Water And Ion Absorption By Polyethylene In Relation To Water Treeing

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ABSTRACT

Water absorption by polyethylene (PE) is discussed in relation to water treeing. Two steps have been considered: the first is water diffusion into undamaged PE, the second is water migration into growing water-tree channels. A critical discussion of published data is presented. Diffusion of water and Na^+ ions into a low density PE film is studied by a radiotracer method in the absence of water-treeing. Na^+ permeation is found to be very low ($P < 4\times10^{-15}$ cm^2/s). A water permeability of 4.5×10^{-10} cm^2/s has been measured and is not affected by an applied uniform dc or ac electric field.

1. INTRODUCTION

One of the important problems which has appeared in the electrotechnical field during the last few years is that of water treeing [1]. With polyethylene insulated power cables this consists in a degradation of the polyethylene when they are exposed to humidity. Water treeing may lead to breakdown after some years. As indicated by its name, water treeing is related to the presence of water in electrical insulation. Thus several publications have been concerned with water absorption and with the influences of ions on an applied electric field. The results, however, are contradictory. Auckland and Cooper [2] have studied water absorption in low density polyethylene (LDPE) in the presence of an electric field and shown that the water absorption depends on the electric field, on the nature of the ions, and on the conductivity of the solution. Moreover, they have shown that ions are absorbed by the polyethylene. On the contrary, Chan and Jaczek [3] have observed that the water absorption in crosslinked polyethylene (XLPE) cables, where microvoids are present, is the same with or without an electric field. Mizukami et al. [4] noticed an increase in water absorption with an applied field especially at high temperature. It seems likely that these contradictions are due to different experimental conditions. It is thus important first to try to classify the questions which arise about the absorption of water and ions.

The first case to consider is that of pure polyethylene without water trees. Water diffusion parameters in polyethylene (solubility and diffusion coefficient) are known from vapor permeation experiments but the electrotechnical applications lead to other questions:

- What is the influence of the microvoids [5,6] which exist in XLPE?

- Do ions migrate into PE from the aqueous solution as could be assumed from the Auckland and Cooper results or those of the Sazhin et al. [7] injection experiments?

- Which role does the electric field play? Does it influence the water migration directly, or through the ions, or does it induce a polymer degradation which in turn will induce a modification in water diffusion?

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This leads to the consideration of the second case, that of the PE which contains growing water trees. Then the water and ionic migration, and the influence of the electric field, are quite different. We have made experiments in this field, which will be published elsewhere [8]. Briefly, we have shown that the water absorption is approximately proportional to the third power of the tree length, that is, to the water-tree volume. The water absorption kinetics reflects the water tree growth and is thus influenced by the electric field in the same manner. This has been observed for trees growing from a needle point filled with aqueous solution, so that there is no problem of limited water supply. The case of bow-tie trees growing inside the insulation may be different and their growth may be partially controlled by water diffusion through the PE.

The aim of this paper is to present some results about the first questions: water and ionic diffusions in PE containing no water trees and the influence of an electric field on them. The discussion will take into account the published data and try to explain the contradictions.

2. EXPERIMENTAL

Polyethylene

The experiments have been performed on a low density polyethylene (ATO-1002-CN-22) containing no additives and in particular no antioxidant. No oxidation was detectable by IR. The films were 50 μm thick.

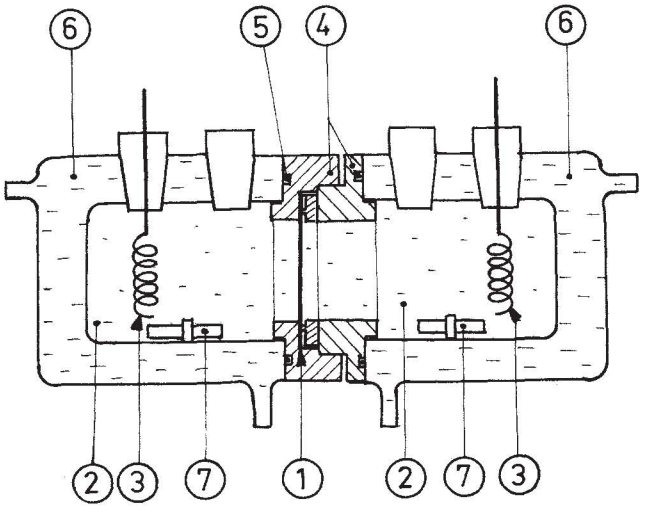

Fig. 1: Permeation cell

(1) PE film
(2) 10^{-1} M/1 NaCl solution
(3) silver electrodes
(4) Teflon(R) film holder
(5) gasket
(6) thermostated water circulation
(7) magnetic stirrer

Permeation Cell

Permeation experiments have been performed with a glass cell schematically represented in Fig. 1. The glass has been silanized to avoid ion absorption on the cell walls. The solutions were continuously stirred with a magnetic stirrer. All experiments have been done at 50°C, the temperature being controlled by water circulation. Each cell compartment contains a silver electrode dipped in conducting 10^{-1} M/1 NaCl solutions. A conventional electrical circuit allows the application of a dc or ac voltage to the film and measurement of the current flow.

Radioactive Solutions

Each cell compartment was filled with a 10^{-1} M/1 NaCl solution, one of them being tagged with a radiotracer. For water permeation, tritiated water was used. It had an activity of 90 mCi/l which yielded a counting rate measured by liquid scintillation of 2.5×10^{7} counts per minute per gram of water (CPM/g). For Na^{+} permeation the solution was tagged with Na^{22}. The activity was about 8 mCi/l and the counting rate 10^{11} CPM/Na.

Evaluation of the Permeation

The permeability of the film is characterized by the permeation $P = D\,k$ (cm^2/s) where D is the diffusion coefficient (cm^2/s) and k is the partition ratio, ratio of the concentrations in the polymer film and in the solution (dimensionless number) [9]. The amount of diffusant Q, which has passed through the film in time t is plotted versus permeation time t. In the steady state Q increases linearly with time and $dQ/dt = FS$ where S is the surface area of the film and F the flow rate. F is related to the permeability P by

$$F = P(C_1 - C_2)/l \qquad (1)$$

where l is the film thickness and C_1 and C_2 the concentrations in the solution upstream and downstream. C_2 is low and is neglected in comparison to C_1.

$$P = \frac{l}{S}\,\frac{1}{C_1}\,\frac{dQ}{dt} \qquad (2)$$

$Q = C_2 V$ where V is the volume of the downstream cell. The concentrations C are proportional to the activities A so that

$$P = \frac{lV}{S}\,\frac{1}{A_1}\,\frac{dA_2}{dt} \qquad (3)$$

Sorption

Na sorption experiments have been carried out by soaking PE samples for various times in 0.1 M/1 NaCl solution tagged with Na^{22} at 50°C. Soaked samples were rinsed in cold water for a few seconds, after which the outer surfaces were dried with a cloth.

Water sorption experiments from a 0.1 M/1 NaCl solution were conducted in the same manner. The water content was measured with a Du Pont moisture analyzer 902.

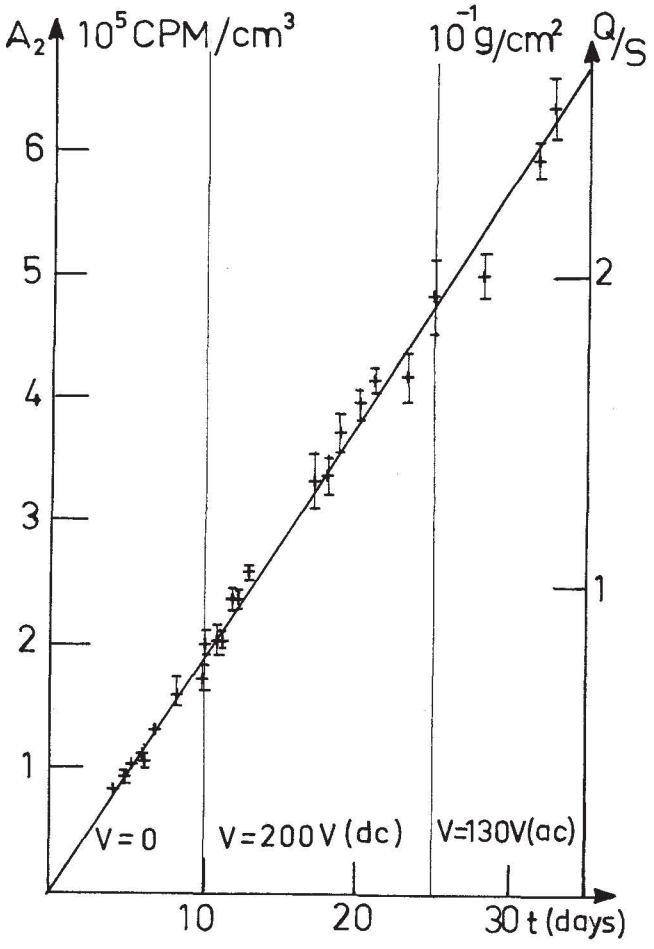

Fig. 2: Water diffusion through a 50 μm thick LDPE film at 50°C: the water flux Q/s t is the same without electric field and for successive applications of 200 V (dc) or 130 V (ac).

Verification of the State of the PE Film

Before each permeation experiment we have made an electrical test to be sure that the film did not contain any holes. The film was judged free of holes if application of 500 V produced a current of less than 0.1 nA/cm^2. Samples containing holes gave a current of more than 1 μA/cm^2 for a voltage less than 10 V.

During all permeation experiments the electrical state of the film was tested from time to time to be sure that we were concerned with molecular diffusion and not migration through channels.

3. RESULTS AND DISCUSSION

1. *WATER*

1.1. *Diffusion without Electric Field*

Fig. 2 gives the plot of water permeation. The slope gives a value of the permeability P of 4.5×10^{-10} cm^2/s. The permeability value is in good agreement with those given in the literature ($P\sim2$ to 4×10^{-10} cm^2/s at 50°C) which have been obtained by vapor or liquid permeation [9-11]. According to the literature, this case corresponds to a solubility of the order of 10^{-4} (100 ppm) and a diffusion coefficient D of about 2×10^{-6} cm^2/s. Water sorption analysis leads to values of about 30 ppm. Taking into account that, for a 50 μm thick sample and a diffusion coefficient of the order of 10^{-6} cm^2/s, desorption may reach more than 50% during the handling time, the order of magnitude of the solubility may well be about 100 ppm. The solubility and the coefficient of diffusion D for water absorption in XLPE cables obtained by Chan and Jaczek [3] are quite different ($D\sim10^{-9}$ cm^2/s at 60°C). This discrepancy can be explained by a clustering effect [9,12]. It has been shown by these authors and others [5,6] that XLPE contains microvoids of the order of 1 μm in diameter. This explains why the water absorption may be so high (some hundreds or thousands ppm) although the real solubility of water in PE without microvoids is low (≤ 100 ppm). The water clustered in these microvoids does not contribute to the diffusion. Only the small amount of soluble water contributes to it with its usual D so that the apparent global diffusion coefficient is reduced. Such a case has been observed in other hydrophobic polymers such as polysiloxane [12]. This answers one of the questions of the introduction: microvoids increase the solubility so that PE seems to be not hydrophobic and decrease the apparent diffusion coefficient. Moreover, it must be recalled that clustered water may be present even if there are no microvoids: at high temperature water sorption in LDPE notably increases [13,14] and it has been shown by calorimetric measurements that most of this water gets clustered [13] when the temperature decreases.

1.2. *Influence of an Electric Field*

Successive applications of a dc voltage of 200 V (E = 4 V/μm) and 50-Hz ac voltage of 130 V (E = 2.6 V/μm) do not modify the water permeation. Such an experiment is illustrated in Fig. 2, where, taking into account the precision of the measurement a single line is obtained for the three cases. Note that the creation of water trees has not been observed in the films, in agreement with what could be expected from the experimental conditions. Moreover, the electric field used was uniform to avoid influence of dielectrophoresis.

Our experiment shows that an electric field either static or alternating has no influence on water diffusion. This is in agreement with Chan and Jaczek results [3], which means that for molecular diffusion, as long as trees are not present, water diffusion is not influenced by an electric field. This result is apparently in contradiction with that of Mizukami et al. [4]. But as the thickness and the nature of the sample are unknown, it is not possible to evaluate diffusion coefficients from their curves and to know . if the long diffusion times involved (order of 1000 h) are related to a clustering effect or not. It is not even clear if the influence of the electric field which in fact seems significant only at high temperature (90°C), is due to water tree formation.

It is difficult to compare our results with those of Auckland and Cooper [2] because the situation is different. In particular, their sample is known to be lightly oxidized. This could explain the high level of water absorption. Moreover it probably contains microvoids as is shown by the variation of density induced by a variation in the molding pressure [15]. In fact, as will be shown later, under very special conditions we have obtained results which appear similar to theirs.

2. *IONS*

2.1. *Absorption without Electric Field*

No Na^+ ion permeation has been detected up to a maximum experiment time of 14 days, so that taking into account the precision of the method the maximum value for P is 4×10^{-15} cm^2/s. It indicates that ionic permeability is far less than that of water.

This could be due to a lower diffusion coefficient or more probably to a lower solubility. Up to now it has not been possible to answer this question. The Na^+ sorption measurements that we have tried to make are not conclusive. The k-value obtained was rather imprecise and of the order of 10^{-4} to 10^{-3}. Saturation seems to be attained after 20 minutes which should correspond for a 50 µm thick sample to a diffusion coefficient of more than 10^{-8} cm^2/s. These values would give a permeability of the order of 10^{-12} cm^2/s, in disagreement with the permeation value of less than 4×10^{-15} cm^2/s. It seems thus that in this sorption experiment we do not measure a slow absorption but a rapid surface adsorption.

2.2. *Influence of an Electric Field*

Application of a dc voltage of 200 V for 4 days, followed by 370 V for 5 days does not lead to any detectable change. In the same way, an ac voltage of 190 V at 50 Hz for 9 days gives no measurable permeation.

It may be noticed that for ionic conduction the behavior of PE in contact with water is entirely different from its behavior when it is in contact with a swelling liquid. In the latter case field-enhanced ion absorption occurs [16].

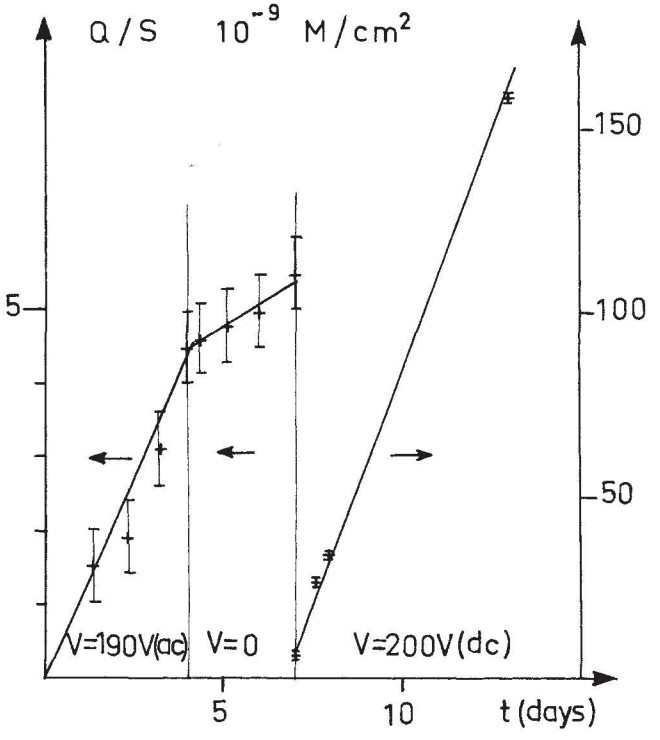

Fig. 3: Na^+ ion diffusion for a damaged film: the Na^+ flux Q/St measured without voltage (v=0, left scale) is increased by application of an electric field, ac (V = 190 V, left scale) or dc (V = 200 V, right scale).

2.3. *Influence of the State of the Film*

During Na^+ permeation experiments, an evolution in the state of the film has been observed. After a variable time (from 1 to more than 14 days), when no ionic permeation is detectable, an ion flux is observed, which corresponds to P = 1 to 4×10^{-13} cm^2/s. When the film is in this new state, the ion migration is reflected by an increased current ($I\sim$1 nA/cm^2 for 50 V and $I\sim$ 1µA/cm^2 for 300 V). When the film is in this state, the application of an electric field affects the ionic permeation: P is increased by a factor of 100 with a dc voltage of 200 V and by a factor of 5 with an ac voltage of 190 V (Fig. 3). (It must be noticed that this case is different from that of a film with a hole, for which the permeability is more than 10^{-12} cm^2/s, and the current more than 1 µA/cm^2, for an applied voltage <10 V).

Interpretation of this case is rather difficult and it is not possible to give more than conjecture. However, it shows once more that a degradation of PE completely changes the diffusion conditions. Several mechanisms may be put forward to explain the alteration of the film. For example, due to the high energy γrays (1.3 MeV) emitted by Na^{22}, a decomposition of water may occur and lead to the formation of peroxides. This may lead to PE oxidation and an increase in water absorption. It is also known that γrays may lead to direct scission of the chains making microvoids formation or oxidation easier [17]. All these mechanisms must lead to an increase in water absorption which could explain an increase in ionic permeation. We may thus have obtained in an indirect way a situation comparable to that of Auckland et al. who have used an oxidized PE able to contain much water. They observed an ion absorption by PE indicated by the decrease in the solution conductivity. The influence of an electric field in this case is an agreement with our result.

4. CONCLUSION

This study is concerned with a parallel investigation of water and ionic diffusion in a low density polyethylene.

- We have measured water diffusion ($P \sim 4\times10^{-10}$ cm^2 at 50°C) by a radiotracer method and shown that it is not affected by an electric field. This is in agreement with results obtained with XLPE containing microvoids.

- Na^+ ion permeation is lower than 4×10^{-15} cm^2/s. An ionic permeation sensitive to the presence of an electric field appears after degradation of the polymer film.

Thus the electric field has no influence on water diffusion in undamaged PE.

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