Comparison of water treeing in an amorphous and in a semicrystalline polymer

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In this paper, we compare the growth and the structure of water trees in amorphous polystyrene and semicrystalline low-density polyethylene. The structure and the growth of the water trees observed in each of the polymers are very different. These different aspects are discussed in terms of mechanical fatigue, and the role played by the crystalline layers in the resistance of semicrystalline polymers to water treeing is pointed out.

(Keywords: water treeing; amorphous polymers; semicrystalline polymers; polystyrene; polyethylene)

INTRODUCTION

Owing to its outstanding dielectric properties, polyethylene is used as insulating material for high-voltage cables. However, traces of moisture arising from environmental conditions of cable manufacture and installation, combined with the presence of an alternating electric field magnified on cable defects, induce a degradation of the cable insulation named water treeing. It was shown[1,2] that water treeing may be considered as a fatigue phenomenon and should be related to the crazing phenomenon appearing in the bulk of a polymer or at the front of a crack, when the material is submitted to dynamic mechanical stress. Water treeing can occur in a number of amorphous or semicrystalline polymers[3–6] and the rates of treeing in these different materials have been compared. The reasons for doing such experiments were practical: development of better insulation, or demonstration of the merits of a particular material or class of materials. But no final conclusions on the understanding of water treeing were achieved. The processes leading to water tree initiation and growth, and then to cable breakdown, are probably the result of a complex interacting series of chemical, physical and structural phenomena. Nevertheless, the degradation of the material due to water treeing appears as mechanical damage, which may be assumed to be due to the effect of mechanical stresses induced in the polymer by forces of electrical origin. Since crazing, to which water treeing may be compared, is dependent on the nature and the structure of polymers, we have investigated[7,8] the influence of structural parameters of polymers on water treeing. It appears that such correlations represent an important tool leading to the understanding of water treeing. Since the propagation sites of water-filled microcavities constituting a water tree are the inter- and intraspherulitic amorphous spaces, it was of interest to determine the role played by such areas and by the tie molecules that join the crystalline lamellae. So, to do that, we have chosen to compare the growth and structure of water trees in an amorphous polymer such as polystyrene (PS) and in a semicrystalline one such as low-density polyethylene (LDPE).

EXPERIMENTAL

Because water treeing has proved to be a complex and often baffling problem, it was of prime importance to study this phenomenon under carefully controlled laboratory conditions.

Water trees were grown using the water needle method in injection-moulded specimens[8]. Their geometry allowed us first to generate a water tree in a well defined area represented by the tip of the water needle, and secondly to observe continuously, under a microscope, the growth of the water tree[8].

The geometry of the specimens and principally the tip of the water needle was rigorously controlled as well as their isotropy in the active zone. Such isotropy was obtained by annealing at 80°C for 48 h under nitrogen. Owing to such controls, the reproducibility of the experimental results was very good.

The experimental conditions were the following. The radius of curvature of the needle was 10 ± 1 μm, the amplitude of the voltage was 10 kV (maximum) at the frequency of 1500 Hz, and the distance between the tip of the needle and the opposite plane electrode was 2.5 mm. The high-voltage electrode was a platinum wire in contact with a solution of NaCl in water with a concentration of 0.1 mol l^{-1}. All experiments were done at room temperature. The length of the trees was measured along the needle axis. For each experiment, the time dependence of the water tree length was obtained over an average of 12 specimens. Some characteristics of tested materials are given in *Table 1*.

RESULTS AND DISCUSSION

Figures 1, 2 and *3* show the structure of a water tree in a PS sample after it was submitted to the alternating voltage for 3, 6 and 412 h respectively. *Figure 4* shows the structure of a water tree in a LDPE sample after 120 h under voltage. Comparison between *Figures 3* and

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Table 1 Some characteristics of the tested polymers

Polymers	PS	LDPE
Density ($\mathrm{g\,cm^{-3}}$)	1.05	0.920
Melt flow index[a] (g/10 min)	2.2	2
Melting temperature (°C)	180	110
Glass transition temperature (°C)	−80	+75
Crystallinity (%)	Glassy	43
Tensile strength ($\mathrm{kg\,cm^{-2}}$)	480	150
Elongation at break (%)	1.8	700

[a] At 200°C under 5 kg

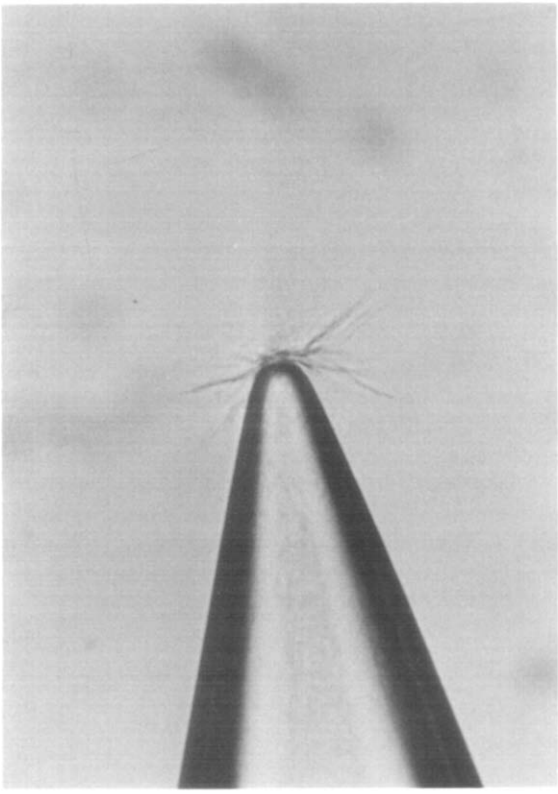

Figure 1 Structure of a water tree in a polystyrene sample after it was submitted to an alternating voltage for 3 h: × 570; $U = 10$ kV (max); $f = 1500$ Hz

4 shows the clear differences appearing in the water tree structure of an amorphous and a semicrystalline polymer, respectively PS and LDPE. In LDPE, water trees are made up of non-interconnected microcavities filled with water[2,9]. In the case of PS, we clearly observe that a water tree initiates and grows, in the first stage of its propagation, as a water-filled channel-like structure growing from the tip of the water needle (*Figures 1* and *2*). However, we can say that such a structure is not due to an electrical tree, because no evidence of carbonization was detected by u.v. analysis. Such an observation is in good agreement with that of Shaw *et al.*[5]. Moreover, our test method has allowed us to distinguish three different areas (*Figures 3* and *5*) constituting a water tree in PS. In zone 1, which is like a dark sphere, we note an important concentration of water denoted by a very low intensity of transmitted light. Channels constitute zone 2, which is followed by zone 3, where strings of microcavities are observed at the front of each channel. So, in PS, a water tree is comparable to a group of cracks (represented by the water-filled channels) with crazes or

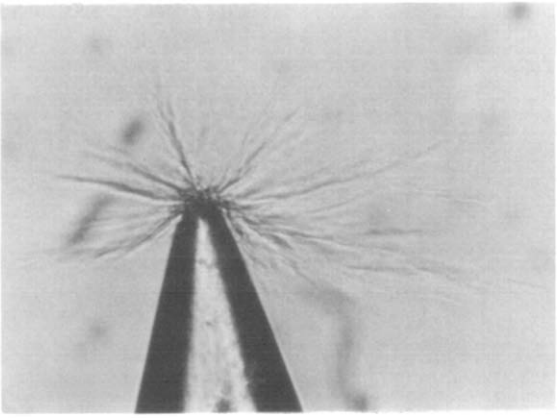

Figure 2 Structure of a water tree in a polystyrene sample after it was submitted to an alternating voltage for 6 h: × 570; $U = 10$ kV (max); $f = 1500$ Hz

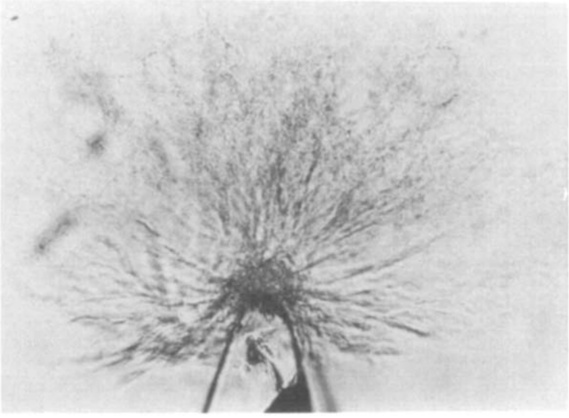

Figure 3 Structure of a water tree in a polystyrene sample after it was submitted to an alternating voltage for 412 h: × 570; $U = 10$ kV (max); $f = 1500$ Hz

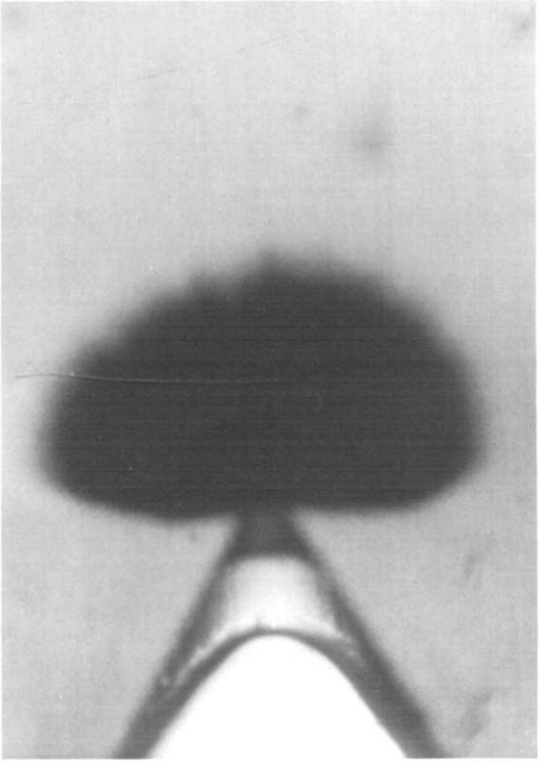

Figure 4 Structure of a water tree in a low-density polyethylene sample after it was submitted to an alternating voltage for 120 h: × 570; $U = 10$ kV (max); $f = 1500$ Hz

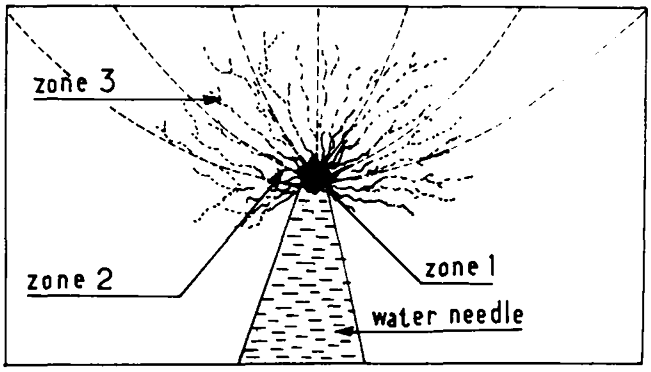

Figure 5 Diagram of the structure of a water tree in a polystyrene sample showing three different zones. The broken curves show the distribution of electric field lines in the plane-point geometry of our specimens

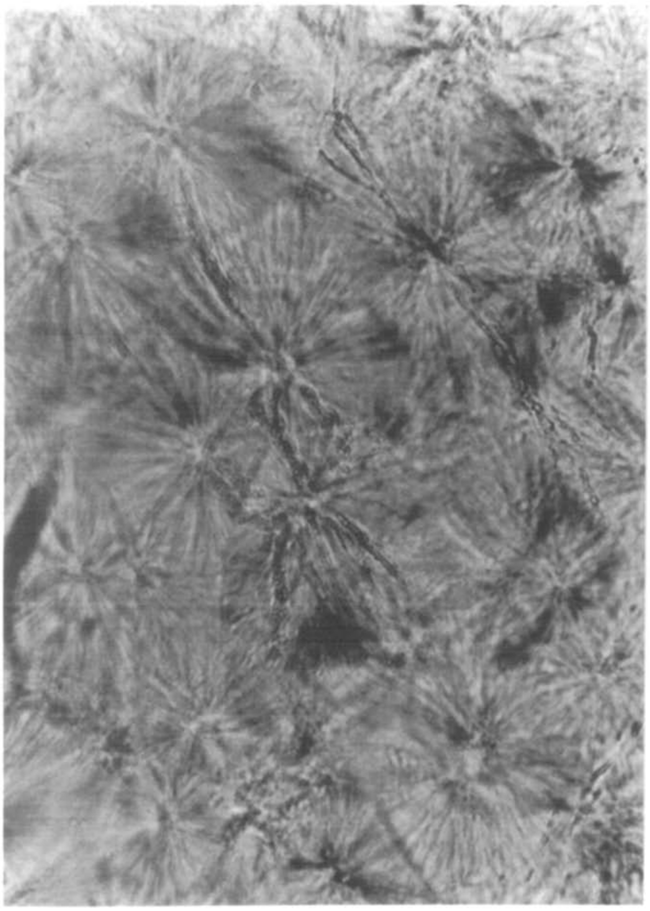

Figure 6 Structure of a water tree in a polypropene sample (×475) showing microcavities in the spherulites

cavitation initiation at the front, as is observed in fracture mechanics[10–13]. In our experiments in PS, because the frequency of the voltage was sufficient to stop space-charge creation, we can say that the electric field at the tip of the water needle reaches $320\ \text{V}\ \mu\text{m}^{-1}$, and induces an alternating electrostatic pressure of $10^7\ \text{N m}^{-2}$. The value of the electrostatic pressure is comparable to the mechanical stress inducing a fatigue failure as shown by the Wohler curves of PS[14]. On the contrary, in semicrystalline polymers such as LDPE, polybutene and polypropene, we have never observed any 'crack-like' structure initiation with the same value of the electric field at the tip of the water needle. We have only seen initiation and propagation of microcavities in the intra- or interspherulitic amorphous areas (*Figure 6*), which are joined by the tie molecules. We can expect that, in the case of LDPE, the energy due to the electric field is lower than the energy necessary to break the tie molecule chains, but sufficient to induce plastic deformations, themselves inducing local density fluctuations and consequently initiation of microcavities. So, water treeing in semicrystalline polymers, as previously assumed[2], is a phenomenon more comparable to microcavitation appearing in front of a crack than to cracking. The presence of tie molecules makes the polymer less brittle and conflicts with channel initiation, consequently giving the material a better water treeing resistance. In fact, in fracture mechanics as in water treeing[8,15–17], it was shown that the higher the molecular weight of a polymer, the higher the mechanical resistance to mechanical fatigue and to water treeing. Such resistance can be attributed to greater chain entanglement and consequently to a greater number of tie molecules in higher-molecular-weight materials. In contrast, in low-molecular-weight samples, as well as in amorphous ones such as PS, which is glassy ($T_g = 75°\text{C}$) at the temperature of our experiments (room temperature), materials are more brittle and more subject to cracking. Moreover, in amorphous material, it was shown that the crack paths are not determined by the spherulitic structure as in semicrystalline polymer[18–20] but by the local stress field[21]. In agreement with observations, we note, in our water treeing experiments on PS, that channels and microcavities respectively comparable to cracks and crazes propagate in the direction of the electric field (*Figure 5*), which plays the role of a fatigue mechanical stress. The curves of *Figure 7* show that, in PS, the microcavities propagate more rapidly than the channels, and their propagation rate is comparable to that observed in LDPE. The propagation of microcavities in PS obeys a power law $l = at^b$ as in LDPE. In our experiments, the coefficients a and b were of the same order for both materials. The initiation of microcavities was observed only after 20 h under voltage, a delay corresponding to a channel length of about 40 µm. In fact, close to the tip of the water needle we can expect that the dissipated energy is sufficient for channel-like crack structure initiation without any visible crazing phenomenon. Meanwhile, as the channels advance, the

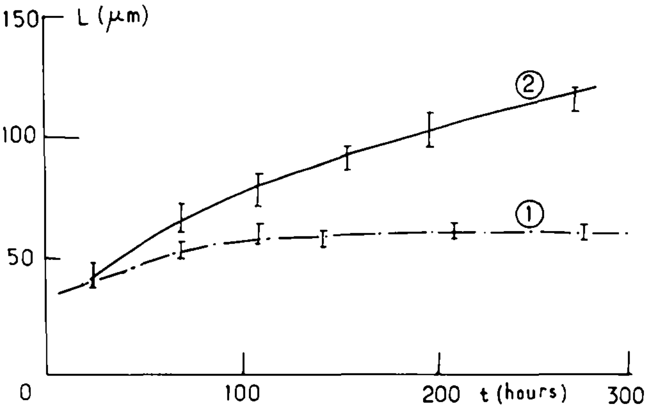

Figure 7 Growth kinetics of water trees in polystyrene: (1) channel-like structure; (2) zone of microcavities

energy available to form new channel surface decreases with decreasing electric field, a phenomenon denoted by the asymptotic behaviour of the channel propagation (*Figure* 7). No asymptotic behaviour of the propagation rate of microcavities was observed, but we can note a slowing down of this rate when the distance to the water needle tip increases, as observed in LDPE. This decrease could be correlated to the decrease of the local electric field.

CONCLUSIONS

The work presented here shows the comparison of water treeing in two polymers of very different nature. One of them is low-density polyethylene (LDPE), which is semicrystalline, and the other is polystyrene (PS), which is amorphous. Whereas the structure of a water tree resembles the crazing phenomenon, a water tree in PS near its initiation site presents a channel-like structure followed by strings of microcavities, which seems to be related to the cracking phenomenon. The propagation of these strings of microcavities in PS obeys a law of the same type as the law describing the propagation of microcavities in the amorphous areas of LDPE.

In water treeing as in cracking and crazing, the role played by the tie molecules joining the inter- and intraspherulitic crystalline areas through the amorphous zones is essential, because they make the material less brittle. Principally in the case of water treeing their presence conflicts with crack initiation, leading to a greater resistance towards breakdown of the polymeric insulation of high-voltage cables.

Finally, comparison of our experimental results given in the present and previous papers[1,2,7,8] with those of fracture mechanics corroborates the fact that, independently of other physical and chemical mechanisms, water treeing is first of all mechanical damage of the polymer due to the action of the alternating field playing the role of a cyclic mechanical stress.

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