the serie of NR rubber.

The study of ageing factors on the rubber can be performed by recording the FT-IR with ATR (attenuated total reflection) spectra. In Fig. 9 are compared the FT-IR spectra for EPDM samples with two types of fillers: Ultrasi and Ultrasil +Si69 at 60 phr filler content. The effect of the filler type can be better evidenced from the variation of amplitudes of some specific lines in the range 1400–2500 cm^{-1}, than from the occurrence of new spectral lines. The temperature effect on the

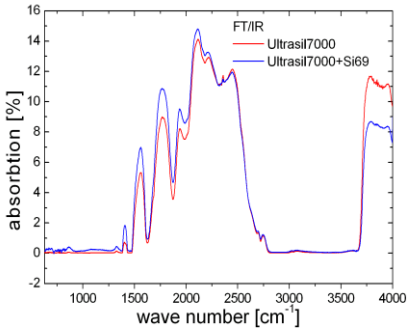

Fig. 9 The absorbtion FT/IR spectra recorded for EPDM with Ultrasil (red) and Ultrasil+Si69 (blue) fillers before ageing.

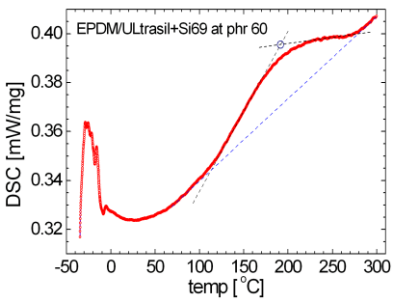

Fig. 10 The DSC curve for EPDM with Ultrasil+Si69 filler obtained in the – 35 °C ÷ 300 °C temperature range.

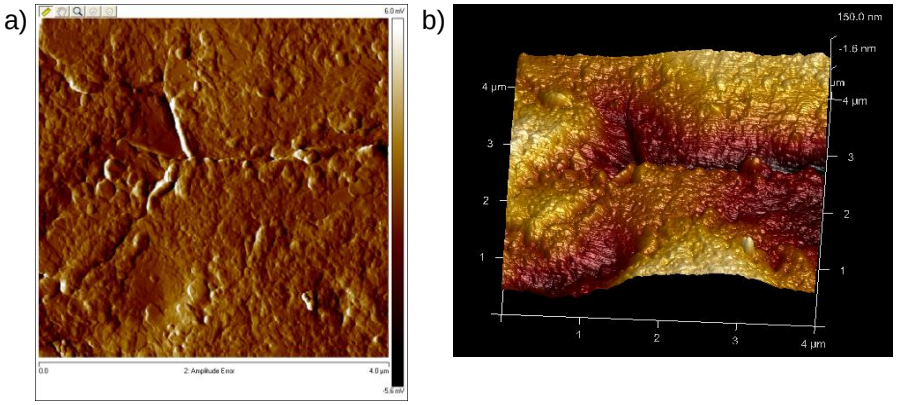

Fig. 11 AFM images of the NR1 natural rubber surface a) in amplitude and b) 3D representation by combining the amplitude and phase informaton.

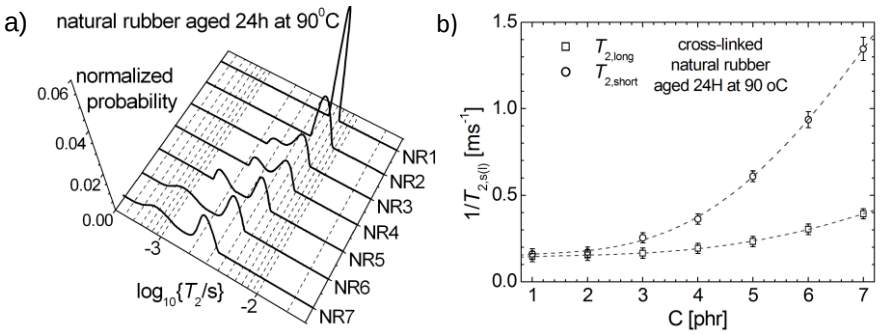

Fig. 12 a) The T_2 distribution curves for the serie of aged NR for 24 h at 90 °C measured at surface with the NMR-MOUSE®; b) the dependence of short and long components of relaxation rates $1/T_{2,s(l)}$.

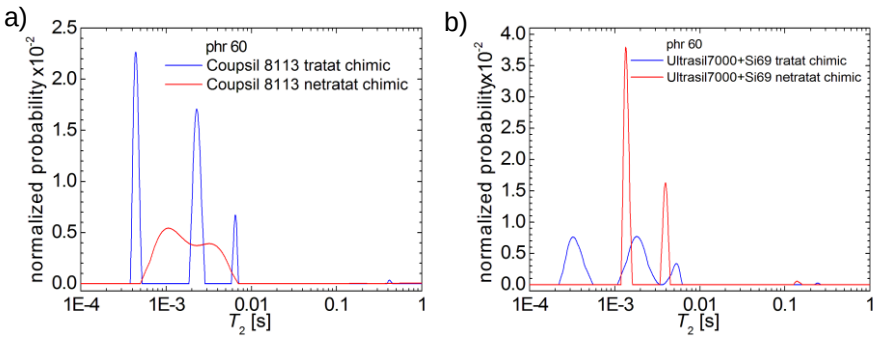

Fig. 13 The distribution of relaxation times T_2 for filled EPDM elastomers a) Coupsil and b) Ultrasil+Si69, chemically aged (blue) and non-treated (red).

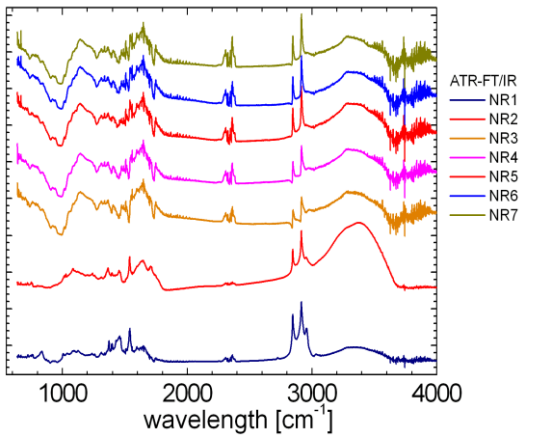

Fig. 14 The ATR-FT/IR spoectra measured at natural rubber surface aged 24 h under the UV radiation function of cross-link density (NR1-NR7).

intensity of polymeric chains interactions with filler clusters can be evidenced from the DSC curves. In Fig. 10 such curve is presented for EPDM with Ultrasil +Si69 recorded with a velocity of 10 K / min. One can observe a deviation in the range 150-250 °C.

A specific method for the study of surface effects is based on the atomic force microscopy. In Fig. 11 are presented as examples, two AFM images (2D and 3D) of a NR1 natural rubber. The AFM measurement of samples subjected to the action of intense heat source are not trivial, since the sample surface is sticky. This fact restrains the sensitivity of the AFM sensor at palpation.

The elevated temperature can have an ordering effect of the polymer chains. This effect was observed for the distribution of relaxation times T_2 measured at NR1-7 rubber surface (Fig. 12a). From these distributions one can get the relaxation ratios $1/T_2$ of short and long components which can be correlated with the rubber cross-link density C (Fig. 12b).

Another study was related to the modifications which occur in the distribution of relaxation T_2 of filled EPDM samples after the treatment with various corrosive agents. In Fig. 13 are compared the T_2 distributions of EPDM filled with Coupsil and Ultrasil+Si69 at 60 phr filler content. We demonstrate that the filler type is important, thus while for the sample EPDM/Coupsil after the chemical treatment the width of lines becomes narrowest with an order of magnitude (Fig. 13a) for the sample EPDM/Ultrasil+Si69 the effect is vice-versa (Fig. 13b).

The effects of UV radiation were revealed by DQ NMR measurements and also from ATR FT-IR spectra. In Fig. 14 such ATR-FT/IR spectra measured at the surface of a series of natural rubber aged for 24 h under UV radiation with the wavelength λ = 253.7 nm produced by a bulb with the power P = 30 W located at 15 cm on top of the exposed surface. Differences between samples can be observed in the 2800-3000 cm^{-1} spectral range.

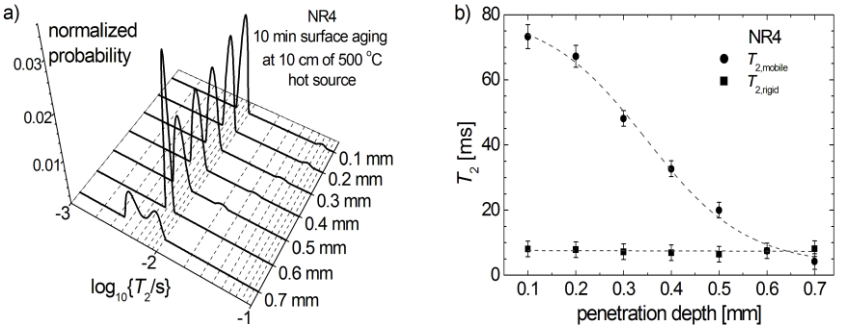

Fig. 15 a) The T_2 distribution curves for NR4 measured with the NMR-MOUSE® function of sensitive volume; b) the variation of rigid and mobile T_2 components function of penetration depth.

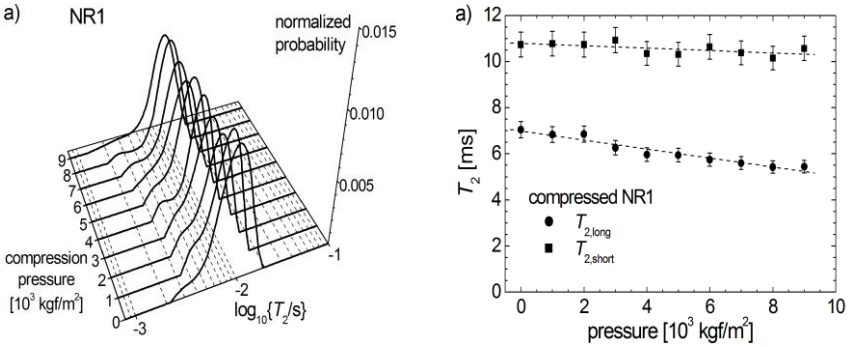

Fig. 16 a) The T_2 distribution curves for NR1 measured at surface with the NMR-MOUSE® function of external pressure; b) the variation of rigid and mobile T_2 components function of pressure obtained from the spectral deconvolution of curved presented in a).

The penetration depth of the effects of extreme temperatures obtained by exposing an rubber sample closed to a hot suource (500 ^{o}C), was determined from the measurement at NR4 surface of the T_2 relaxation times distributions function of unilateral sensor sensitive volume position (Fig. 15a). We can observe two peaks, one relatively fixed and one mobile with values dependent on the temperature effect (Fig. 15b). In this case the corresponding distribution to the non-affected sample is obtained at a depth of 0.7 mm. The short and long relaxation times obtained from T_2 distribution of NR1 natural rubber subjected to external pressure show a decreasing linear dependence function of the external pressure values (Fig. 16).

The dissemination of results

1. C. I. Horvat, X. Zhu, D. Türp, R. A. Vinokur, D. E. Demco, R. Fechete, O. Conradi, A. Graichen, D. Anokhin, D. A. Ivanov, M. Möller, *Perfluorosulfonic acid ionomer – silica composite membranes prepared using hyperbranched polyethoxysiloxane for polymer electrolyte membrane fuel cells*, Int. J. Hydr. Energy, 37 (19) 14454–14462 (2012).
2. C. Filipoi, D. E. Demco, X. Zhu, R. Vinokur, O. Conradi, R. Fechete,M. Möller, *Water self-diffusion anisotropy and electrical conductivity of perfluorosulfonic acid/SiO_2 composite proton exchange membranes*, Chem. Phys. Lett., 554 143–149 (2012).
3. D. Demco; A.-M. Oros-Peusquens, L. Utiu, R. Fechete, B. Blümich, N. J. Shah, *Molecular dynamics parameter maps by ^{1}H Hahn echo and mixed-echo phase-encoding MRI*, J. Magn. Reson. (2012) DOI: 10.1016/j.jmr.2012.11.005.
4. D. Moldovan, Metode moderne RMN pentru caracterizarea materialelor avansate, ISBN: 978-973-53-0902-2, Ed. Risoprint Cluj-Napoca (2012).
5. N. Cioica, R. Fechete, O. Cozar, C. Cota, *Investigate the effect of some plasticizers on the macrostructure of corn starch used to obtain biodegradable packaging*, INMATEH - Agricultural Engineering, Volume 36, Issue 1, 2012, Pages 69-70, (2012).
6. E. Jumate, D. C. Moldovan, R. Fechete, D. L. Manea, *The porosity and exchange processes in Portland cement pastes by 1D and 2D NMR relaxometry*, First International Conference for PhD students in Civil Engineering, 4-7 Noviembrie, Cluj-Napoca, CE-PhD, 421-427(2012).
7. D. Corpodean Moldovan, R. Fechete, D. E. Demco, *Characterization of the ^{1}H Double Quantum Fourier and Laplace Spectra of Aged Natural Rubber Samples*, Poster presented at EUROMAR 2012 International Conference, Dublin, Ireland, 1-5 Iulie (2012).
8. R. Fechete, D. Corpodean Moldovan, D. E. Demco, *Morphology of Filled EPDM Rubber by Laplace Distribution of ^{1}H NMR Spin-Diffusion Decays*, Poster presented at EUROMAR 2012 International Conference, Dublin, Ireland, 1-5 Iulie (2012).

Data
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