Scientific report

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

January – December 2015

The objectives for year 2015

O6c The characterization of proton conduction in polymeric electrolyte membranes in interaction with ultraviolet radiation

The self-diffusion coefficient, IR and Lapalce spactra measurement for thin films PEM membranes aged by exposure to UV radiation

An UV lamp with wavelength λ = 253.7 nm located on top of the probe at a distance of 10 cm was used to study the structural modification effects of PEMs membranes after UV radiation expose over 1, 2 and 3 hours. For these membranes and for an additional non-irradiated Nafion membrane the transmission IR spectra were measured using the ATR accessory of FT-IR spectrometer. The spectra are presented in figure 1. Here we can observed a clear effect of irradiation associate with destruction of i) functional groups (<$CFCF_2$>; <CF_2CF_2>, <OCF_2CFO>; <CF_2>; <CF_3>; <$SO_3^-H^+$>) (high wavelengths number) and ii) polymer backbone ([$(CFCF_2)_m$-$(CF_2CF_2)]_n$) that leads to the increase of transmittance (small wavelengths number).

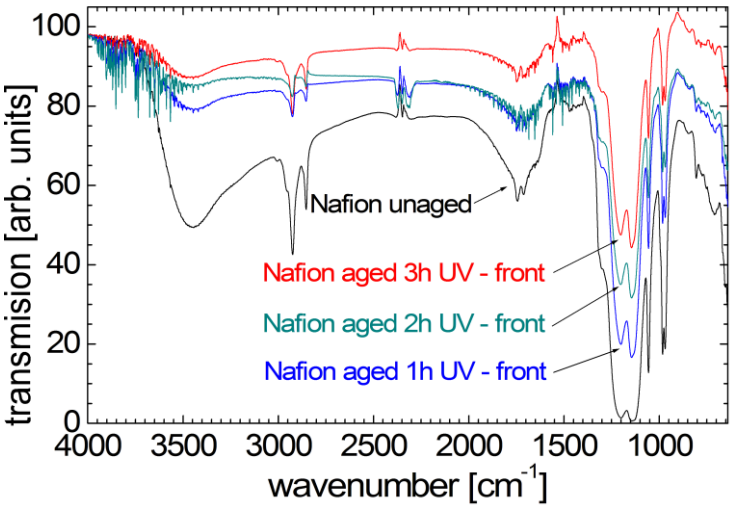

Fig. 1 FT-IR ATR spectra of PEM membranes irradiated with UV radiation at 1, 2 and 3 hours.

The structural modification effects of Nafion 117 probe subjected to an increased dose of UV irradiation can be also observed from the distributions of relaxation time T_2 (measured for bound water and free water proton) obtained from CPMG echoes train decay curves in function of echo time (Fig. 2). It was shown that the inverse of the relaxation times (measured at maximum of the main peaks-Fig2b) increases linearly with increase of the CPMG echo time, τ (Fig. 3a). If we considered the linear dependence (like is shown in the inset of Fig. 3a) by fitting the experimental data we obtain a value of effective self-diffusion coefficient of water in Nafion membrane which decreases to ~66% after 3 hours of UV irradiation (Fig 3b).

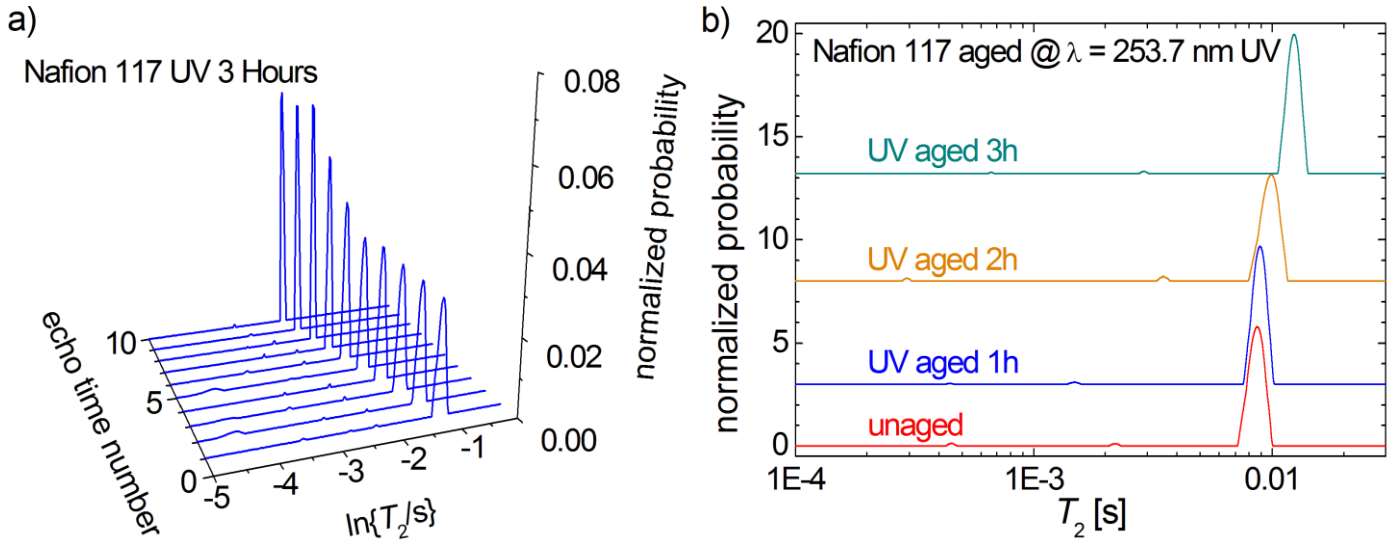

Fig. 2 The distributions of relaxation times for PEM membrane UV irradiated: a) at 3 hours in function of CPMG echo time and b) in function of irradiation time for an echo time of 1.07 ms.

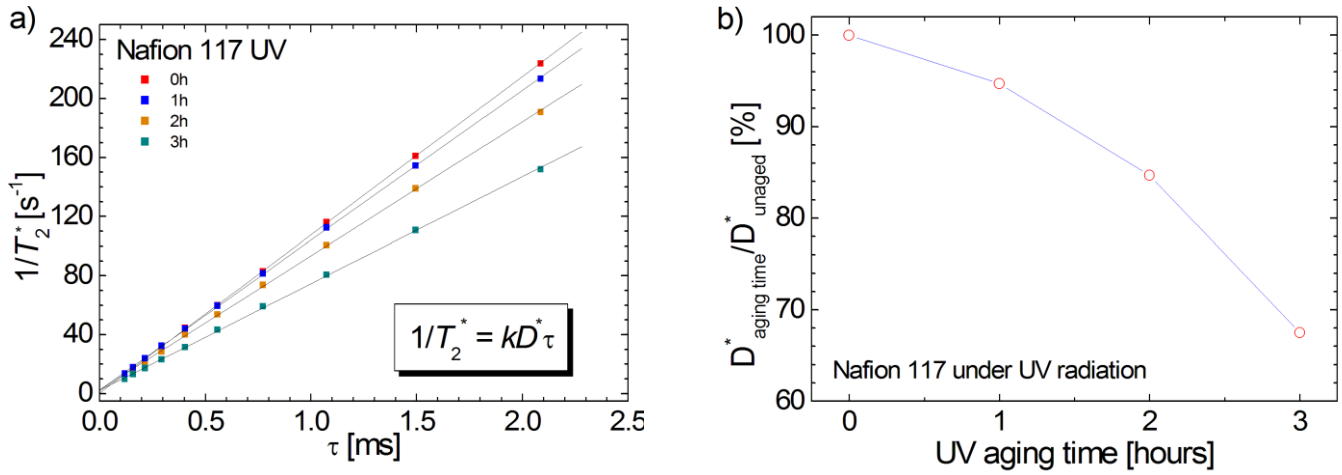

Fig. 3 a) The relaxation time ratio $1/T_2$, represented in function on the echo time and relationship with self-diffusion coefficient D^*; b) Self-diffusion coefficient D^* for PEM membranes UV irradiated reported at $D^*_{non\text{-}irradiated}$ for non-irradiated probe.

AFM imagines obtained by exposure to UV radiation of thin films aged PEM membranes

The UV irradiation effect on the PEM membranes, in particular on the Nafion 117, it can be well observed from AFM measurement (atomic force microscopy) before irradiation (Fig. 4) and after irradiation (Fig. 5). The images were measured in amplitude (up figs. a) and b)) and in phase

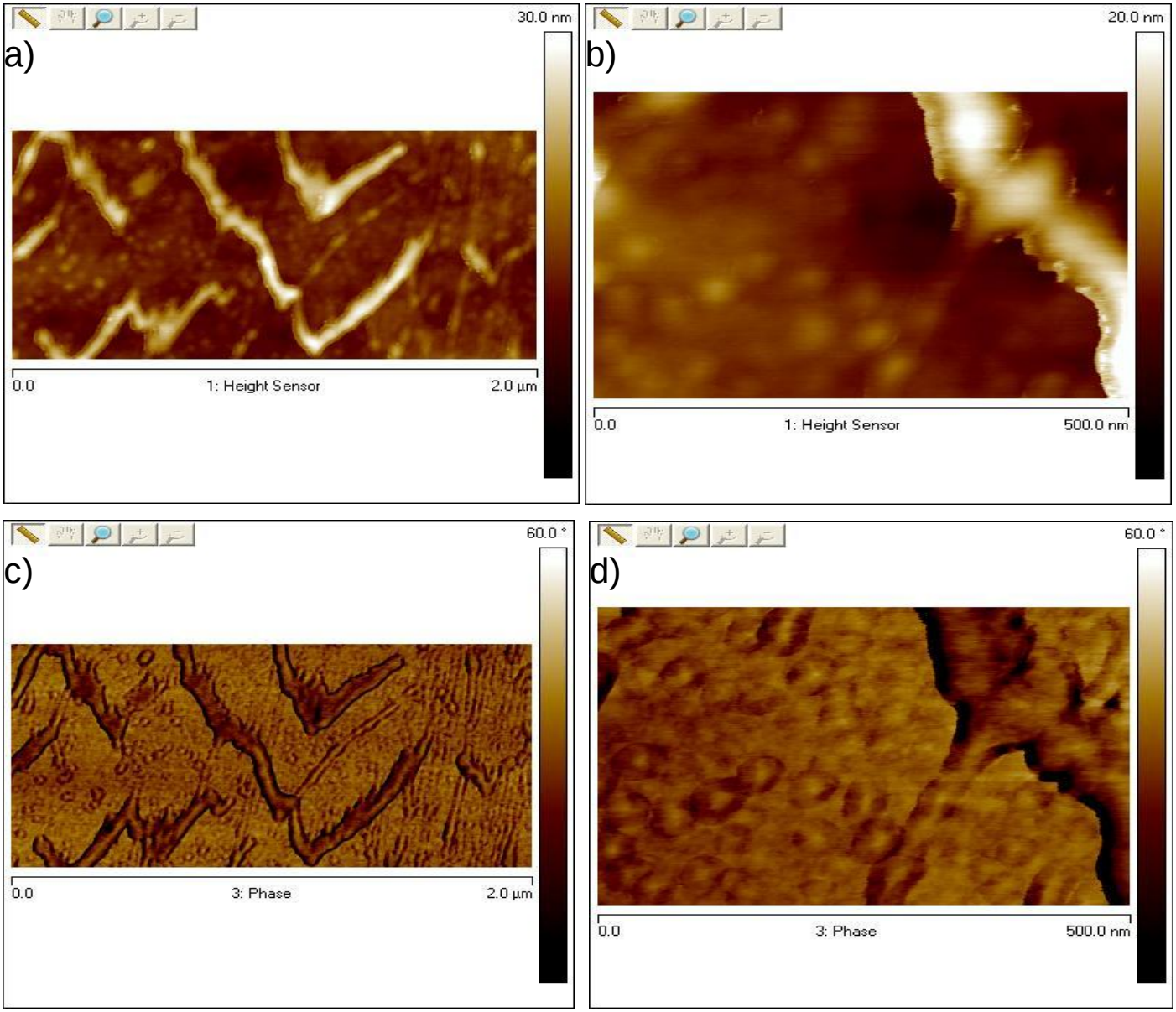

Fig. 4 AFM images of non-irradiated Nafion 117 PEM membranes at different magnitudes.

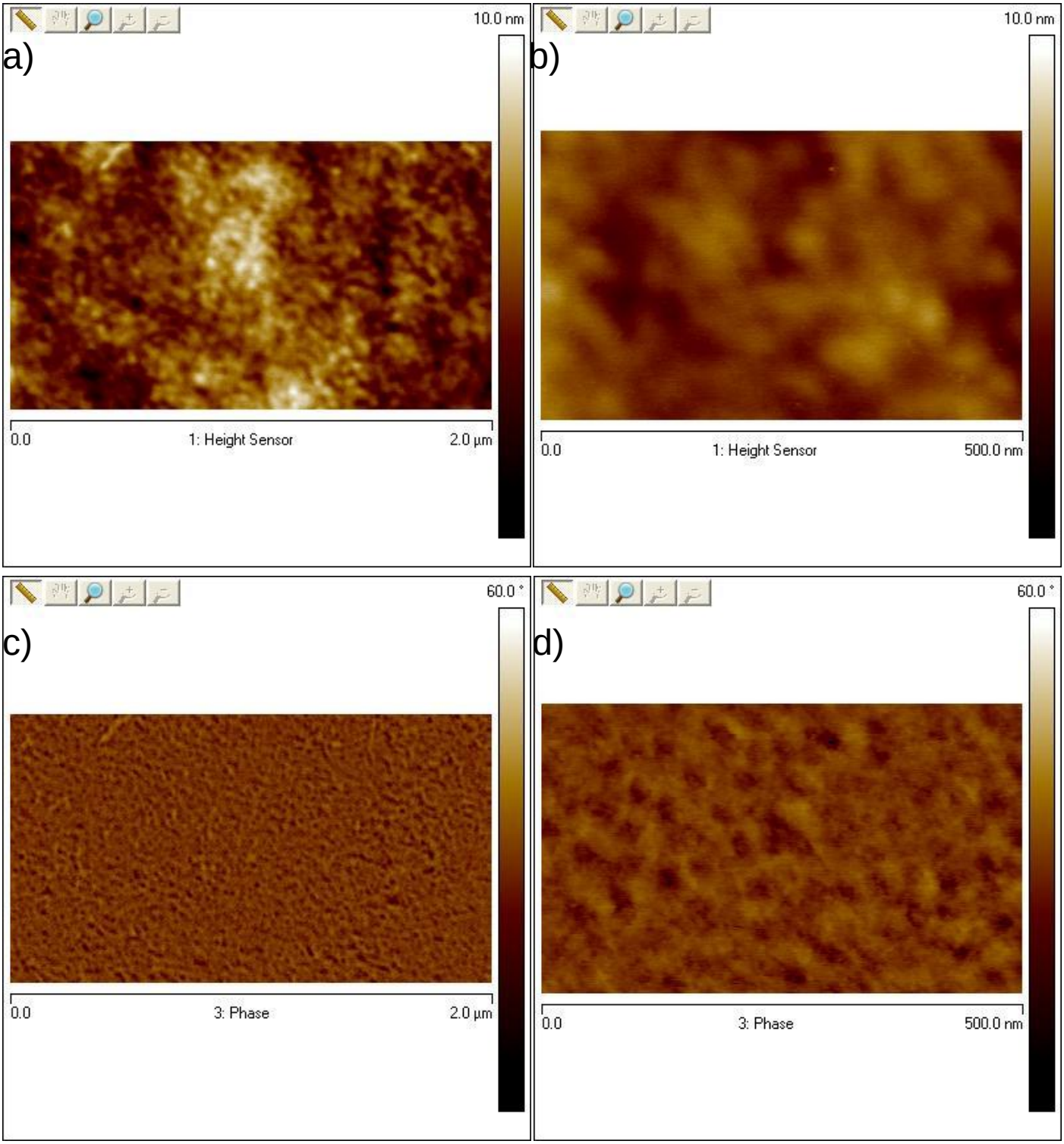

Fig. 5 AFM images of irradiated Nafion 117 PEM membranes at different magnitudes.

(down figs. c) and d)) and the results was obtained with different resolution from 500 nm (left) to 2 µm (right). The AFM images obtained for the non-irradiated sample (Fig. 4) show the cannels network (the dark color representing a small value) allowing the proton conduction of membrane and the polymeric network (the light color representing the high value). The thickness of the polymer chains can be measured from the AFM images and is of the order of 100 nm while the cannels diameter is from 130 nm - to 450 nm (local measured in the AFM images); in the same time the cannels length can exceed 1 µm. This well-defined cannels network disappears after UV irradiation (Fig. 5) via a dramatically destruction of polymer network. The amplitude AFM images manage to surprise only the local multilayered cannels network with inserts of polymer fragments, while the phase AFM images present even a quasi-uniform distribution of the irradiated membrane surface. At an increased resolution, the AFM images show a more porous and less connected structure. The electric conduction in these membranes is assured by the deep cannels network.

O7-I) The effect of mechanic deformation at high temperature on the proton self-diffusion processes in hydrated PEMs membranes

The NMR measurements of the parameters sensitive to the structural modification for Nafion membranes mechanically deformed at the high temperature.

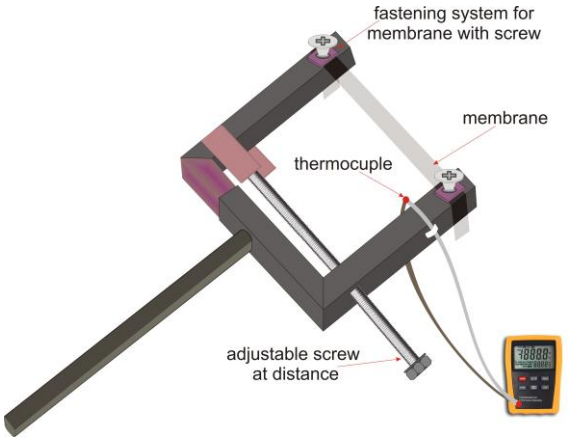

Fig. 6 Elongation mechanism of PEM membrans at high temperature.

To study the temperature effects on the mechanically deformed PEM membranes a stretching mechanism was made. This mechanism is provided with an extendable arm and to which was attached a thermocouple for temperature measurement, like in Fig. 6. The membrane is fixed in both heads and it can be stretched using the adjustable screw. A series of four Nafion membranes 15 cm x 1 cm size were fixed in the device and placed near an oven set at 1000 ^{o}C. The membranes were stretched at different ratios (form λ= 1.076 to λ = 1.312) with an adjustable screw. For all probes the temperature were measured using the thermocouple to be 70 ^{o}C ± 5 ^{o}C. Then, for each degree of elongation of the PEM membrane the relaxation time distribution T_2 was measured in function on the echo time (Fig. 7). This parameter is sensible also to the ^{1}H self-diffusion coefficient of PEM membrane. Notable effects can be observed in function of the λ ratio.

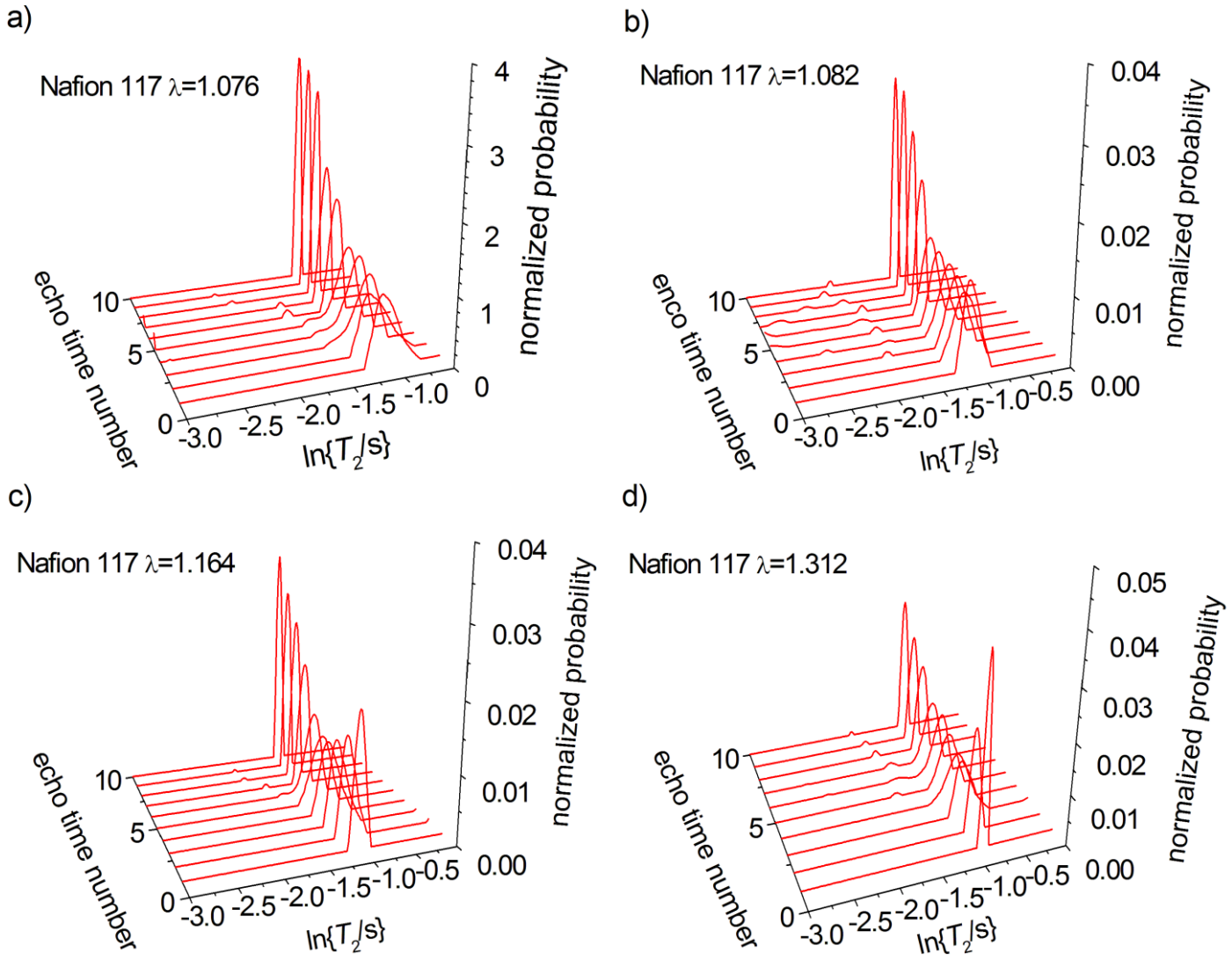

Fig. 7 The distributions of relaxation times for PEM membranes mechanical deformed at high temperature for 4 values of the stretching retios a) λ = 1.076, b) λ = 1.082, c) λ = 1.164 si d) λ = 1.312, measured for several values of echo time in the CPMG pulse sequence.

The characterization of mechanical deformation effect

The distributions of T_2 relaxation times presented below (Fig. 8) were measured for four values of stretching ratio λ (the length of deformed membrane reported at the initial length). The effect of deformation of PEM membranes is clearly observed especially on most mobile components characterized by the peak localized at high value of T_2, which is shifted toward higher values of T_2, indicating an increase of mobility under the action of mechanical deformation most probability by the stretching of molecular chains.

If we compare the mechanical deformation effect (Fig. 8) with the effect of UV radiation (Fig 2b) we observe that: the structure of peaks in the distribution T_2 is the same, but the mechanical stretching leads to an increased heterogeneity and a larger mobility (T_2 values of 10 or higher) of polymeric chains while the UV radiation leads to breaking of the chemical chains and formation of smaller chains.

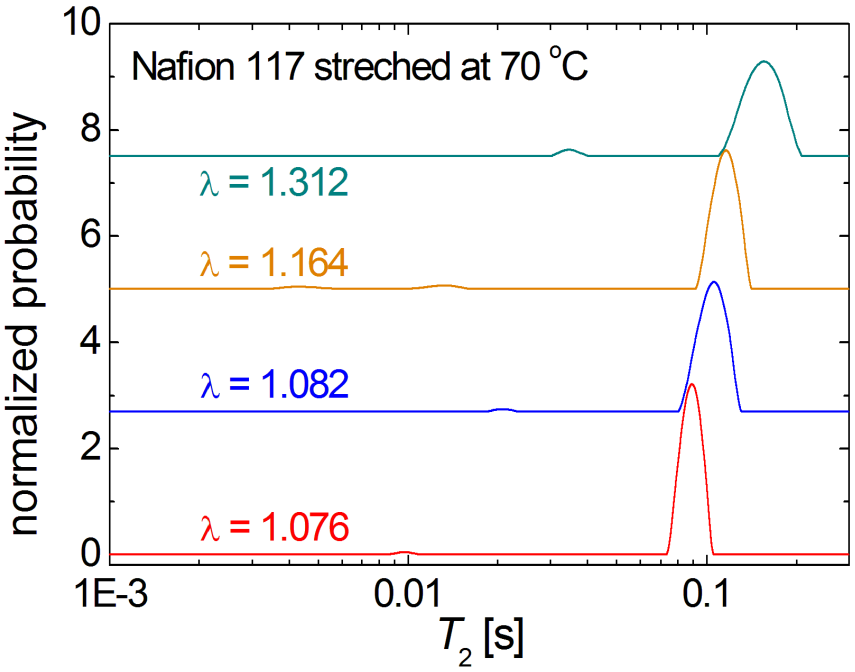

Fig. 8 The distrubution of relaxation time for PEM membrane subjected to streching at a temperature of 70 °C ± 5 °C for 4 value of stretching ratio λ. The echo time was 1.07 ms.

Results

1. R. Şipoş, R. Fechete, R. I. Chelcea, D. Moldovan, Z. Pap, Z. Pávai, D. E. Demco, Ovariectomized rats' femur treated with fibrates and statins. Assessment of pore-size distribution by $_1$H-NMR relaxometry, Rom. J. Morphol. Embryol., 56, 743-752 (2015).
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All the objectives and activities were totally achieved.

Data
29.11.2015

Project Manager PN II Idea 307/2011,
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