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Pore dimension of water trees in PE: NMR studies

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Abstract

In PE films aged under electric field the crystallisation of water (and melting of ice) has been studied by quadrupolar NMR, this technique allows one to determine the concentration of water as low as 10^{-4}. It is shown that the pore dimensions of the tracks forming the water trees of the order of 2.5 nm, are independent of the ageing time. The mobility of water in these water trees and in porous glass, of similar pore dimensions, are compared. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Pore dimension; Water trees; Polyethylene films

1. Introduction

Insulating polymers have been widely used in power cables. The most common material used in high and medium voltage cables is polyethylene. Under service conditions electrical ageing of the insulation is inevitable and may in the long run give rise to costly cable failure. At the first stage of ageing water treeing may occur. Even if it is not a direct cause of dielectric rupture their presence considerably reduces the breakdown voltage. Water trees appear as bush structures filled with water with a length ranging from 10 μm to about 1 mm, they are composed of disconnected pores (also called tracks) of diameter in the nanometer range. However, up to now, there is no non-destructive technique for measuring the lateral dimension of such microscopic tracks. The track surface is hydrophilic allowing diffusion of water (and other polar species, such as ions). Inception of water trees starts in the presence of an aqueous solution (with ions) and an alternate high electric field. Studies have shown the influence of many factors in the inception and growth of water trees such as temperature, mechanical stress, type and concentration of ionic salts, applied electric field (frequency and amplitude), polymer morphology and composition, etc. Due to the complex mechanisms involved in the nucleation and propagation of water trees in polymer insulators, conflicting results have been reported; models involving electromechanical and electrochemical processes are still under development [1–5]. The aim of this paper is to show that quadrupolar NMR gives information on the amount of water absorbed in these materials and on the size dimension of the tracks created by electrical ageing.

2. Experimental

In this work, low density polyethylene (LDPE) from Borealis, with a density of ≈ 0.92, was aged under an AC electric field (6 kV/mm at 50 Hz) in the presence of an aqueous solution of sodium chloride (1 M) at a constant temperature of 45°C for different time periods (475 and 900 h). Disc shaped samples of ≈ 200 μm thickness and diameter of ≈ 30–35 mm were press-moulded from pellets. Afterwards, the samples were sandblasted in order to increase the number of initiation sites for water trees, and then the amount of water in the aged material. For ageing, a modified Cigré cell [3,4] was used with the aqueous solution acting as electrodes on both sides of the disc shaped samples (planar electrodes), as can be seen in Fig. 1. The aged LDPE samples and the virgin sample (weight: 200 mg) were soaked in heavy water for 2 days. Water in these materials cannot be detected by differential scanning calorimetry (DSC).

NMR experiments on the aged film swollen with D_2O were performed with a Bruker AM250 spectrometer equipped with a 5 mm broad-band probe without field/frequency lock control. The film is rolled in the NMR tube, the magnetic field is perpendicular to the film

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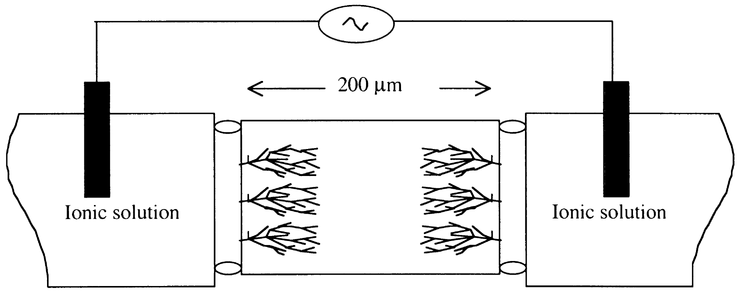

Fig. 1. Electrical ageing set-up for disk shaped LDPE samples with a diameter of 5 cm, the film thickness is 200 μm. Water trees with an average length of 20–50 μm are formed on both sides of the film.

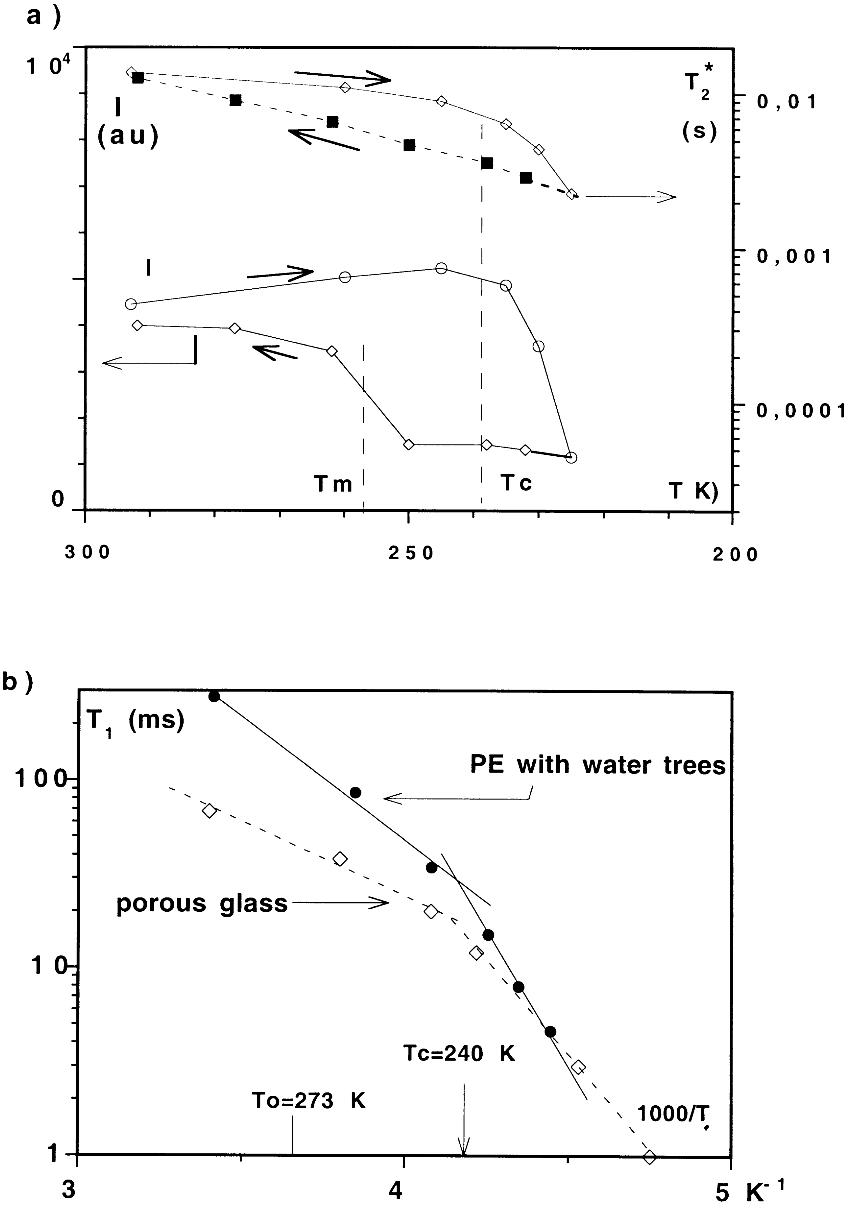

Fig. 2. (a) Evolution of the quadrupolar deuterium NMR signal due to heavy water absorbed in PE water trees: surface area *I* in arbitrary units and effective transversal relaxation time T_2^*. (b) Spin–lattice relaxation time T_1 of heavy water in PE water trees and in silica glass of dimension 2.5 nm, in decreasing temperature.

thickness, that is to say perpendicular to the propagation of the water trees through the sample, during the electrical ageing. Temperature was controlled in the range of 210–300 K by a Bruker VT100 system (±1°C regulation). ^{2}H spectra were recorded at a frequency of 38.376 MHz. The transients (FID) were obtained using a $\pi/2$ pulse width (14 μs) and a recycle delay of 2 s, 800 transients were usually added to obtain spectra with a good signal-to-noise (S/N) ratio. The FID signals were typically sampled with 4 K real data points over a 10 000 Hz spectral width, and an exponential line broadening of 5 Hz was used (which is small compared to the experimental line width). Peak areas and line widths were obtained by deconvolution with a single Lorentzian shaped curve. T_1 values were obtained by the inversion-recovery method (delay$-\pi-\tau-\pi/2-$acq.)$_n$ using 12 different τ(values to obtain the T_1, following standard procedures [6].

3. Results and discussion

The concentration of water in these films (polymer weight 0.3 g) has been measured by comparing the NMR integrated signal intensity (peak area after 800 scans) containing deuterium water in pores with a standard sample containing a similar amount of heavy water. For an electrical ageing of 900 h, a weight fraction of $c = 6 \times 10^{-4}$ of water is found. The virgin sample after 8000 scans did not present an NMR signal, so one can estimate that the (mobile) water concentration is at least 500 times less than in the aged material. In Fig. 2a, the total intensity I of the NMR peak and the effective transversal relaxation time, T_2^*, (deduced from the line width $w = 1/\pi T_2^*$) as a function of temperature, during cooling and heating experiments is reported. In Fig. 2b a comparison of the T_1 spin–lattice relaxation times of deuterated water in a PE film with water trees and in porous glass (Silica Gelsil glass from Geltech company) of pore dimension $d = 2.5$ nm is given. These porous glasses have been studied by various techniques, in particular by DSC and dielectric spectroscopy [7,8]. Between each measurement the corresponding time is about 1 h (30 min for thermal equilibrium and 30 min for measurement).

When the temperature is decreasing, at first the total intensity increases: this is the classical Curie law observed in bulk water and in porous glass. Near 260 K the signal decreases abruptly by a factor of 5, similarly, in the same temperature domain the relaxation time T_2^* decreases. Such effects could be due to the freezing of water as a result of crystallisation or to amorphisation passing through the glass transition at T_g.

When temperature is increasing, at first the signal intensity is constant and then increases abruptly at 240 K, the width w of the NMR peak decreases continuously. The important hysteresis observed in the intensity measurement cannot be interpreted in terms of a glass transition: the glass transition of water is about 140 K and the hysteresis of such a transition is generally very weak. The broadening of the glass transition in most compounds is larger (20–30 K) than the width observed here (<10 K). Also, this transition must not be confused with the λ transition observed near 228 K in pure bulk water [9]. These effects must be interpreted in terms of crystallisation; such important hysteresis effects were already observed in porous silica glass [10–13] filled with water and in butyl rubbers containing small pores [13]. In these materials, DSC measurements were possible because the amount of water was large ($c = 0.80$ instead of 10^{-4} in aged PE).

The melting and crystallisation depression temperatures, $\Delta T_m = T_m^0 - T_m$ and $\Delta T_c = T_c^0 - T_c$, of water in porous glass has been measured by various authors [10–14], T_m^0 and T_c^0 being the ice melting and crystallisation temperatures in bulk water. As shown by Neffati [7], the depression ΔT_m of water in various porous glass and polymers containing holes always obeys the same Thompson equation: $\Delta T_m = 49/d$ (d in nm). Brun [10,11] has shown that the crystallisation depression verifies a similar expression: $\Delta T_c = 64.7/(d - 0.6)$, this equation which is the basis of thermoporometry applies only if the cooling rate is lower than 0.6 K/min. In our NMR study, the equivalent cooling rate is of the same order, about 1 K/min.

It is important to note that the melting depression $\Delta T_m = 15 \pm 0.5$ K of ice in PE films, observed by NMR, is of the order of that observed in silica glass of pore dimension $d = 2.5$ nm (Neffati [7]). The crystallisation depression $\Delta T_c = 40$°K observed by this technique gives the same value of 2.2 nm when the Thomson–Brun equation is applied. The same value of ΔT_c is observed in butyl rubbers containing pores of the same dimension filled with water [7,8] One concludes that the sharp transitions observed by NMR in PE containing water trees are due to the first order crystal–liquid transition, confined in very small pores of dimension 2.5 ± 0.5 nm. It is important to remark that the width of the melting transition, less than 10°C, is smaller than the width of the DSC endotherm peak observed in silica glass, 15–20°C. This suggests that the distribution of pore size in aged PE is sharper than that in porous glass.

In Fig. 2b, one notes that after crystallisation at T_c around 240 K for these two types of materials, the spin–lattice relaxation time T_1 decreases more rapidly than before crystallisation. Assuming isotropic reorientation the relaxation rate $1/T_1$ due to quadrupolar interactions is given by: $1/T_1 = (3/8)(e^2qQ/\mathrm{h})^2(1 + \eta^2/3)\tau_c$, where ($e2qQ$/h) is 2π times the nuclear quadrupole coupling constant in Hz, η is the asymmetry parameter (of the order of 1) and τ_C the reorientational correlation time [6]. It has been found experimentally by Liu et al. [14] that this correlation time varies as $\tau_C \approx 1/T_1 \approx 1/d$ for strong polar liquid interacting with the surface, and as $1/\mathrm{d}^2$ for non-polar liquid interacting weakly with the surface. This last scaling law has been theoretically explained by Korb et al. [15]. In porous materials crystallisation of water has mainly two effects on the confinement of water: (a) when ice is formed in the larger pores, the proportion of small pores filled with liquid water increases; (b) crystallisation cannot lead to ice crystallites matching exactly the surface of the pores (the surface can have a fractal dimension between 2 and 3), therefore some liquid water becomes confined between the pore surface and the crystallites, the larger pores are replaced by small pores during the process of ice formation. These two effects increase the correlation time in the low temperature domain when crystallisation occurs. The $T_1(T)$ curves of water in water trees PE and in silica glass are very similar because crystallisation occurs at the same temperature, at $T_c = 240$ K. The same behaviour is observed in butyl rubbers containing pores of the same dimension [7]. One notes, however, a difference in the values at high temperature: probably this effect could be due to the different interaction of water with the functional groups attached to PE and silica surfaces [16,17].

We have performed similar studies on PE aged during 375 h under the same electric field. The intensity and the line width varies in the same manner as that reported here, therefore the structure of the water trees seem to be very similar during its growth.

4. Conclusions

NMR spectroscopy demonstrates that water crystallises in the small pores formed in PE when submitted to electrical ageing. This property permits one to estimate the dimension, $d = 2.5 \mp 0.5$ nm, of the pores via the Thompson and Brun relations. The accuracy of NMR permits one to measure the mobility and the amount of liquid and crystallisable water in weight fraction as low as 10^{-4}, this accuracy can be easily improved by increasing the amount of material in the NMR tube, and by increasing the NMR frequency and the scan number. The study of different films aged under different ageing times and electric fields show the same trends in the crystallisation temperature of water. Therefore, the dimension of the pores (tracks) are of the same order: this indicates that during the growth of water trees, new canals (or pores) are formed and there is no thickening of the pores previously formed at the beginning of the process (Fig. 1). Ice formations in PE containing water trees and in silica glass of pore are very similar; the hydrophilic character of silica glass is due to the OH groups attached to the surface, it is also well known that the surfaces of pores in PE contain various polar groups due to the oxidation during electrical ageing [5]. One emphasises however, that in polymers some additional effects could occur: the electrical treatment produces polar groups grafted on the surface of the pores and certainly with a certain thickness, also some chains are disrupted; so the interface should not be considered as sharp but continuous with a gradient of density of polar groups concentration and, therefore, of mechanical properties. These effects should also have an influence on the dynamics of confined water.

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