

Influence of the molecular weight of low density poly(ethylene) on water treeing in relation to mechanical damaging

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The influence of the molecular weight of low density poly(ethylene) on the propagation of water trees is studied and compared with environmental stress cracking data. Water treeing is interpreted as a mechanical damaging of the polymer due to the action of local stresses of electrical origin. The propagation of water trees is discussed in terms of plastic deformations of the amorphous inter- or intraspherulitic spaces, induced by stretching action of dynamic forces of electrical origin on the tie molecules.

(Keywords: poly(ethylene); molecular weight; water tree; mechanical damage; dynamical and electrical stress)

INTRODUCTION

Polymers, and more particularly low density poly(ethylene) (LDPE), are still normally used as insulation for alternating current high-voltage extruded cables. Such materials offer many advantages in comparison to the more classical oil-impregnated paper. Nevertheless, they run the risk of long-term degradation which could bring about the breakdown of the insulation.

The coupling action of high electric field with traces of water, which may be introduced into the cable during manufacturing or installation, induces a degradation phenomenon of the insulator which is called 'water treeing'. From a macroscopic point of view, a water tree mainly consists in non-interconnected water-filled microcavities. The presence of such a degradation reduces the dielectric strength of the insulator. Thus, water treeing is one of the main factors in the failure of polymeric insulation of extruded power cables.

Today, despite the numerous studies on the subject over the last 10 years, the basic mechanisms of water treeing are still not well understood. A better understanding would be of great importance because it could lead to the synthesis of new materials having a better resistance to such a degradation. The processes leading to water tree initiation and growth and then to the cable breakdown are very likely the result of a complex interacting series of physical, chemical and structural phenomena. Nevertheless, the degradation of the material due to water treeing appears as a mechanical damaging which may be assumed to be due to the effect of mechanical stresses induced in the polymer by forces of electrical origin.

In a previous paper¹, Meyer and Filippini proposed a mechanism in which water treeing was compared with fatigue environmental stress cracking. Such an analogy was supported by arguments related to the magnitude

and the frequency of the electrical stress^{2,3} which have similar actions to those of mechanical stresses leading to the propagation of cracks. In fact, it was shown that a water tree, which is a strained region containing microvoids, is related to a craze rather than to a crack⁴.

The magnitude and the frequency of the mechanical stress are not the only parameters acting in the propagation of cracks and crazes. Structural and morphological parameters also play an important part in such phenomena⁵⁻⁸. So, if water treeing and crazing are similar phenomena, we can expect that the effect of these last parameters acts in the same direction for both these degradations. In this way, we have chosen to present a study of the effect of the molecular weight on the resistance of such materials to water treeing, and to compare the results with mechanical data on the same polymers.

EXPERIMENTAL

Water trees were grown using a laboratory model. The specimens (*Figure 1*) were injection moulded so that their upper parts are water reservoirs used for the lower parts (imprints of sharp needles), which are therefore always provided with water. This ensures that at the tip of this water needle, which has a well-defined curvature radius ($r = 10 \mu\text{m}$), a water tree initiates and propagates in the presence of an alternating electric field. Moreover, this lower part, containing the water needle, is an area of a smaller thickness allowing us to continuously display the growing of the degradation on a video monitor screen by means of a microscope and a video camera during the application of the electric field (*Figure 2*).

Due to the scatter of the results at least 12 specimens were used to obtain the growth kinetics of water trees in each material. All experiments were performed at room temperature, using a solution of NaCl in water with a concentration of 0.1 mol l^{-1} . The voltage was applied to the specimen through a platinum wire in contact with the

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liquid. The amplitude of voltage was 7 kV r.m.s. applied across a point/plane distance of 2.5 mm. The frequency was 1500 Hz. The length of the water trees was measured along the needle axis. All measurements were performed in the initial stage of water tree growth, up to a length of about 150 μm , where the electromechanical effects seem to be predominant².

MATERIAL AND CONTROL OF THE MORPHOLOGICAL PARAMETERS

Two groups of different samples, made up of trading materials used for cable insulation were studied. In group I are polymers A and B, respectively, free of additives. The polymers C and D of the second group contain the same

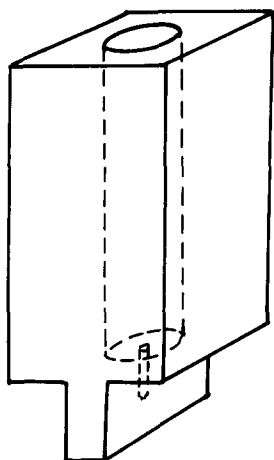


Figure 1 Geometry of an injection moulded specimen

antioxidant in the same proportion. Some characteristics of these products are given in Table 1.

Because residual strains and oxidation of the materials are expected to favour the propagation of water trees, the specimens were first deaerated for 4 days then annealed at 80°C for 24 h under nitrogen blanket. The aim of annealing is to reduce the residual strains appearing during the moulding of the polymer. After such a procedure, observations under optical polarizing microscope ($\times 500$) have shown that our samples were isotropic in the area of water tree growth.

It is difficult to distinguish between the effects of the structural parameters of a polymer, i.e. the spherulite size, the crystallinity and the molecular weight, because of their strong interactions. Concerning our LDPE specimens, the moulding conditions, the annealing temperature and the cooling kinetics were adjusted in order to reduce morphological differences between the samples. After such treatments, diffraction patterns have shown that the magnitude of the spherulite size was about 1 μm in all materials. The crystallinity of each sample was controlled by dynamic scanning calorimetry. The analysis of the obtained thermograms showed that the differences in the crystallinity level between the samples of each group were less than 1%. Hence, if differences appear in the water tree propagation curves for the different specimens of each group, such an effect is due to the difference in their molecular weights.

RESULTS AND DISCUSSION

Figures 3 and 4 show examples of variations of the length of water trees as a function of time for groups I and II, respectively. A clear difference appears in the behaviour

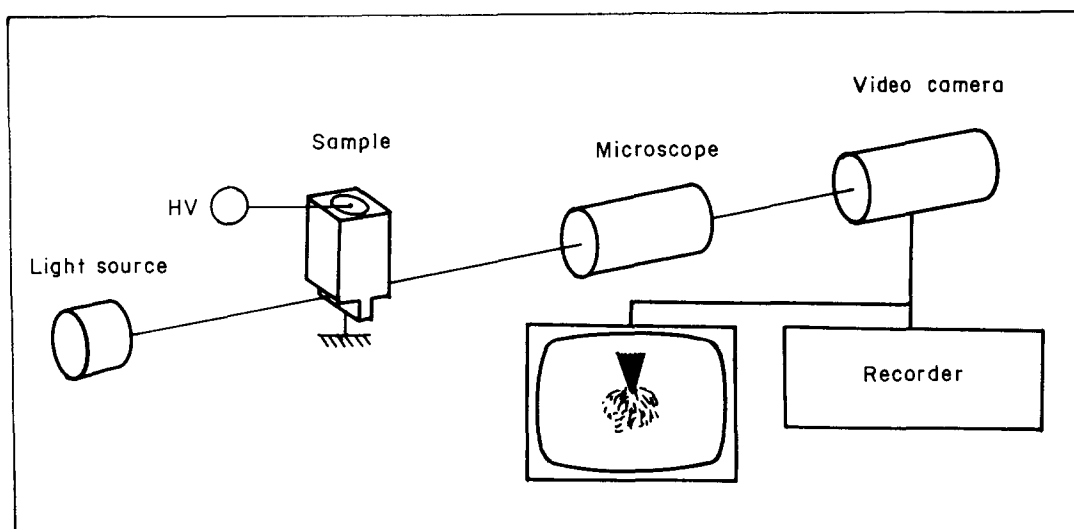


Figure 2 Experimental device

Table 1 Some characteristics of the polymers studied

	Polymer	Antioxidant	Density (kg m^{-3})	MFI (deg min^{-1})	Molecular weight, \bar{M}_w
Group I	A	No	0.922	0.25	119 000
	B	No	0.923	2.3	81 100
Group II	C	Yes	0.921	0.15	161 000
	D	Yes	0.918	20	48 000

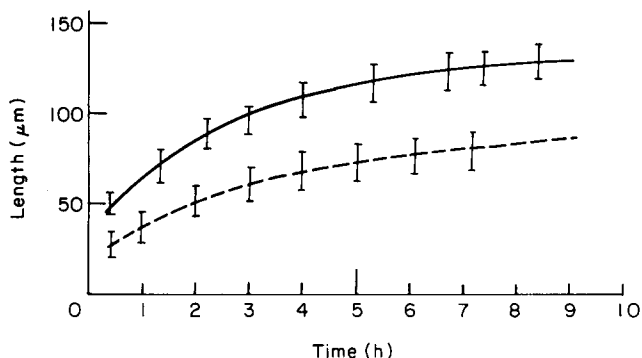


Figure 3 Length of water tree as a function of time in polymers without antioxidant: polymer A ($M_w=119\,000$, ---) and polymer B ($M_w=81\,100$, —)

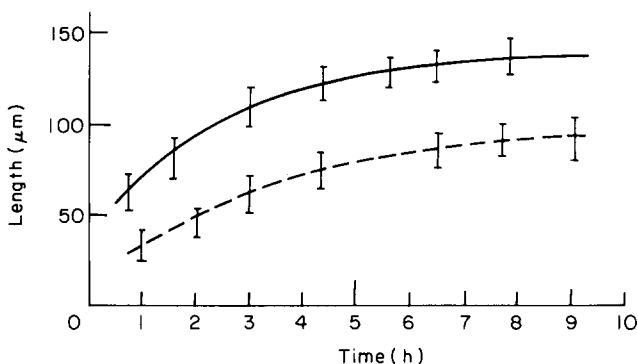


Figure 4 Length of water tree as a function of time in polymers containing an antioxidant: polymer C ($M_w=161\,000$, ---) and polymer D ($M_w=48\,000$, —)

of the different samples of each group. At this first stage, due to the fact that in each group each sample has the same crystallinity and the same spherulite size, we can conclude that for each group of LDPE, the molecular weight has the same effect: the higher the molecular weight, the lower the water tree propagation rate. As a digression, experiments were also conducted on non-annealed samples and we found that, first the molecular weight acts in the same way as in annealed samples, and second the effect of annealing is to reduce the propagation rate of the water trees (Figure 5), probably by acting on the homogeneity of the sample.

The resistance of materials A, B, C and D to experimental stress cracking, was estimated using prebended tensile samples in presence of Anterox CO 630 at 10% dilution in water. The average life time of each material is given in Table 2. We can see that, in each group the material which has the highest molecular weight also has the highest environmental stress cracking resistance. This result is in agreement with data concerning high density polyethylene (HDPE)⁷: the authors notice a qualitative correlation between the resistance of HDPE in the fatigue regime and molecular weight. Hence, our experiments allow us to corroborate the analogy between fracture mechanics and water treeing. For both phenomena, the molecular weight acts in the same way: by increasing it gives the material improved resistance to mechanical or electrical stress.

The electromechanical interpretation of water treeing assumes that the microcavities are created under the action of dynamic stresses of electrical origin, in a similar

way to that of crazes appearing in polymers submitted to a mechanical stress. Thus, our experiments are additional proof in favour of the interpretation of water treeing as a mechanical damaging in the polymer.

Concerning the effect of the molecular weight, we may say that the higher the molecular weight of a polymer, the higher the chain entanglement. Consequently, it is reasonable to suppose that in high molecular weight materials, the concentration of the molecules is higher than in materials with lower molecular weight, thus giving a higher mechanical strength to interlamellae and interspherulitic bonds. Then, such materials should have a higher elasticity limit inducing a greater resistance to fatigue. So, the structure of interlamellae and interspherulite spaces, related to the size of the molecular chains, and consequently to molecular weight, should play an important part in water treeing. The mechanical stresses due to the fatigue action of the electric field and to the pressure forces induced by the penetration of water are likely to induce plastic deformations of tie molecules. So, local density fluctuations could appear in the inter- or intraspherulitic areas facilitating the formation of the microcavities.

CONCLUSIONS

We have presented experiments on the effect of the molecular weight of LDPE on the kinetics of the damaging phenomenon of polymers under the action of an electric field called water treeing. Our results demonstrate that the higher the molecular weight, the higher the resistance of the material to water tree growth, as observed in fracture mechanics. There is additional proof that water treeing and stress cracking or crazing are related phenomena: in one case, the mechanical damaging of the polymer is induced by local stresses due to a mechanical load, in the other it is induced by local stress due to an electrical field.

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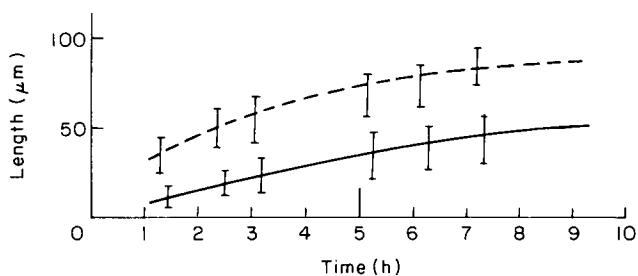


Figure 5 Effect of annealing on the propagation curve of a water tree: annealed polymer A (—) and non-annealed polymer A (---)

Table 2 Life time of the polymers studied in environmental stress cracking testing

Polymer	Group I		Group II	
	A	B	C	D
Life time	48 h	6 min	96 h	4 min

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