

Scientific report

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

January -December 2014

The objectives for year 2014

O6b The development of a new tool based on the two dimensional correlation maps, 2D Laplace inversion and MONTE-CARLO simulations for the characterization of the free ↔ bound water exchange processes by the measurement of the proton exchange velocity and channel proton conduction in PFSA/SiO₂ membranes.

Writing of new NMR pulses sequences specific to 2D T_2 - T_2 and T_1 - T_2 correlation maps measurements

A non-exponential character of the relaxation curves for PFSA/SiO₂ membranes was observed. This led to a development of a new model of Laplace transform which contains a complex nucleus composed as a sum of multi-Gaussian + multi Exponential components (see eq. 1). In fig. 1a is presented the FID curve registered for a PFSA membrane containing 10 wt.-% SiO₂. A new Laplace inversion algorithm was used to fitted experimental data (see continue line in the fig. 1a). One notes that the introduction of Gaussian components is obtained a better approximation of

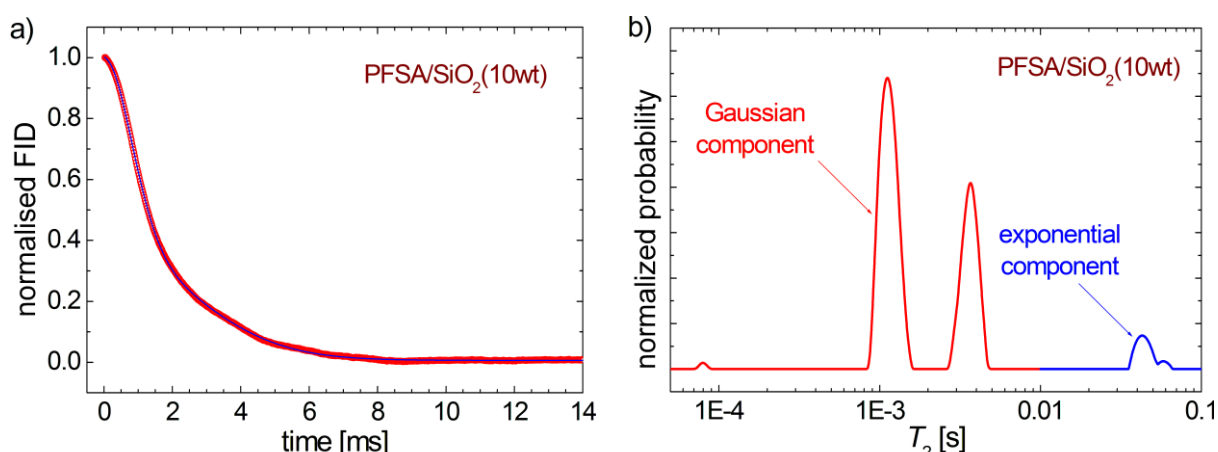
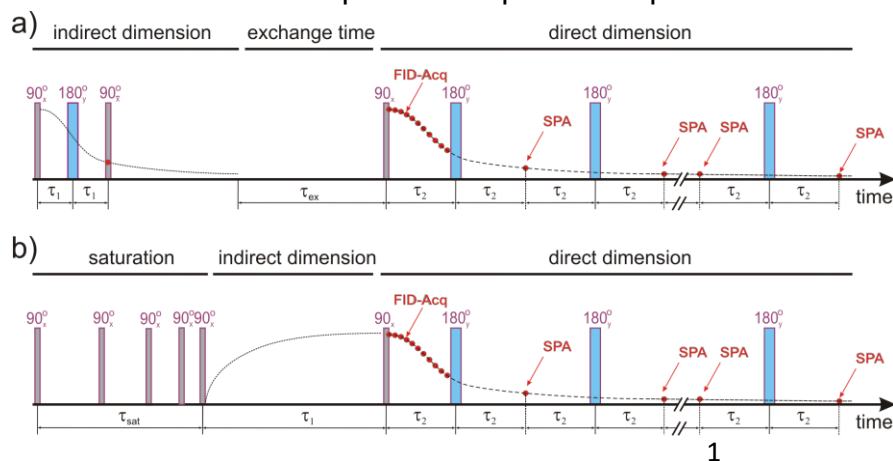


Fig. 1 a) FID curve is obtain for PFSA/SiO₂ (10wt) membrane; b) The $T_{2,Gauss}$ and $T_{2,exp}$ relaxation time distribution obtained by analysis of FID curve presented in Fig. 1a.

experimental data. The distributions of the relaxation time corresponding to the Gaussian and exponential components are presented in Fig. 1b.

The CPMG pulse sequence assumed a stroboscopic recording (between pulses) of the spin system response with a periodicity related to the echoes time apparition; typically, this time is larger than 70 μ s and thus the Gaussian character notable at small times is lost. Thereby, were written a new NMR pulses sequences specific to 2D T_2 - T_2 and T_1 - T_2 correlation maps



measurements and which keeps this character. Pulses sequences are present in fig. 2. Thereby, in the direct dimension we have a complex acquisition of the signal as a FID sum of Gaussian component and classic CPMG.

Fig. 2 a) Specific NMR pulses sequence of PFSA/SiO₂ hydrated membranes for 2D correlation of a) T_2 - T_2 and b) T_1 - T_2 .

The development of a new Laplace inversion algorithm to obtain the T_2 - T_2 exchange maps of free and bound water from hydrated PEM membranes

The 1D FID decay curves were analyzed after development of a new Laplace inversion algorithms based on complex nucleus of multi-Gaussian combined with multi-exponential:

$$M(t) = \int_{T_{2,\min}^{\text{Gauss}}}^{T_{2,\max}^{\text{Gauss}}} f_{\text{Gauss}}(T_2^{\text{Gauss}}) \exp\left[-\left(\frac{t}{T_2^{\text{Gauss}}}\right)^2\right] dT_2^{\text{Gauss}} + \int_{T_{2,\min}^{\text{exp}}}^{T_{2,\max}^{\text{exp}}} f_{\text{Gauss}}(T_2^{\text{exp}}) \exp\left[-\left(\frac{t}{T_2^{\text{exp}}}\right)^2\right] dT_2^{\text{exp}}. \quad (1)$$

After the development of new Laplace inversion algorithms the 2D T_2 - T_2 correlation maps were properly analyzed. These algorithms are based on Gaussian and exponential kernels like are describe herein:

$$M(\tau_d, \tau_i) = \int_{T_{2,d,\min}^{\text{Gauss}}}^{T_{2,d,\max}^{\text{Gauss}}} \int_{T_{2,i,\min}^{\text{Gauss}}}^{T_{2,i,\max}^{\text{Gauss}}} \exp\left[-\left(\frac{\tau_d}{T_{2,d}^{\text{Gauss}}}\right)^2\right] f_1(T_{2,d}^{\text{Gauss}}, T_{2,i}^{\text{Gauss}}) \exp\left[-\left(\frac{\tau_i}{T_{2,i}^{\text{Gauss}}}\right)^2\right] dT_{2,i}^{\text{Gauss}} dT_{2,d}^{\text{Gauss}} \\ + \int_{T_{2,d,\min}^{\text{exp}}}^{T_{2,d,\max}^{\text{exp}}} \int_{T_{2,i,\min}^{\text{Gauss}}}^{T_{2,i,\max}^{\text{Gauss}}} \exp\left[-\left(\frac{\tau_d}{T_{2,d}^{\text{Gauss}}}\right)^2\right] f_2(T_{2,d}^{\text{exp}}, T_{2,i}^{\text{Gauss}}) \exp\left[-\left(\frac{\tau_i}{T_{2,i}^{\text{Gauss}}}\right)^2\right] dT_{2,i}^{\text{Gauss}} dT_{2,d}^{\text{exp}}. \quad (2)$$

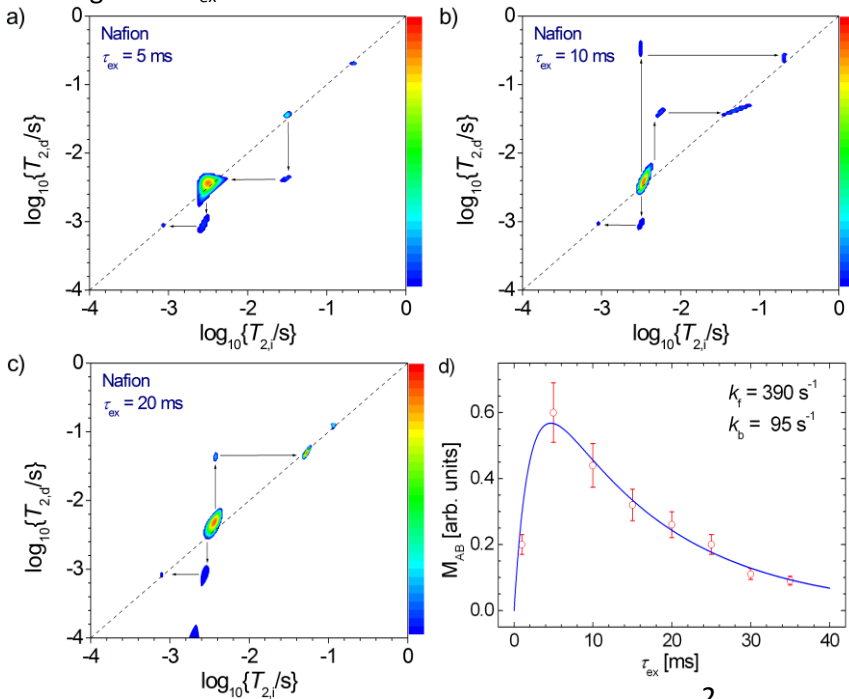
Several series of 2D NMR T_2 - T_2 exchange maps were recorded. These are obtained in function of the SiO_2 contained (0, 1, 2, 3, 5 and 10 wt) in hydrated PEM (PFSA/ SiO_2) membranes (see fig. 3) and in function of exchange time (see Fig. 4a, 4b and 4c). Such a map obtained for

PFSA/ SiO_2 (10wt) for an exchange time of 50 ms is presented in fig. 3. A series of 2D T_2 - T_2 exchange maps were measured in function of exchange time (see fig. 4).

The differential equations which describe the relaxation and exchange between two coupled spin systems A and B are described by the below system:

$$\begin{cases} \frac{dM_A}{dt} = -k_{AB}M_A + k_{BA}M_B + R_A^1(M_A^\infty - M_A) \\ \frac{dM_B}{dt} = -k_{BA}M_B + k_{AB}M_A + R_B^1(M_B^\infty - M_B) \end{cases}, \quad (3)$$

Fig. 3 2D T_2 - T_2 exchange maps for PFSA/ SiO_2 (10wt) membrane hydrated 100 % at an exchange time $\tau_{\text{ex}} = 50$ ms.



where $M_{A,B}$ are the system magnetization A and B, k_{AB} and k_{BA} are the exchange velocities, and $R_{A,B}^1 = 1/T_{1,A,B}$ are the transverse relaxation time rates. We can calculate the exchange velocity k_f (free to bound) and k_b from the integral areas amplitude of the extra-diagonal peaks as we can see in Fig. 4d.

$$M_{A \rightarrow B}(\tau_{\text{ex}}) = \frac{k_{A,B}}{\lambda_+ - \lambda_-} e^{\lambda_+ \tau_{\text{ex}}} (1 - e^{-(\lambda_+ - \lambda_-) \tau_{\text{ex}}}), \quad (4)$$

Fig. 4 2D T_2 - T_2 exchange time maps obtained for 100 % hydrated Nafion 117 membrane at an exchange time a) $\tau_{\text{ex}} = 5$ ms, b) $\tau_{\text{ex}} = 10$ ms and c) $\tau_{\text{ex}} = 20$ ms; d) The values of amplitude integral areas of the extra diagonal peaks and exchange rates values characteristics to free $\leftrightarrow$ bound water exchange.

Correlation of the experimental T_2 - T_2 exchange maps with simulated maps

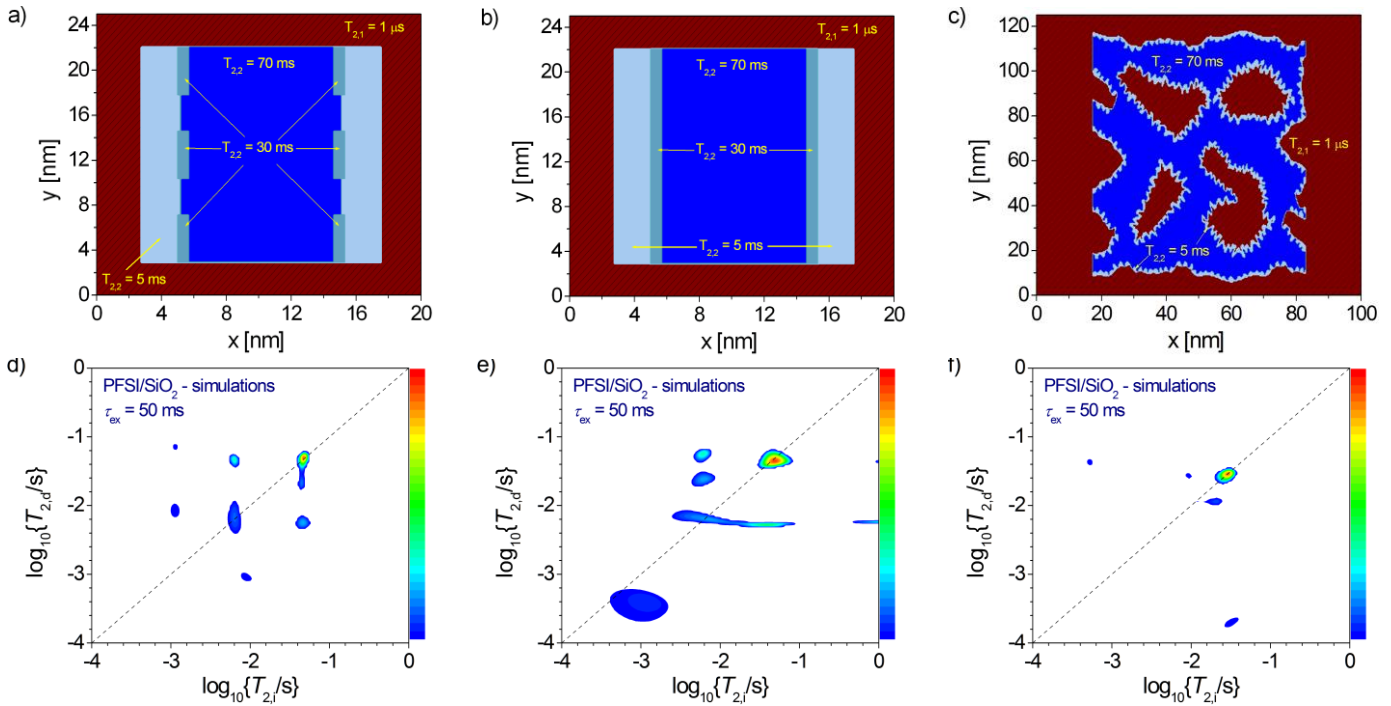


Fig. 5 The T_2 distribution maps of an ideal situation of 3 components communicating a) directly, b) indirectly, and c) a semi-ideal case. T_2 - T_2 exchange maps corresponding to 3 maps are presented in figs. d) e) and f) for $\tau_{ex} = 50 \text{ ms}$.

The ideal maps were simulated with MONTE-CARLO method with 3 components which communicate directly (Fig. 5a) or indirectly (Fig. 5b) and two dimensional T_2 - T_2 maps were compared with measured maps.

07a The characterization of proton conduction in polymeric electrolyte membranes in interaction with various solvents at different adsorption contents/pH and ultraviolet radiation.

Absorption measurements of different solvents in PEM membranes

Absorption of several solvents with different pH in PEM membranes was measured. We obtain a relatively small variation of the absorption curve for different pH values but we observed two absorption times, among which one very fast (below 1 minute) and which leads to a fast hydration with $\sim 80\%$ from a total mass of water of absorption hydrated. The second absorption time is of the order of hundreds of minutes which mean that a complete hydration can be achieved into several hours up to one day. The absorption time values are slightly dependent of pH solvent. Degradation effect of polymeric chains is observed (see the read decay curve from fig. 6) for solutions with small pH (acid). To explore the channels dimension in PEM membranes, several absorption measurement of different spherical (Toluene) and linear molecules have been performed. We show that the Octane solvent ($\sim 9.2 \text{ \AA}$) cannot be delves into the PEM.

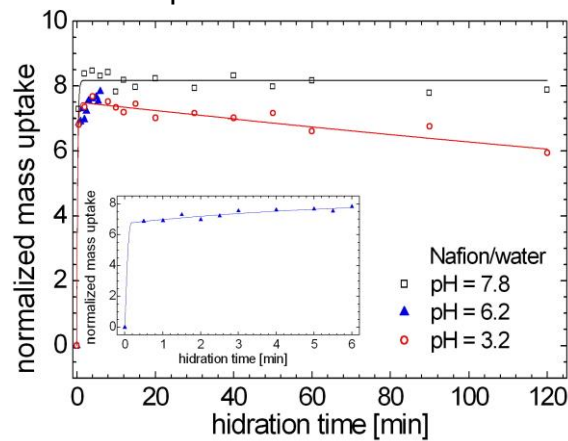


Fig. 6 Absorption curves for different solvents (solutions with different concentration of H_2O_2 in distilled H_2O) for values of pH 3.2, 6.2 and 7.8.

Table 1. The list of compatible solvents and the corresponding pH values (in solution 50 % solvent 50 % distilled water).

Solvent	Molecular type	Maxim dimension	pH	Absorption compatibility in PEM
Toluene	Spherical	4.5664 $\text{\AA}$	6.8	Yes
n-Hexane	Linear	6.6384 $\text{\AA}$	6.9	Yes
Octane	Linear	9.2642 $\text{\AA}$	7.1	No
n-Decane	Linear	11.8952 $\text{\AA}$	-	No

The measurement of PGSSE diffusion curve for PEM membrane with different solvents with various concentrations

The PGSSE decay curves were measured for PEM membrane with different concentration, solvent from 0 to 100wt $\text{H}_2\text{O}_2/\text{H}_2\text{O}$. In fig. 5a are presented the decay curves of the stimulated echo for solution of $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ with 20wt, 35wt, 100wt. The data were analyzed by inverse Laplace transform and bimodal distributions of diffusion coefficient were obtained. The macroscopic parameter, namely their pH, was observed to be linearly correlated with solvent percentage but diffusion coefficient present a maximum for a concentration of 35wt $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ and a pH of ~ 5.7 . Comparing with PEM probe in which the distilled water was absorbed, the signal (STE) is more intense. The data quality is much better thanks to numerous numbers of protons (H_2O_2) in membranes. Membranes in deionized water are yellow (pH = 4.18) and in 35% H_2O_2 are transparent-colorless. Then we may argue that at surface, intense oxidation process taking place (cleaning). If the cannels dimensions are not changing then, the H_2O_2 presence which has a larger mass than H_2O leads to a much smaller diffusion coefficient (D proportion with $1/M$). Of course the situation is more complex because we have also $D(\text{H}_2\text{O})$ which is much large plus the effects related to the presence of free - bound water.

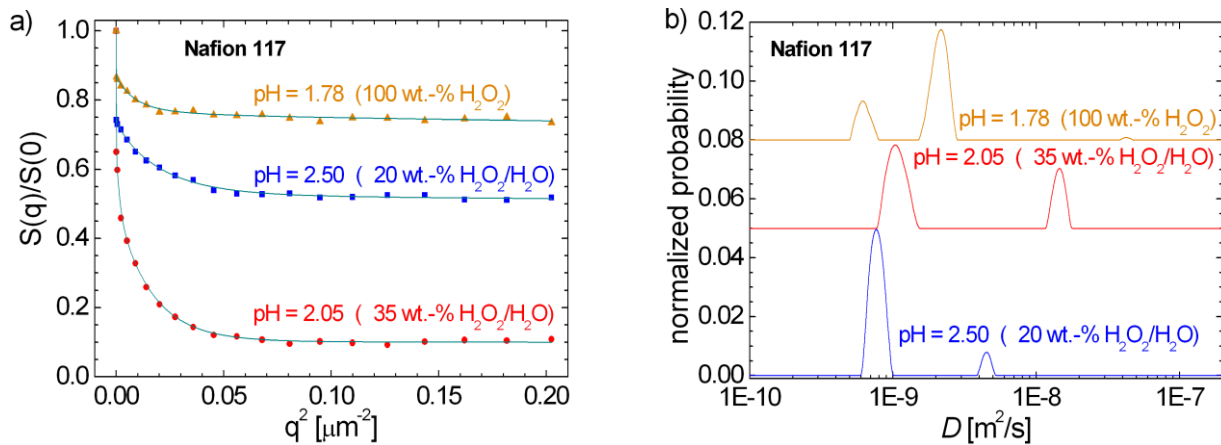


Fig. 7 a) PGSSE decay curve obtained for PEM membranes in function of pH absorbed solutions from 1.78 to 4.18; b) The distributions of self-diffusion coefficients for H_2O_2 and H_2O molecules obtained by Laplace inversion of PGSSE curves.

CPMG and Hahn echo decay curves measurements for PEM membranes after the interaction with different salt solutions and repeated cycle of UV radiation

For increasing of pH value of solvents, salt solutions (ions of different salts) have been used. Various decays of CPMG type (fig. 8a) were measured and compared. We observed a strong dependence of the relaxation times on the solution pH. With the increase of the pH value, the relaxation time distributions (fig. 8b) are shifted to larger values. CPMG and Hahn echo decay

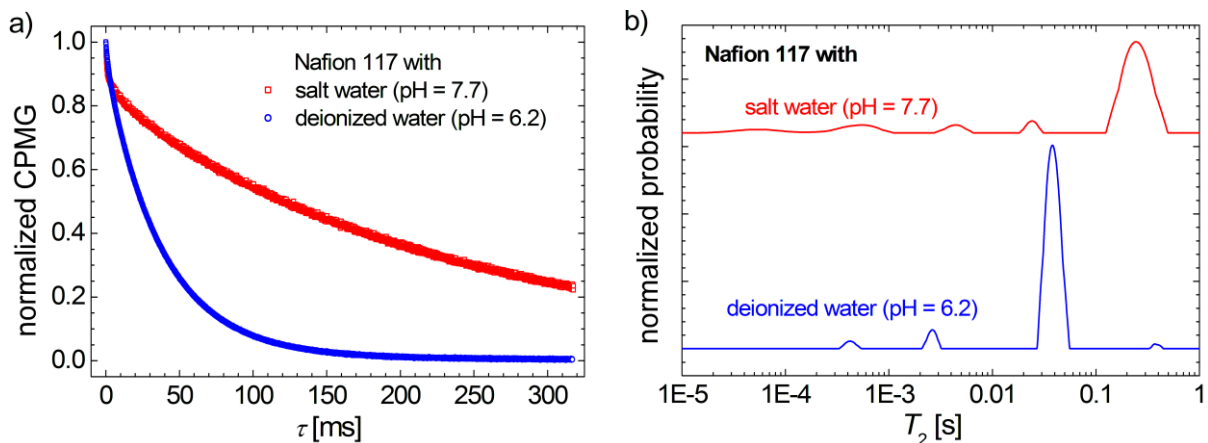


Fig. 8 a) Decay curve of CPMG echo train for PEM membranes 100 % hydrated with deionized water (pH = 6.9) and salt solution (pH = 7.8) and b) fitted relaxation time distribution T_2 .

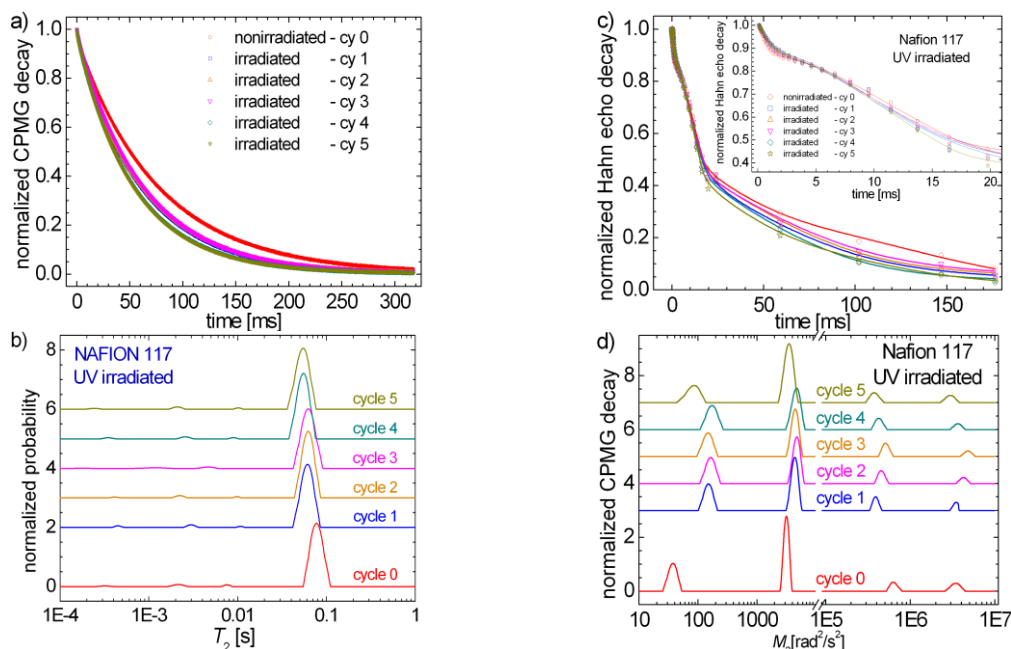


Fig. 9 Decay curves a) CPMG and c) Hahn echo for PEM membrane 100 % hydrated subjected to several cycles of UV radiation for 30 min and corresponds distribution b) T_2 and d) M_2 .

measurements were performed for PEM membranes espoused to repeated cycles (each 30 min) of UV radiation. One notices a slight dependence of the T_2 relaxation time and M_2 second van Vleck moments distributions function of cycle numbers.

Results:

1. R. Fechete, D. E. Demco, X. Zhu, W. Tillmann, R. Vinokur, M. Möller, Water states and dynamics in perfluorinated ionomer proton exchange membranes by ^1H one- and two-dimensional NMR spectroscopy, relaxometry, and diffusometry, Chem. Phys. Lett. 597 6-15 (2014).
2. N. Cioica, R. Fechete, C. Filip, I.B. Cozar, C. Cota, E.M. Nagy, NMR and SEM Investigation of Extruded Native Corn Starch with Plasticizers (submitted to Romanian Journal of Physics 2014).
3. Nicolae Cioica, Radu Fechete, Ramona Chelcea, Constantin Cota, Mihai Todica, Cornel V. Pop, Onuc Cozar, Water Absorption And Degradation Of Packages Based On Native Corn Starch With Plasticizers, (submitted to Studia UBB Chemica 2014).
4. Ramona I. Chelcea, Remus S. Sipos, Radu Fechete, Dumitrita Moldovan, Ioana Sus, Zoltan Pávai and Dan E. Decmo, One-Dimensional Laplace Spectroscopy Used For The Assessment Of Pore-Size Distribution On The Ovariectomized Rats Femur, (submitted to Studia UBB Chemica 2014).
5. E. Jumate, D. L. Manea, C. Aciu, L. Molnar, R. Fechete, Innovative Materials Made by Adding Cellulose to Cement Mortars, (submitted to Thomson Reuters Conference Proceedings Citation Index-ScienceSM -ISI Web of Science, 2014).
6. Nicolae Cioica, Radu Fechete, Ramona Chelcea, Constantin Cota, Mihai Todica, Cornel V. Pop, Onuc Cozar, Water Absorption And Degradation Of Packages Based On Native Corn Starch With Plasticizers, Advanced Spectroscopies on Biomedical and Nanostructured Systems BioNanoSpec, Cluj-Napoca, Romania, September 7-10, 2014 - Poster.
7. Ramona I. Chelcea, Remus S. Sipos, Radu Fechete, Dumitrita Moldovan, Ioana Sus, Zoltan Pávai and Dan E. Decmo, One-Dimensional Laplace Spectroscopy Used For The Assessment Of Pore-Size Distribution On The Ovariectomized Rats Femur, Advanced Spectroscopies on Biomedical and Nanostructured Systems BioNanoSpec, Cluj-Napoca, Romania, September 7-10, 2014 - Poster.
8. E. Jumate, D. L. Manea, C. Aciu, L. Molnar, R. Fechete, Innovative Materials Made by Adding Cellulose to Cement Mortars, The 8th International Conference Interdisciplinary in Engineering INTER-ENG, 9-10 oct. 2014, Tg. Mures, Romania – oral presentation.

All the objectives and activity has been fully fulfilled.

Data

29.11.2014

Project manager PN II Idea 307/2011,

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