A percolation theory analysis of surface potential decay related to corona charged polypropylene (PP) electrets

T A Yovcheva, G A Mekishev and A T Marinov

Department of Experimental Physics, University of Plovdiv 'P Hilendarski',
Tzar Assen Street 24, 4000 Plovdiv, Bulgaria

E-mail: temiov@pu.acad.bg

Abstract

We have studied the behaviour of 20 μm thick PP corona charging electrets, stored before and after they were charged, at various conditions of controlled relative humidity. The electret surface potential was measured for 250 days using a vibrating electrode with compensation. The time dependence of the surface potential was analysed by the percolation model for the 2D case. We have developed computer software for nonlinear programming. We have compared the experimental curves to the theoretical ones. We calculated the basic parameters that determine cluster formation and growth to an unbounded cluster, leading to a fast neutralization of electret charges.

The percolation model allowed us to analyse electret surface discharge and to reveal the significant influence of the humidity level at which they have been stored. This is extremely important and should be taken into account in the study of the stability of electret sensors and devices that are used at room temperature and function under real conditions at various humidity levels.

1. Introduction

In many papers [1–7] the electret effect and the influence of various factors on it have been explained by two theories: the phenomenological theory, in which the various polarization mechanisms play the primary role and charge injection is secondary, and the charge injection theories, in which the field produced by externally injected charge enables various polarization processes to develop. However, in both cases the processes occurring in the bulk of the dielectric have been studied while the possible influence of the surface on charge relaxation has been neglected. There are experimental data, however, to testify to such an influence [8–10].

In [8] the charging of electrets in corona discharge was carried out using a metal mask. The mask was put upon the sample and the charge was deposited on the central area of the

Table 1. Relative humidity (RH) in the different desiccators.

No of desiccators	1	2	3	4	5
Relative humidity (%)	0	32–33	52–55	75–76	98–100

sample surface, thus the peripheral band of the sample remained free of charge. That caused a decrease in charge decay rate. According to [9], the creation of a certain mechanical relief of the electret surface, in the form of a ditch, impedes the decay of the charge and increases the stability of the electret obtained. The same effect would be observed if charge distribution were made non-uniform, where the charge is deposited as separate islands, distributed over the electret surface [10]. Therefore, surface charge relaxation should not be neglected under certain conditions. Charge drift through the dielectric bulk happens primarily in studies of the physical properties of the electrets, especially when some thermostimulated charge methods are involved. Still, electret stability of electronic devices, in a real working environment and accounting for the influence of humidity, is due to the surface charge. Currently there has only been one attempt, that we know of, to explain the electret effect out of the phenomenological or the injection theories and to use the percolation model instead [11–13].

The aim of this work is to investigate a surface potential decay of corona-charged electrets, stored at various humidities, and use a percolation model to explain their behaviour.

2. Experimental details and results

Nonmetalized samples of polypropylene (PP), Bulgaria, have been studied. The sample thickness was 20 μm and all samples had a diameter 30 mm. Samples were cleaned for 4 min in an ultrasonic bath with alcohol, rinsed with distilled water and dried under room conditions. Before charging in a corona discharge, they have been stored in desiccators at various relative humidities (RH) (table 1) for 50 days at room temperature.

Just before being put into the corona discharge, each of the samples was placed on a metal electrode, all of them 30 mm in diameter. The charging of electrets in the corona discharge was carried out by means of a conventional three-electrode system—a grounded plate electrode, corona electrode (needle) and a grid placed between them. The voltage of the corona electrode was -5 kV and the charging time was 1 min. The electret surface potential (V_{eo}) was limited by the grid potential and was of the order of -670 V.

The electret surface potential has been measured by the method of the vibrating electrode with compensation.

After charging the samples, the initial electret surface potential (V_{eo}) was measured. Then the electrets were put in desiccators at room temperature and the surface potential (V_e) was measured periodically out of the desiccators.

A few groups of samples have been studied. Our previous analysis [14] has shown that the electret behaviour is basically determined by the storage conditions after charging. Hence we have reported the results of two groups of samples: the first one designated as 51–55 and the second one designated as 11, 22, 33, 44, 55. The first figure stands for the desiccator where the samples were placed before charging in the corona discharge; the second one indicates the desiccator where they were placed after charging. We have denoted the first group as 5C and the second one as CC where C = 1, 2, 3, 4, 5.

Figures 1 and 2 represent the time dependence of the surface potential of the two groups—5C and CC respectively. All points are mean values obtained from six samples. The initial values of the electret surface potential for all six samples in each series from the two groups differ insignificantly and the difference ranges from 0.4% to 1% for the different series.
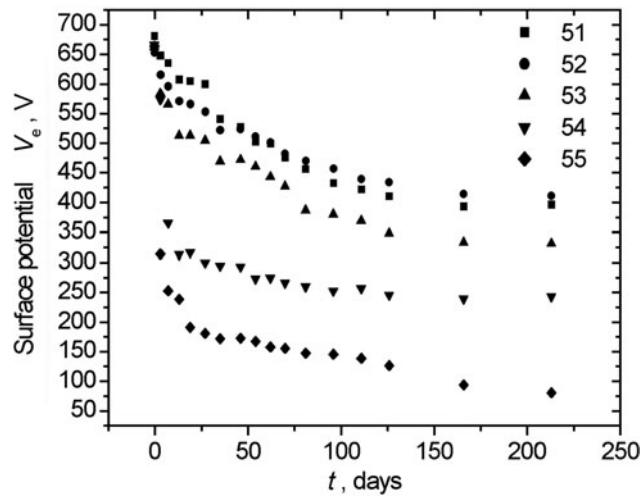
Figure 1. Time dependence of the surface potential for the 5C samples.
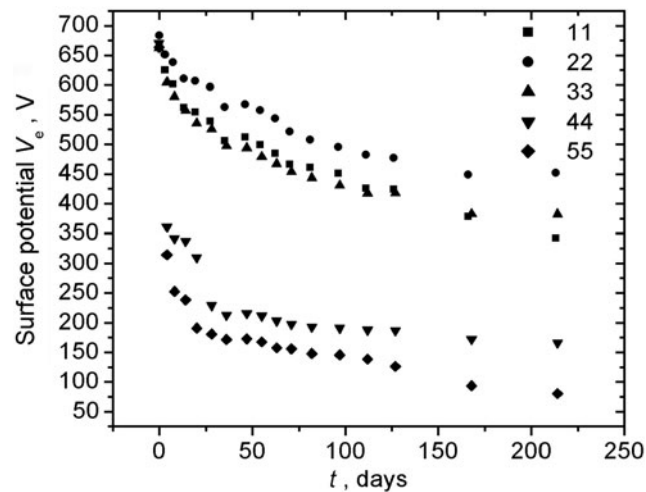

Figure 2. Time dependence of the surface potential for the CC samples.

Since the time of storage depends on the relative humidity, this difference changes. Figure 3 represents an example of the confidence intervals for the average values of the -90% confidence level by the error bar for the samples stored at different RH values: 33%, 55% and 100%.

The results presented in figures 1 and 2 show:

(i) no matter whether the samples before charging are kept at a relative humidity of about 100% (figure 1) or at various relative humidities (figure 2) their behaviour is determined mainly from the storage conditions after charging;

(ii) in both groups (5C and CC) considerable charge decay is observed if the electrets are kept after charging at relative humidities higher than 55%;

(iii) the difference in charge decay of electrets from different series should not be explained as a result of injection of the surface charge into the bulk and its subsequent transport through the sample.
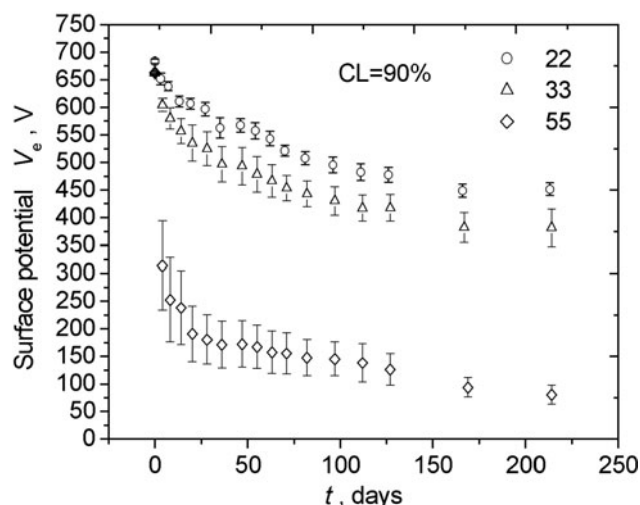
Figure 3. Time dependence of the surface potential for the samples 22, 33, 55. The error bars mark the confidence intervals for the mean values (90% confidence level).

Immediately after polarization, moisture is adsorbed quickly. As the surface adsorption centres are unevenly distributed, the local electric conductivity is characterized by a great dispersion, i.e. the electrical properties of the surface are inhomogeneous. Because of the heterogeneous structure of the sample surfaces and the spatially fixed random properties of the various humidity media, it is not appropriate to use the surface resistivity in order to describe the electret surface charge relaxation.

That is why we assume that the percolation model is an appropriate one to describe the surface potential decay. Normally percolation models are used to explain the insulator–conductor transition in composite materials where conducting particles are dispersed within the isolator medium. In such cases, the concentrations of the dispersed particles remain steady in time.

If an electret is stored at a certain humidity, water-molecule clusters are formed on its surface, due to moisture adsorption, and they generate a percolation lattice. The concentration of the adsorbed molecules varies as a function of time, i.e. the structure and density of the percolation lattice also changes with time. A model that accounts for these changes is the model of Kuzmin and Tairov.

3. Percolation model by Kuzmin and Tairov

The percolation model proposed by Kuzmin and Tairov [11–13] describes charge transport resulting from electret surface discharge caused by environmental humidity. This model is based on the simultaneous utilization of the percolation theory and the Kolmogorov's concept for a two-dimensional (2D) kinetics of nucleus formation.

Whenever an electret is placed into an environment with certain humidity, water molecules from this environment adsorb onto the surface of each of the samples. Conductivity channels are formed on the surface and they combine into clusters that are separated from each other. The aggregation of these clusters represents a 2D percolation lattice.

As the concentration of the adsorbed water molecules gets higher, the individual clusters may interconnect and hence create an unbound cluster. The unbound cluster is formed when

the fraction of the surface covered by adsorbed molecules θ reaches the percolation threshold or the critical percolation density θ_c, i.e. when $\theta = \theta_c$. According to [15] in the case of a 2D percolation lattice $\theta_c = 0.44 \pm 0.02$. Since water conductivity is much greater than that for the material of the electret itself, the unbound cluster shunts the surface of the electret and causes fast neutralization of the electret charge; surface potential decay is then observed. Consequently, the fraction from the electret surface that is interconnected with the unbound cluster does not contribute to the value of the surface potential. So the time dependence of the surface potential may be described by the following equation:

$$V_e(t) = V_{eo}[1 - P(\theta(t))], \tag{1}$$

where V_{eo} is the surface potential of the electret, measured straight after the electret was obtained, and $P(\theta)$ is the density of the percolation cluster. $P(\theta)$ defines the probability for a randomly chosen point from the surface to belong to the specified cluster, and it represents a dimensionless quantity. The density of the percolation cluster is a function of the surface fraction $\theta(t)$ covered by the adsorbed molecules at a moment t.

In order to define $\theta(t)$, Kuzmin and Tairov assume the following [11, 13]:

(i) the mean area of the incipient adsorption centres, called nuclei, is infinitely small in comparison with the total surface of the electret;

(ii) all the adsorption centres are generated randomly on the surface of the electret at a finite rate $\alpha(t)$ per unit area;

(iii) all the adsorption centres have the same convex shape;

(iv) as soon as they are generated and adsorb water molecules all the nuclei have the same rate of growth $v(t)$.

At the moment of charging $t = \tau_0$, the following dependence is describe for $\theta(t)$:

$$\theta(t) = 1 - q(\tau_0, t) \exp\left[-\int_{\tau_0}^t \alpha(\xi) S(R(\xi, t)) \, d\xi\right] \tag{2}$$

where $q(\tau_0, t)$ is the fraction of the surface that has remained free from the adsorbed phase at the moment of charging τ, $R(\xi, t)$ is the radius of those nuclei which have originated after the sample was charged, and $S(R)$ is the surface of nuclei having radius R.

Provided that before charging the samples have been stored in a controlled stationary environment, a thermodynamic equilibrium is established. Then, if we assume that the samples are charged at a moment $\tau_0 = 0$, the function $q(\tau_0, t)$ can be replaced by $q(0)$. Taking this into account and writing $S(R) = \pi(\int_{t'}^t v(\xi) \, d\xi)^2$, the formula (2) may be represented as:

$$\theta(t) = 1 - q(0) \exp\left[-\int_0^t \alpha(t')\pi \left(\int_{t'}^t v(\xi) \, d\xi\right)^2 dt'\right] \tag{3}$$

where $\alpha(t)$ is the rate of nuclei formation at the moment t' and $v(\xi)$ is the rate of nuclei growth as a result of water molecule adsorption. The authors propose the following law for $\alpha(t)$:

$$\alpha(t) = \beta\delta(t) + \alpha_0 \tag{4}$$

where β is the concentration of the nuclei generated at the time of charging, $\delta(t)$ is the Dirac pulse function and α_0 is the steady rate of nuclei generation per unit area after the electrets have been obtained. The rate of nucleus growth $v(t)$ is supposed to decrease following an exponential law:

$$v(t) = v_{01} \exp(-t/\tau) + v_{02} \tag{5}$$

where v_{01} and v_{02} are constants.

Table 2. Parameters obtained after computer calculation. CL = 90%.

Samples	α_0 (10^9 m^{-2} s^{-1})	V_{es}/V_{eo}
51	0.36 ± 0.05	0.58 ± 0.02
52	0.45 ± 0.06	0.63 ± 0.03
53	0.07 ± 0.006	0.50 ± 0.02
54	0.08 ± 0.005	0.36 ± 0.002
55	0.10 ± 0.01	0.12 ± 0.003
44	0.12 ± 0.02	0.25 ± 0.004
33	0.10 ± 0.01	0.58 ± 0.02
22	0.40 ± 0.04	0.66 ± 0.02
11	0.10 ± 0.003	0.51 ± 0.02

By averaging the data for the various 2D percolation lattices, and using the regression analysis method, the authors found, with a 95% confidence level, the following relations for density of the percolation cluster [13]:

$$0 \leqslant \theta < \theta_c \qquad P(\theta) = 0$$
$$\theta_c < \theta \leqslant 0.533 \qquad P(\theta) = \sum_{i=0}^{4} a_i(\theta - \theta_c)^i \qquad (6)$$
$$0.533 < \theta \leqslant 1 \qquad P(\theta) = \theta$$

where $\theta_c = 0.428$, and this value is close to the one reported in [15] for the 2D percolation lattice.

It is shown in [12] that at the moment when an unbounded cluster appears there are three different types of transitions:

(a) the unbounded cluster is formed some time after charging the electret;
(b) the unbounded cluster originates at the moment the charging is accomplished; and
(c) the unbounded cluster already existed at the time of charging.

4. Application of the percolation model to experiments

Using this percolation model, we devised computer software for nonlinear programming, using the Flexyplex software package. The software processes the experimental data by minimizing the chosen function, in this case equations (1) and (3), by the least squares criterion χ^2, selecting the most appropriate parameters for which the probable value ranges have been defined:

$$q(0) = (0-1);$$
$$\alpha_0 = (0-1) \times 10^9 \text{ m}^{-2} \text{ s}^{-1};$$
$$v_{01} = (0-1) \times 10^{-13} \text{ m s}^{-1};$$
$$v_{02} = (0-1) \times 10^{-15} \text{ m s}^{-1};$$
$$V_{es}/V_{eo} = (0-1).$$

Here, V_{es} is the standing surface potential. The values obtained for these parameters are presented in table 2 and figures 4 and 5.

The dependences of the pre-exponential constant and the free term, describing the rate of nuclei growth (equation (5)), on humidity for groups 5C and CC are presented in figures 4, 5 respectively. It is seen that the rate of nuclei growth increases rapidly after the break point (RH = 55%).
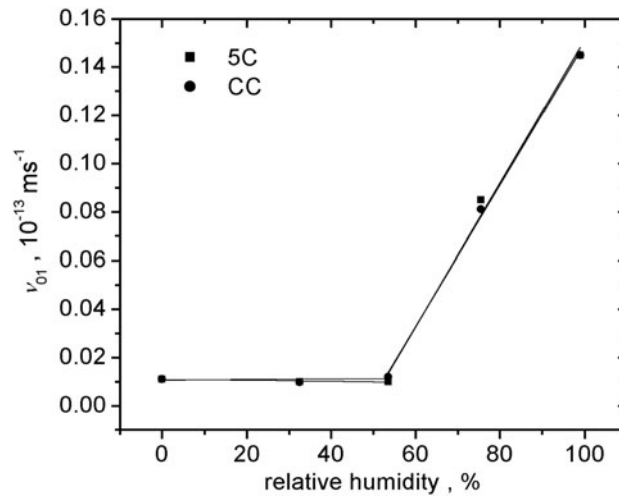
Figure 4. Dependence of the pre-exponential constant (equation (5)), describing the rate of adsorbed nuclei formation, on humidity for groups 5C and CC.
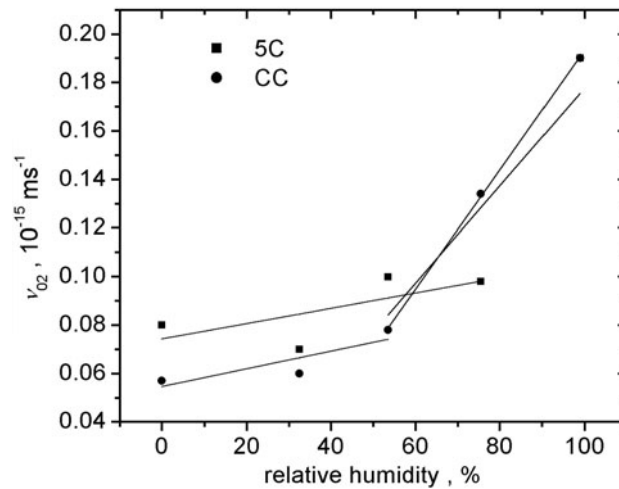

Figure 5. Dependence of the free term, describing the rate of adsorbed nuclei formation (equation (5)), on humidity for groups 5C and CC.

The surface potential time dependence curves for all the samples obtained from experimental studies, and the theoretical calculations, look like the results displayed in figures 6–8. The results obtained show a good conformity of theory and experiment.

5. Discussion

The good agreement between the experimental and theoretical curves (figures 6–8) shows that the percolation model describes well the electret behaviour under various humidity conditions. Additionally, for all the studied samples, the surface potential decays evenly with no plateau (figures 1, 2), i.e. the unbounded cluster originates at the moment when charging ends. The
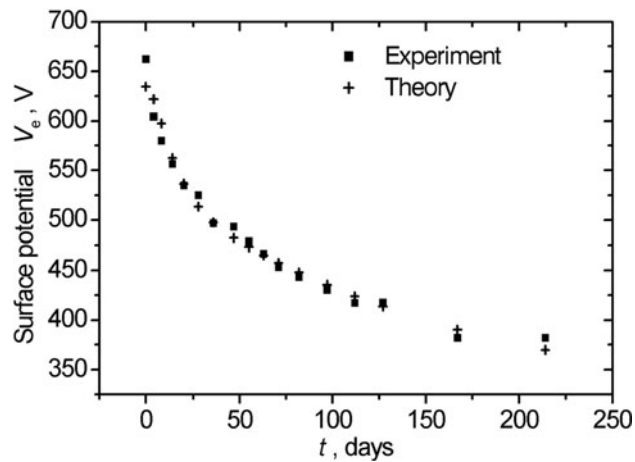
Figure 6. Time dependence of the surface potential for the 33 samples.
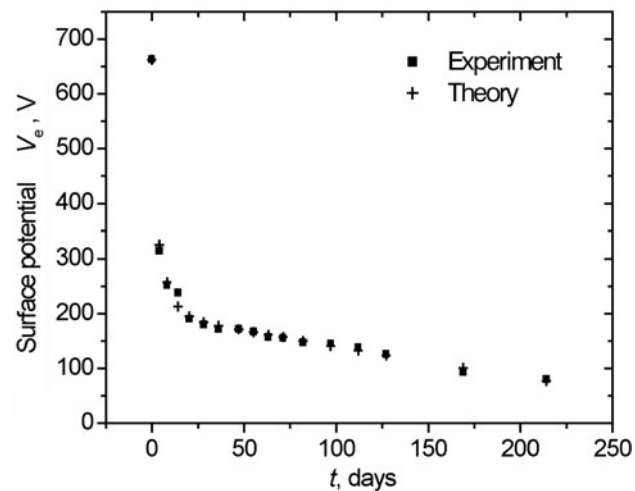

Figure 7. Time dependence of the surface potential for the 55 samples.

values of q are the same for all the samples ($q = 0.57$), which is in good agreement with the theoretical estimate ($q \approx 0.5715$) given for this case in [12]. According to the estimate given in [13], a percolation transition may occur if the relative humidity is higher than 60%. The results we obtained did not confirm this, and showed that such a transition may also take place at lower relative humidities.

We assume that moisture adsorption is stimulated by electrization, and further cluster growth depends on the storage medium after the charging of electrets. After the unbounded cluster is formed, when $\theta = \theta_c$, further growth of $P(\theta)$ is due to the fact that already existing isolated clusters or newly formed clusters join it. The clusters that remain unconnected to the unbounded cluster are ineffective with reference to electrical conductivity and do not contribute to the surface potential decay. Some authors believe that part of the unbounded cluster is ineffective with regard to electrical conductivity, especially in the 2D case [16–22], but we found this to be the case if we applied a voltage to the ends of an uncharged sample
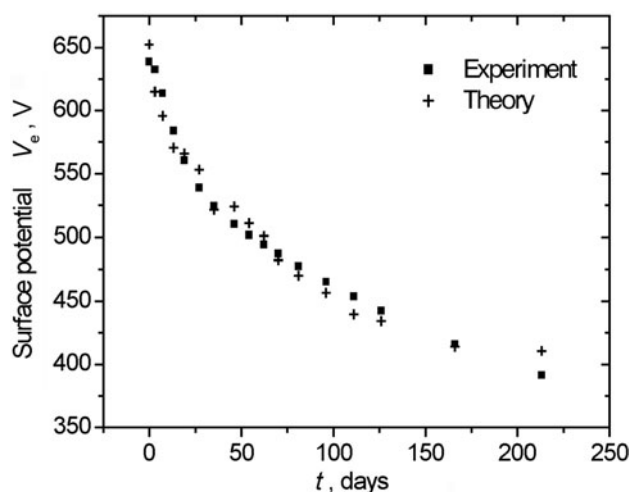
Figure 8. Time dependence of the surface potential for the 52 samples.

covered by an unbounded cluster. However, if the unbounded cluster is formed on the surface of an electret, the so-called thickenings, duplication chains or dead ends will contribute to the surface discharge of the electret.

The dependences of the constants that characterize the rate at which the adsorbed nuclei grow as a function of relative humidity are displayed in figures 4 and 5. For humidity values as high as 55%, v_{01} hardly changes and v_{02} grows almost insignificantly. When the humidity goes over 55% v_{01} and v_{02} increase rapidly, while α does not change (table 2). Therefore, the rate of nuclei growth is decisive for the unbounded cluster kinetics at these humidity values.

When the value of relative humidity is lower than 55% (the break points in figures 4 and 5), the unbounded cluster density $P(\theta)$ growth for all the samples from a given series is slow and does not represent significant differences. Hence, for all six samples the value variation for V_e is not big (figure 3, curve 22). If environmental humidity is about 55% the growth of $P(\theta)$ is unequal for all the samples from a given series and then the value variation of V_e increases with time (figure 3, curve 33). When the relative humidity gets to about 100%, $P(\theta)$ increases almost immediately after the samples are subjected to that humidity and its values for the various samples from a given series differ strongly from each other. As time gets on, the unbounded cluster density values for the different samples become approximately equal. This is why, for this series, the greatest value variation of V_e is observed during the first few days, then these variations become smaller with the progress of time (figure 3, curve 55).

The standing relative surface potential V_{es}/V_{eo} goes down as relative humidity increases from 33% to 100%. When RH = 0%, the value of V_{es}/V_{eo} is lower than that for RH = 33% which probably is due to a lower value of α. To clarify this question we need to conduct a further investigation.

6. Conclusions

The percolation model allowed us to analyse electret surface discharge and to reveal the significant influence of the humidity level at which they have been stored. This is extremely important, and should be taken into account in the study of the stability of electret sensors and devices that are used at room temperature and function under real conditions at various humidity levels.

Acknowledgment

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