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Conduction and charge-injection in polypropylene films aged by corona discharge with streamers

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Abstract. The nature of the surface plays a critical role in the charging ability and the insulating character of insulating materials. By submitting the polymer (for instance polypropylene) to corona discharges with streamers, the corona-activated species change the chemical and morphological properties of the surface. The physico-chemical properties had previously been investigated by electron-micrography and infrared absorption spectroscopy, and both techniques have clearly shown that nodules and crystallites of oxidized constituents of the polymer appear on the surface. By using both surface potential decay and return voltage analysis, the present work will be shown to reveal a significant correlation between the physico-chemical properties of the treated polymer and the transparency of the surface to charges deposited on it by a direct current corona. Whilst the voltage of charged untreated samples decays rapidly and substantially, it decays less, and less quickly, for treated samples. Conversely, whilst the return voltage for untreated samples is hardly measurable, it is quite appreciable for treated samples. These observations cannot be explained in terms of one-dimensional charge transfer models but their interpretation may be based on the defects mentioned above, which modify the local field on the sample during charge deposition.

1. Introduction

Many years ago, Gross showed that the decay of the surface potential of a charged insulating sample was indicative of its dielectric properties, and also that a charged material can retain charges after a momentary short-circuiting, even if it is applied for a time longer than the dielectric relaxation time of the material. This has been interpreted in terms of a memory function, accounting for the absorptive character of the material [1, 2]. Thereafter, studies focused on the interpretation of the surface potential decay in terms of dipolar relaxation, charge migration and conduction in the bulk [3]. The potential return (or reappearance of potential when the charged sample is neutralized after some duration of natural decay) was re-investigated recently by Coelho *et al* [4], who interpreted their results in terms of the attraction of the injected carriers by charges deposited at the time of the neutralization.

In the present work, as well as in [4], potential decay and return have been measured with a vibrating, contactless probe, which is a technique well suited for charge transport studies, since no field between sample and probe can perturb the carriers.

The nature of the surface plays a critical role in the charge storage ability and the insulating character of the material. By submitting the polymer (for instance polypropylene) to corona discharges with streamers, the corona-activated species change the chemical and morphological properties of the surface of the material. By using both surface potential decay and return, the present work will be shown to reveal the correlation existing between the degradation evolution, the electrical properties and the morphological changes that are produced on the sample surfaces by AC corona treatment.

Before presenting the results of our electrical measurements, it seems appropriate to summarize previously published results on the degradation processes of the polypropylene exposed to a corona discharge with streamers [5].

As soon as the sample is exposed to the corona discharge with streamers at about 60% relative humidity (RH), nodules corresponding to the agglomeration of oxidized oligomers start to appear on the surface [6]. Then these nodules grow until they reach a critical size (about 10 μm). After about 7 min of treatment,

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the nodules start to evolve into crystallites through complex mechanisms involving radical reactions, at and only at the point of impact of the streamers [7]. The SEM observations have shown that this transformation is initiated by cracks on the top of the nodules [5]. These crystals become increasingly numerous. Dielectric breakdown happens when crystals are closely packed together, and this behaviour is reminiscent of the dielectric breakdown caused by partial discharges [8]. When the exposure is carried out in a lower relative humidity (about 5% RH), the small crystals appear directly after about 2 min of treatment. Moreover, the lifetime of the sample also depends on the relative humidity, and the lifetime seems to be longer with higher relative humidity, which is against expectation.

Infra-red micro-spectroscopy has shown that the degradation products consist essentially of carboxylic acids, other carbonyl groups and alcohol functions [9]. Oxalic acid, fumaric/maleic acid and succinic acid were the main carboxylic acids identified by capillary electrophoresis [5]. The IR spectra show that the transformation of the nodules into crystals takes place together with an increase in the intensity of carbonyl groups observed at 1720 cm^{-1} and a decrease in the intensity of double bonds (at 1630 cm^{-1}) and of the free hydroxyl groups -OH (3400 cm^{-1}). These changes can be explained in terms of the ozonolysis reaction [10], ozone produced in the discharge reacting with the double bonds of the nodules to give carbonyl groups. Similarly, the hydroxyl function can be attributed to an intermediate product such as hydroperoxide, transformed into carbonyl groups in the presence of ozone. Finally, the crystals appear as the end products of an acid hydrolysis.

2. Experimental

The study was performed on 15 μm thick polypropylene films submitted for various durations to AC corona discharges with streamers in synthetic air of different relative humidities (about 5–60% RH). To study the evolution of the electrical properties with respect to the degradation processes, the ageing discharges were supplied by means of an AC (50 Hz) 10 kV peak voltage applied to a metal tip of 50 μm radius through a 25 MΩ resistance that prevented the insulating film undergoing premature breakdown.

After treating samples for different times of AC corona, we studied the evolution of the surface potential decay and potential return rates as a function of the duration of treatment.

The sample was then corona-charged by a tip at high DC voltage regulated in current at 25 μA, with a grid at −3 kV interposed between tip and sample, as close as possible to the sample surface in order to provide a uniform charge distribution and control the number of surface charges. The deposition time was 5 s. Under such conditions, the electrical field across the dielectric film was about 200 MV m^{-1}, namely higher than the charge injection field [11]. The sample was then transferred under a non-contacting probe (Monroe 168-1).

Return potential studies consist of monitoring the surface potential after temporary neutralization of the charged surface with an AC corona discharge. All operations are controlled by a microcomputer.

However, since fast polarization and/or recombination processes may affect the initial decay and return rates, the time derivative dV/dt has been replaced here by the ratio $\theta(t)$:

$$\theta(t) = [V(t) - V(0)]/t \qquad (1)$$

where $t = 10$ s has been chosen. Fast polarization and surface recombination processes take a few seconds. Transfer time from charging to measurement position takes less than 1 s. Since the initial decay rate may exceed 1 V s^{-1}, and since the dynamical voltage probe resolution is of the order of 10 V, our time interval of 10 s is to be considered as a good compromise.

3. Results

3.1. Electrical measurements

To study the influence of the degradation of the polypropylene films on their electrical properties, we submitted different samples to corona discharges with streamers, for different durations.

Each sample is then DC corona-charged for 5 s and the surface potential decay is monitored for 1 min. Figure 1 gives an example of the decay at about 60% RH for treated and non-treated samples and presents the decay rate $\theta(10)$, as defined above, for samples submitted to corona ageing for various times in dry and humid air. Surface potentials vary from −3000 to −2600 V in 1 min and θ drops sharply from 27 to about 5 V s^{-1} after about 30 s exposure at the discharge with streamers in wet air, or 2 min in dry air (a similar behaviour is observed for three intermediate levels of relative humidity). For longer treatment in dry air, θ remains very small until breakdown takes place after 15 min. For longer treatment in wet air, θ somehow recovers, and breakdown takes place after 30 min treatment.

To study the return voltage, the sample is first charged as before, then left decaying for 1 min, and neutralized by AC corona for 5 s. The surface potential return is recorded for 4 min.

Figure 2 shows the rate of potential return versus treatment time. For samples treated at low humidity, $\theta_R(10)$ increases until the breakdown occurs. For samples pre-treated at about 60% RH, $\theta_R(10)$ first increase sharply and then undergoes some variations before breakdown. In all cases, the return rate varies inversely to the decay rate, at least for short corona treatments.

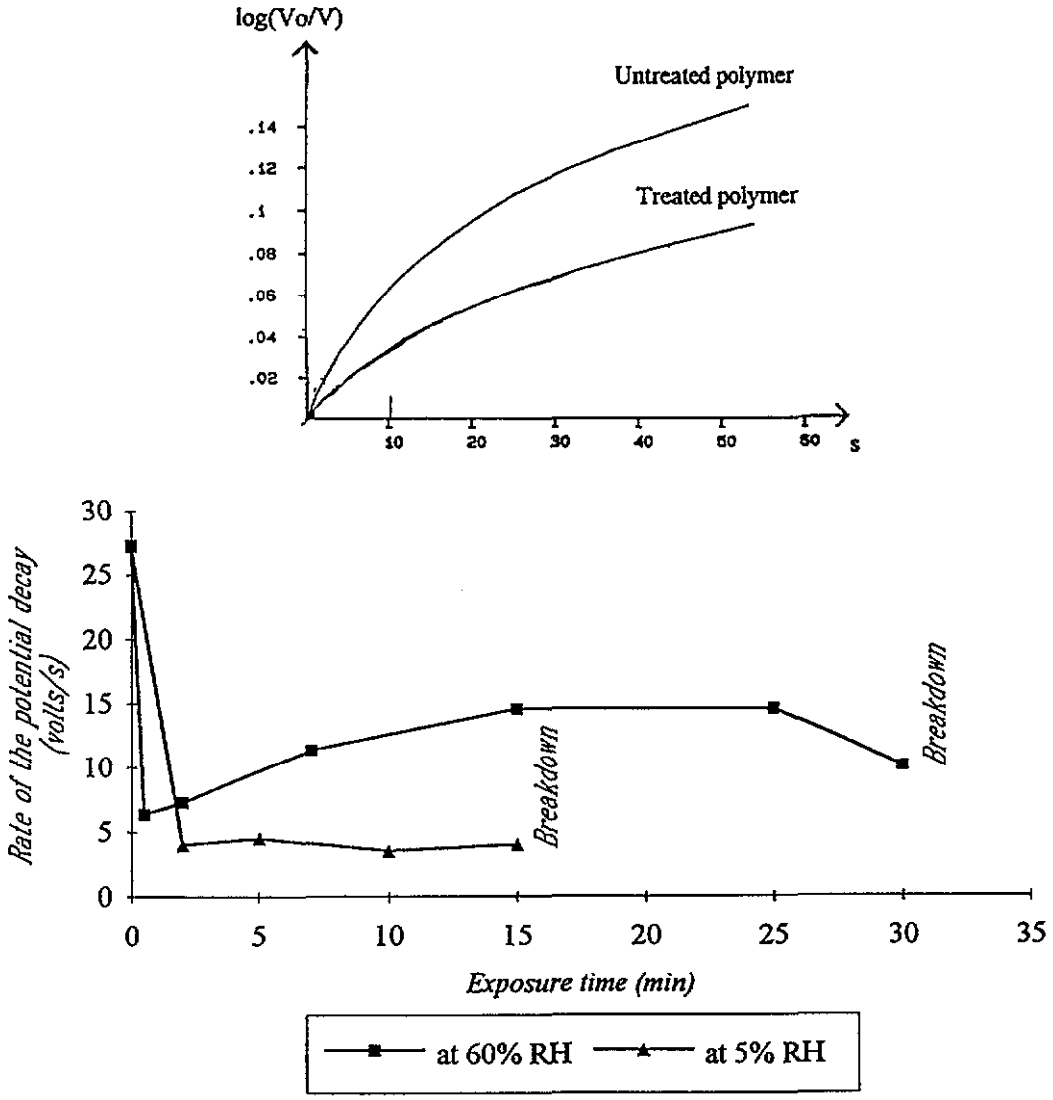


Figure 1. Rates $\theta_D(10)$ of the surface potential decay after corona-charging the polypropylene films (15 μm thick) previously treated by corona discharges with streamers (10 kV, 50 Hz) versus the exposure time.

3.2. Surface morphology and correlated electrical observations

The surface of the polypropylene films is affected during treatment, just as has been mentioned above [5]; namely, nodules appear on the surface during the treatment at about 60% RH and their size increases until they coalesce to form crystals (figure 3). Then dielectric rupture takes place at the point at which the density of the crystals is highest (figure 4). For treatment carried out at about 5% RH, no nodules are observed, and the crystals appear directly on the surface (figure 5). In a humid ambience, nodules appear after roughly 1 min exposure to the AC corona with streamers; then their size and density increase. The crystals appear after about 7 min exposure, but, at low relative humidity, they appear earlier. These delays are characteristic of our discharge conditions (tip–sample distance, tip radius, applied voltage and so on) but only the energy dissipated on the polymer surface by the streamers governs the appearance of these defects.

Moreover, the bulk of the material seems also to be affected by the relative humidity during treatment. Whilst small channels appear across films treated at high humidity under the points of impact of the streamers, some kinds of dislocations parallel to the surface, revealed by electron-micrography, seem to appear in films treated at low humidity (figure 6).

Finally, after dissolving the surface clusters in water and drying the sample, both decay and return kinetics display a tendency to recover their original patterns.

4. Discussion

In the first step, whatever the relative humidity, the degradation of the polymer is related to the oxidation of the surface, decreasing the surface potential decay rate and increasing the surface potential return rate. This might be due to a trapping effect of ions from

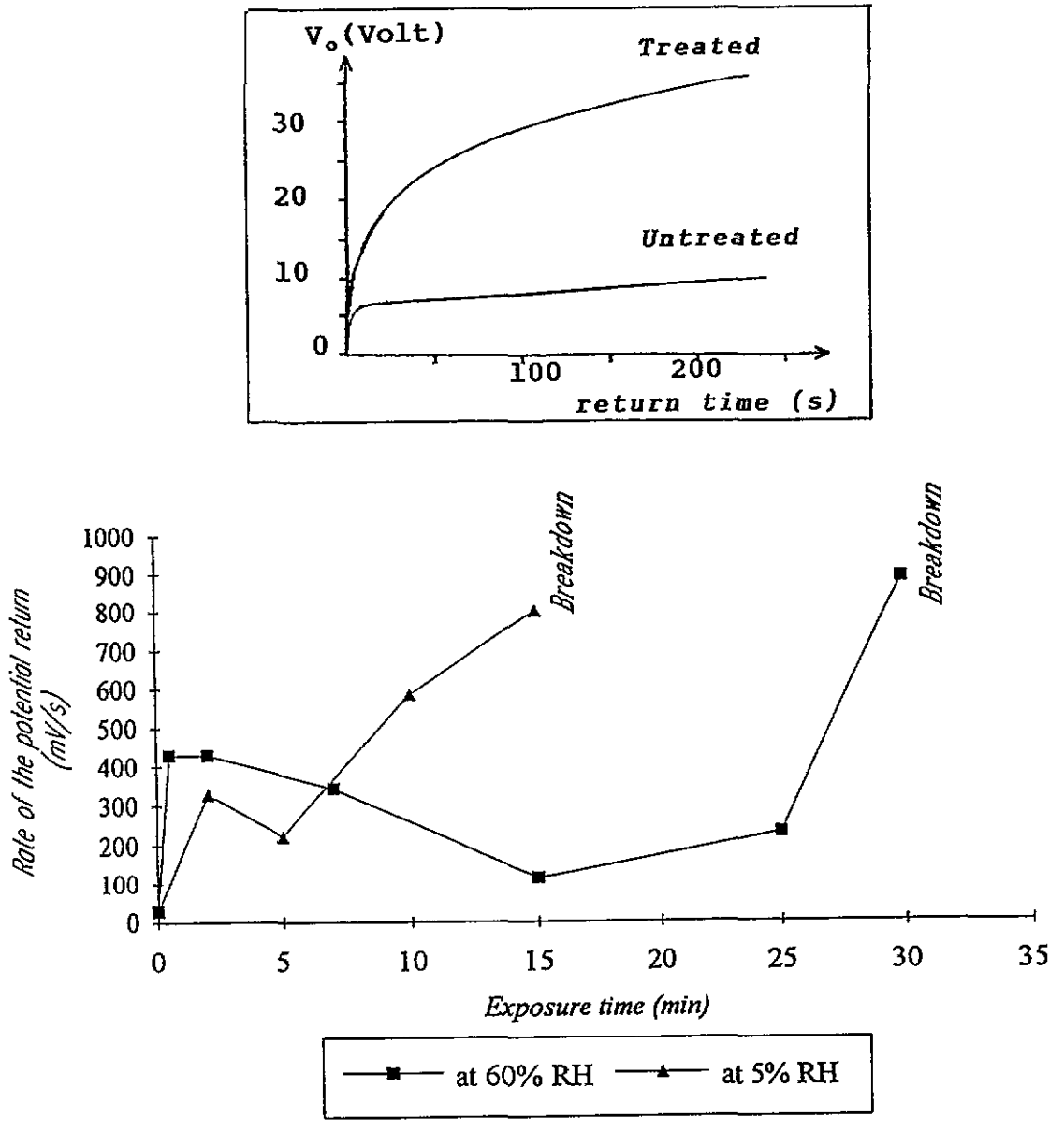


Figure 2. Rates $\theta_R(10)$ of the surface potential return after neutralizing the surface versus the time of the exposure to the discharge.

the corona by the oxidized groups –OH, –C=O and –C=C– produced by the treatment, in agreement with a suggestion by Mizutani and Ieda [12]. These oxidized products can form an electrolyte on the surface of the treated polymer and enhance the leakage of surface charges, but in our experimental conditions (transverse electric field higher than the injection field), this surface transport contribution is negligible relative to the injection of charges, which involves the bulk of the material. So, afterwards, we used the charge-plane model, which supposes the injection of the charges into the polymer.

On the other hand, the ions provided by the streamers with a high kinetic energy at impact may induce a severe degradation of the surface, and even in the bulk of the material.

Using the charge-plane model [4], one can estimate the penetration depth λ after a decay time t, assuming that the duration of the charge deposition (5 s) is short:

$$\lambda = \mu E t. \tag{2}$$

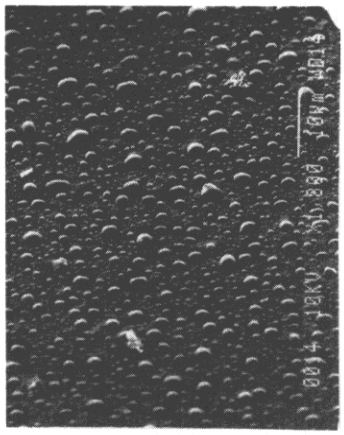
In this relation, μ is the charge mobility which is related to the decay rate by

$$\mu = \frac{L^2}{2V_0^2}\left(\frac{\mathrm{d}V}{\mathrm{d}t}\right)_D \tag{3}$$

and E is the electric field V_0/L across the stressed portion of the sample, which is very thin (15 μm). E is constant, equal to Q/ϵ, as illustrated in figure 7(a) and in our experiments, $t = 65$ s.

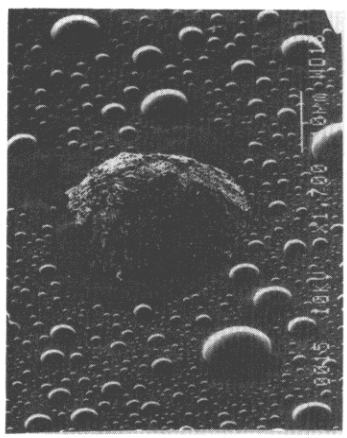
Under the above assumption, λ is then

$$\lambda = \frac{L}{2V_0}\left(\frac{\mathrm{d}V}{\mathrm{d}t}\right)_D t. \tag{4}$$



—10 μm

(a)



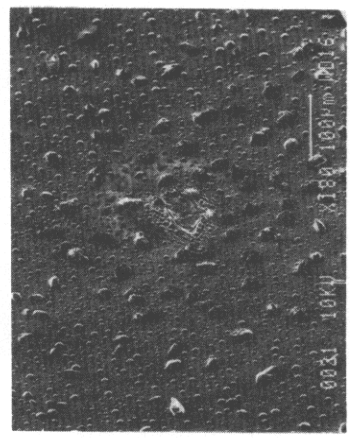
— 10 μm

(b)

Figure 3. Scanning electron microscopy pictures of a polypropylene surface submitted to corona discharges with streamers at about 60% relative humidity: (*a*) at the beginning of the treatment and (*b*) gathering of the oxidized products by the crystallization of the nodules.

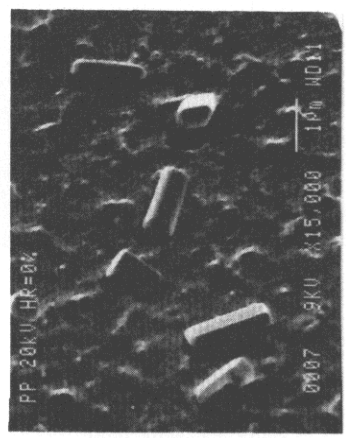
Using the expression (4), λ is of the order of 10 μm for an untreated sample, but only in the range 2–5 μm for a sample treated at 60% RH, and in the range 1–2 μm for a sample treated at 5% RH (table 1). In view of the crudeness of the charge-plane model, the values found for λ are only approximate. Even if the actual mean penetration were 50% of the calculated one, the conclusions would still hold.

Figure 7 shows that, if the charge penetrates to about mid-sample depth, then field cancellation of both sides impedes the building up of return voltage. The nodules and/or crystals appearing on treated surfaces enhance the local field there during charge deposition. These defects charge preferentially so that, for a given total charge, the uniform charge density (outside the altered spots on treated samples) would be smaller than that on the untreated ones, as indicated in figure 8. Hence, the transverse field (and the penetration depth) would also



— 100 μm

Figure 4. A scanning electron microscopy picture of the dielectric rupture of the polypropylene submitted to corona discharge with streamers at about 60% relative humidity.



— 1 μm

Figure 5. A scanning electron microscopy picture of the surface of the polypropylene submitted to corona discharges with streamers at about 5% relative humidity.

be smaller (for a hemispherical conducting sphere on a plane, the field enhancement factor is three, but it can be much higher for sharper defects).

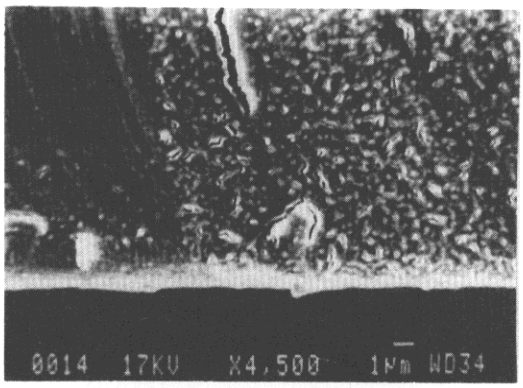
This interpretation is supported by the effect, mentioned above, of removing the clusters generated on the surface by the corona treatment.

4.1. Remarks on the mobility of charge carriers

The effective carrier mobility mentioned so far is the mobility μ_D deduced from the potential decay. Another value of the mobility can be obtained from the return voltage rate [4]:

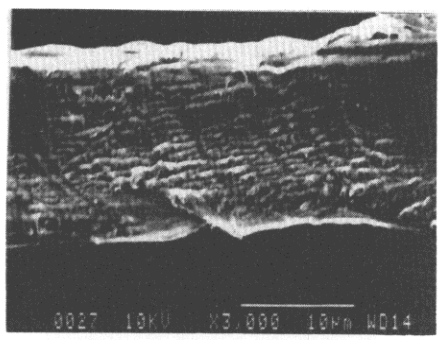
$$\mu_R = \frac{2(dV/dt)_R L^2}{V_\infty^2 - V_0'^2} \tag{5}$$

where $(dV/dt)_R$ is the return potential rate at time t, V_0' the potential before neutralizing the surface and V_∞ the maximum value of the surface potential obtained after



— 2 μm

(a)



— 5 μm

(b)

Figure 6. Scanning electron microscopy pictures of sectional views of polypropylene films under the point of impact of the streamers, treated (*a*) at about 60% and (*b*) at about 5% relative humidity.

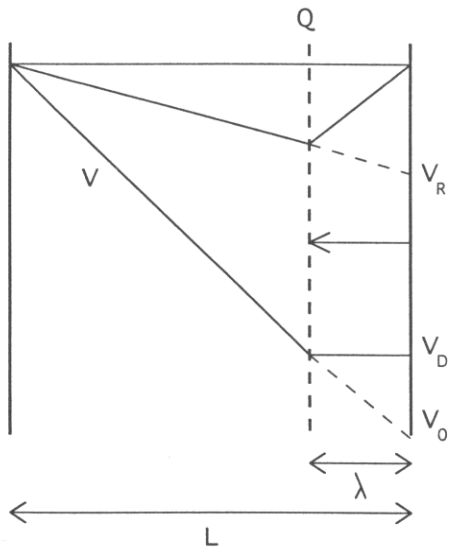
short-circuit. Since μ_D refers to the mobility near the surface and μ_R to that in the bulk, it is not surprising that the values obtained are different. Table 2 shows typical results for non-treated and treated samples. In our experiments, the electric field across the dielectric film is higher than the charge-injection threshold; hence the degradation products decrease the mobility obtained from the decay voltage rate but increase that obtained from the return voltage rate: the oxidized products do not favour the leakage of surface charge.

Whilst μ_R does not seem to depend on the relative humidity, μ_D is higher for samples treated in high RH, indicating an enhancement of the carrier mobility related to the presence of water diffused into the sample.

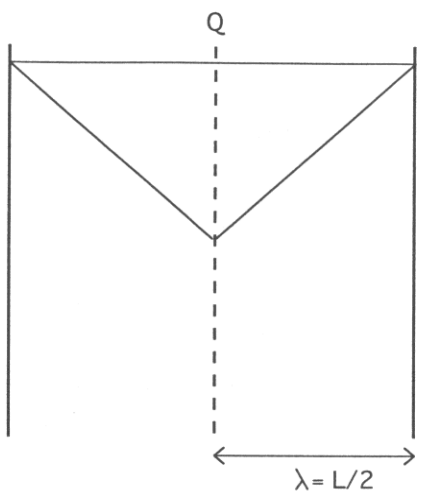
Other workers [13] found that μ in electron-irradiated samples increases with the absorbed dose, and the values they quote for slightly irradiated samples agree with our present data.

4.2. Spontaneous breakdown

Breakdown occurs spontaneously after some period of corona treatment. However, it is interesting to note that it always occurs earlier for samples treated in a drier ambience. This seems consistent with the fact



(a)



(b)

Figure 7. The charge-plane model in a dielectric sample [4]: (*a*) after some time of decay, the penetration depth is small, and a return potential builds up upon short-circuiting; and (*b*) if it reaches about $L/2$, a return potential cannot build up.

Table 1. Variation of the depth of the charges' injection during the exposure to the corona discharges with streamers, calculated according to the potential decay measurements.

Relative humidity	Treatment time (min)	Depth (μm)
	0	10 ± 0.2
High	0.5	2 ± 0.2
	2	2 ± 0.2
	7 to 25	5 ± 0.3
	30	3 ± 0.2
Low	2	1.6 ± 0.1
	5	1.6 ± 0.1
	10	1.1 ± 0.1
	15	1.6 ± 0.1

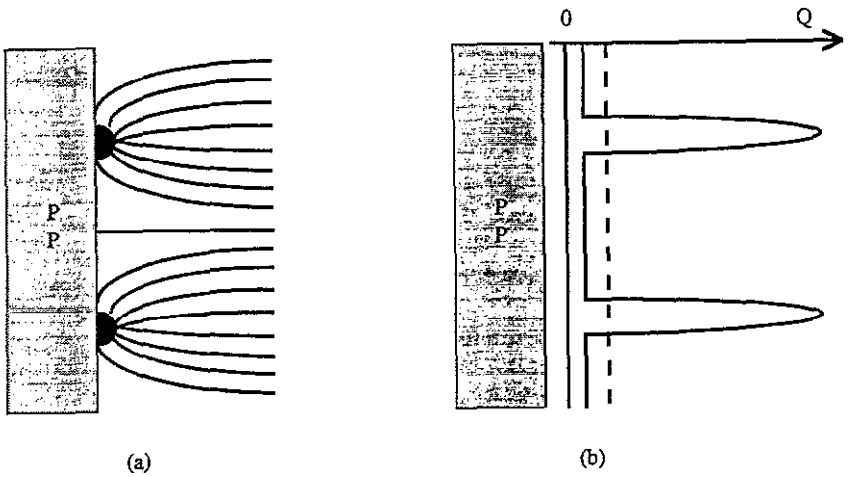


Figure 8. The electrostatic effect of the localized defects on the surface. (*a*) During charge deposition, the defects are charged preferentially. (*b*) The proposed charge density distribution on non-treated (– – –) and treated (——) samples.

Table 2. The variation of the charge mobility in the polypropylene submitted to the corona streamers calculated from the measurements of surface potential decay and return.

	μ_D ($m^2\ V^{-1}\ s^{-1}$)	μ_R ($m^2\ V^{-1}\ s^{-1}$)
Untreated polymer	4×10^{-16}	3×10^{-18}
Low relative humidity	5×10^{-17}	2×10^{-17}
High relative humidity	10^{-16}	2×10^{-17}

that crystals promoted by the aggregation of oxidized sites on the surface, and by creating strong distortions of the local field, appear earlier on samples treated in a drier ambience. The local field distortions create local mechanical strains, which may generate electro-mechanically induced cracks and microcrystals in the bulk, as suggested both by the electron-micrographs (figure 6) and by the enhanced mobility noticed shortly before breakdown, and finally lead to premature breakdown of the sample.

5. Conclusion

This work has revealed a significant correlation between the physico-chemical properties of a polypropylene film treated by an AC corona with streamers and the transparency of its surface to charges deposited on it by a DC corona.

The physico-chemical properties had previously been investigated by electron-micrography and infrared absorption spectroscopy; both techniques have clearly shown that nodules and/or crystallites of oxidized constituents of the polymer start appearing on the surface as soon as the treatment begins.

The electrical transparency observations carried out by means of measurements of the potential decay after charge and return voltage after temporary short-circuiting yield unexpected results. Whilst the voltage of untreated samples decays strongly and rapidly, it decays less, and less quickly, for treated samples. Conversely, whilst the return voltage for untreated samples is hardly measurable, it is quite appreciable for treated samples.

The electrical observations mentioned above cannot be accounted for by one-dimensional charge-transfer models such as those developed earlier for the decay and return voltages [4]. However, the morphology of the nodules and crystallites, which start protruding from the surface as soon as the treatment begins, may account for the results, as suggested below.

It should not be overlooked that the defects mentioned here enhance, by 'edge effects', the local field in the plasma during charge deposition. Consequently, although the average charge density might be roughly the same on treated and untreated samples, the charge uniformly distributed between the defects is smaller on the treated samples, since charge is deposited preferentially on the defects, where it may remain trapped. Since the field across the unperturbed sample area is smaller, the charge penetrates less deeply in untreated samples, and this may cause both a reduced decay and an increased return voltage, as is indeed observed.

This tentative interpretation should of course be confirmed by using a range of decay times, to vary the penetration depth of the deposited charge, and by attempting a high-resolution electrical mapping of the treated surfaces, possibly by scanning tunnelling microscopy, to detect the charge trapped on individual defects.

Nevertheless, it seems well established that the amazing sensitivity of the electrical data to the presence of tiny surface defects is likely to become very useful in the field of surface analysis and in electrical engineering as well.

Acknowledgments

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