# ELECTRICAL PROPERTIES OF CORK AND DERIVATIVES

M.C. LANÇA(1)*, E.R. NEAGU(1,2), C.J. DIAS(1), L. GIL(3), J.N. MARAT-MENDES(1)

(1) Cenimat/I3N, Departamento de Ciência dos Materiais, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal
(2) Department of Physics, Technical University of Iasi, Iasi 700050, Romania
(3) Laboratório Nacional de Energia e Geologia (LNEG), Est. do Paço do Lumiar, 22, 1649-038 Lisboa, Portugal
*carmo@dcm.fct.unl.pt

**ABSTRACT:** The electrical properties of natural cork, commercial cork agglomerates (for floor and wall covering) and a composite of cork/TetraPak® were studied. The composite was developed at LNEG/Portugal and is made of recycled cork and TetraPak® containers.
Measurements of isothermal charge and discharge currents (ICC/IDC) and dielectric relaxation spectroscopy (DRS) were made. The isothermal currents characteristics and the samples electrical conductivity were investigated under different conditions (electric field, temperature and measuring atmosphere). Dielectric relaxation spectroscopy was used to quantify the changes in the permittivity with the samples conditioning. Both experimental techniques showed the strong influence of water content on the electrical properties of cork and its derivatives.

**Keywords:** Cork, electrical properties, recycling.

**RESUMO:** Neste trabalho foram estudadas as propriedades eléctricas de cortiça, natural, de um aglomerado comercial de cortiça (usado para revestimento de paredes e chão) e de um compósito de cortiça/TetraPak®. O compósito foi desenvolvido no LNEG/Portugal e pode é feito a partir de cortiça e de contentores TetraPak® reciclados.
Estes materiais foram caracterizados através de medidas de correntes isotérmicas de carga e descarga (ICC/IDC) e de espectroscopia de relaxação dieléctrica. As características das correntes isotérmicas e a condutividade eléctrica das amostras foram investigadas em diferentes condições (campo eléctrico, temperatura, atmosfera de medida e pré-condicionamento). A espectroscopia de relaxação dieléctrica (DRS) foi também usada para investigar as alterações da permitividade com o pré-condcionamento e humidade das condições de armazenamento da amostra. Ambas as técnicas mostraram a forte influência nas propriedades eléctricas da cortiça e seus derivados da quantidade de água presente nas amostras.

**Palavras chave:** Cortiça, propriedades eléctricas, reciclagem.

## 1. INTRODUCTION

Cork is the outer bark of Quercus suber L (a type of oak that grows in the Mediterranean area) and it is a widely used natural ecomaterial because it is a good thermal and acoustic insulator, has a high friction coefficient and it is impermeable to liquids, chemically stable and fire resistant. This unique set of mechanical, acoustical and thermal properties makes cork and its derivative products ideal for many different applications [1-3]. The structure of cork (in the microscale is a cellular material made of closed cells filled with gas [2,3].) renders the material a dielectric and suggests new possible applications. However, the electrical and in particular the dielectric properties of cork are not well known, and only recently work on this subject was published [4-8].

A composite of cork/TetraPak® was developed at LNEG/Portugal and is made of recycled cork and TetraPak® containers.. The composite is produced by grinding and hot pressing the two components. In order to reduce the amount of water in the final product a wax was added to the material and also the powders are dried previous and after pressing [8]. In some applications this cork derivative can be used as cheaper and environmental-friendly replacement of cork and related materials. New applications are still under study. If value could be added by finding a new application related with the dielectric character, could help to commercialize the material

Studies of electrical and dielectric properties have been previously published for natural cork, commercial cork agglomerate and for the cork/TetraPak® composite [6,7]. But only recently the cork/TetraPak®/Paraffin composite was produced and started to be studied [8]. These studies indicate a strong influence of water content on the value of the conductivity of cork in several orders of magnitude [6]. Similar results were observed for the derivatives [7,8].

In this work the results for natural cork, commercial cork agglomerates and a composite of Cork/TetraPak® or cork/TetraPak®/paraffin were studied and compared. In order to understand the influence of water content samples could be or not dried prior to preparation and/or measurement.

DRS measurements were performed using a broadband impedance analyzer ($10^{-1}$ Hz to 2 MHz) and the temperature range used in the measurements was –100°C to 120°C. After pressing same of the samples were stored either in a dry atmosphere at room temperature or in air at 70°C until measurements were made. ICC/IDC were performed at different temperatures (25°C to 100°C), electric field ($10^3$ – $10^6$ V/m ) and measuring atmospheres (air at ambient relative humidity (RH), primary vacuum, dry air, nitrogen). Samples could be conditioned (dried) prior to measurements (in a $P_2O_5$-loaded desiccator, vacuum, dry air and nitrogen atmosphere or in an oven in air at 50 to 70°C).

The influence of water content was investigated in order to improve the ability of the materials to store space charge and consequently to optimize preparation and storage for possible applications where the combination of the thermal, acoustical and mechanical properties of cork with electrical and dielectric characteristics that might be useful.

## 2. EXPERIMENTAL PROCEDURE

### 2.1 Sample preparation and conditioning

Natural cork was cut into slices on the three different directions: radial (parallel to the tree trunk and perpendicular to the radius of the trunk), axial (perpendicular to the direction of the trunk) and tangential (parallel to the trunk and parallel to the radius) according to the tree trunk. Sample's thickness varied from 1.5 mm to 2.5 mm. Thin samples of natural cork of 75 $\mu$m thickness were supplied by industry and used in the DRS measurement as received or dried.

The cork agglomerate was a commercial agglomerate that is used for wall and floor coverings with 4 mm thickness. It is obtained from cork waste byproducts of the cork stoppers production and from lower quality cork that was not suitable for stoppers. Usually an adhesive is added to improve adhesion of the grains.

The composite was developed at LNEG/Portugal and can be made of recycled cork and TetraPak® containers. The cork/TetraPak® (50/50 % weight) composite is obtained from cork grains and grinded waste of TetraPak® containers. A commercial cork granulate with no additives was used to produce the samples used in this work. It is also possible to use recycled cork, for instance, from used cork stoppers. The cork was further milled to get a powder with a lower grain size. All the TetraPak® is from used containers that are washed and milled to obtain also a powder. The two powders are mixed and hot pressed. In a further attempt to reduce the water content of the grains, it was added to the grains mixture a small amount of commercial paraffin (also grinded). The formulation for the cork/TetraPak®/paraffin composite was 48/48/4 % weight. For the samples of the composite with paraffin the grain mixtures were dried in an oven at 50°C during 1 week prior to pressing. For the two types of composites discs of around 1.5 mm thickness were produce to be used in the DRS and ICC/IDC measurements.

### 2.2. Determination of water content

Samples were dried for 72 h either in primary vacuum or in a $P_2O_5$-loaded-desiccator in order to get a reference weight for dried samples.. After drying, the sample is kept in air at ambient relative humidity (RH) and the weight recovery caused by water re-absorption was monitored as a function of time.

**Table 1.** Water content for natural cork, commercial cork agglomerate and cork/TetraPak® (%weight).

| Cork material | Humidity (%wt) |
|---|---|
| **Natural cork (tangential)** | **3.8** |
| **Commercial cork agglomerate** | **4.0** |
| **Cork/TetraPak®** | **4.6** |

### 2.3. Electrical and dielectric properties measurements

DRS measurements were performed using a NovoControl-GmbH Alpha-N broadband impedance analyzer (frequency range was $10^{-1}$ Hz to 2 MHz) and the temperature was controlled by a NovoControl-GmbH Quatro Criosystem BDS-1100 (temperature range used in measurements was –100°C to +120°C) to an accuracy of 0.1°C.

Isothermal charging and discharging currents (ICC and IDC) method was used to analyze the electrical behavior under a DC electric field (2 to 10 kV/m) at constant temperature (25 and 55°C) in air at ambient relative humidity (RH). These values for the temperature were chosen because 25°C is room temperature (RT) and 55°C is below but nearly the melting temperature of the waxes present in cork (near 60°C ). Each run is composed of a charging (ICC) and a discharging (IDC) step. During ICC, the DC electric field is applied for 1 h. Both the charge and the discharge currents are recorded. Also the charging current was registered to calculate the electrical conductivity of cork and derivatives under different conditions. Current measurements were made using an electrometer (Keithley 617) and a data-acquisition system (the setup measurement was described elsewhere [9]).

## 3. EXPERIMENTAL RESULTS AND DISCUSSION

### 3.1. Water content

The water content (%wt) is defined as the number of grams of water divided by the dry weight. The dry weight (reference) was assumed to be the weight immediately after removal from 72 h in primary vacuum. On Table 1 is given the water content of three different types of cork material at ambient RH and at room temperature (25°C). Before the weighing the samples did not undergo any kind of drying or thermal treatment. After the measurement the samples were placed in primary vacuum for 72h in order to obtain the reference weight. The highest value of water content was observed for the commercial agglomerate, which can be attributed to the polar additives used to improve adhesion, the additives would increase the polar character of the agglomerate and, thus increase water intake. The composite material was produced with no thermal treatment before pressing.

Hence these results compared the three types of cork materials before any attempt to control the water content on the composite.

Results for natural cork obtained by using as reference for weight after drying over $P_2O_5$ atmosphere at room temperature (RT) until an almost constant weight was achieved, showed that the water contents is higher than 3.5 % at ambient relative humidity [6]. In the same work, it was also observed that more than 25 days were necessary for the sample to achieve a constant weight. Compared with the result for natural cork on Table 1, it is possible to conclude that vacuum treatment is more efficient and faster on removing water from cork. According to these results it can be determined that the water removal mechanisms are very slow (which is also confirmed by ICC/IDC results discussed later).

### 3.2. Isothermal currents measurements

In Figure 1 for natural cork, the processes of water desorption and recovery are observed. The sample was dried at RT by placing the cork in primary vacuum for 8 days (curve 1). After this it was kept in a nitrogen atmosphere at normal pressure for 34 days (curve 2). During this time (8 + 34 days) a voltage of 11 V was applied to the 3 mm thick samples and the corresponding charging current density was registered. From curve 1 a relatively fast process of water desorption is seen with a rapid decrease of the current density by several orders of magnitude. And it can be seen that at ambient RH the water present in the cork dominates the conduction mechanisms. The recovery of the current density observed in curve 2 indicates that the water removed while in primary vacuum, was in a thin layer close to the surface. When the sample was kept in the dry $N_2$ atmosphere a very slow process of water diffusion from inner layers to the surface°Ccurs. The current density takes around 30 days to achieve the initial value. The recovery of the electrical conductivity provided a rough estimation of the diffusion coefficient (*D*) considering that Fick´s law is valid [10]. The value obtained for *D* was of the order of $10^{-12} - 10^{-13}$ $m^2s^{-1}$, which is circa one order of magnitude lower than the one reported by Rosa et al. [11]. The difference between the two estimations can be explained by assuming that the diffusion coefficient decreases as the amount of water involved in the process decreases. The results from Figure 1 concern very low amount of water (not detectable by weighing) while the results reported in [11] are obtained for thick samples of cork soaked in water.

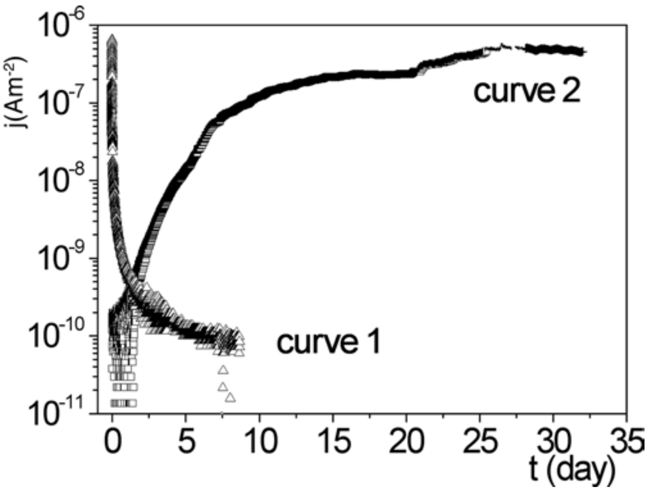


**Fig. 1.** The variation of DC current density through the sample to follow water desorption (in primary vacuum – curve 1), or water diffusion and conductivity recovering (in $N_2$ at normal pressure – curve 2).

The differences observed between natural cork and derivatives could be investigated by comparing the ICC results, like the ones presented in Figure 2. The commercial agglomerate has the highest value for the current density and the lowest is obtained for natural cork with values around two orders of magnitude lower. Intermediate results are observed for the composite. The commercial product has an adhesive incorporated and typically it is a polar material, consequently results in higher current density values. As for the composite, TetraPak® is composed of paper (main component), Aluminum and polyethylene. Even if polyethylene is a very good electrical insulator, Aluminum is a good conductor and paper is hydrophilic. So the last two components would contribute to increase the current in the composite. The discharge current (not presented here) was monitored for 2h and natural cork and the composite show initially values of the same order of magnitude. However for cork there is a much faster decrease in the current density so that at the end of 2h there is almost two orders of magnitude difference between the current densities. The agglomerate current density has a slope similar to the one presented by the composite but the value is one order of magnitude higher.

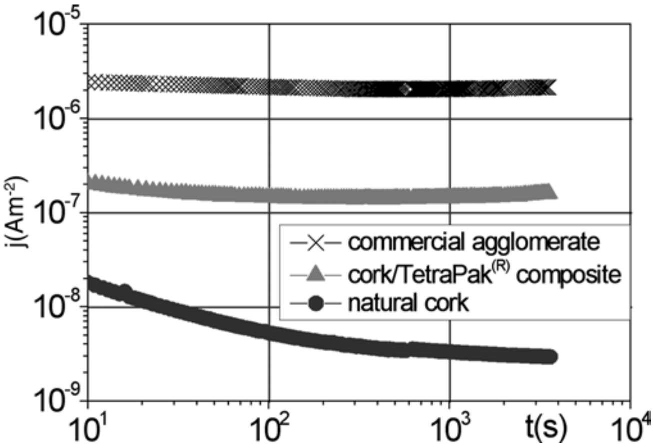


**Fig. 2.** The charging current density for natural cork, cork/TetraPak® composite and commercial cork agglomerate (E = 2 kV/m at 25ºC in air at ambient RH).

The modified cork/TetraPak® composite with added paraffin suffers a pre-conditioning (before samples were pressed the powder was dried at least for a week in air in an oven at 50 to 70ºC) and after pressing were also stored either in air at 70ºC (sample 1) or kept in a $P_2O_5$ atmosphere at RT (sample 2). The comparative results can be seen in Figure 3 for a field of 2 kV/m and 25°C in air.

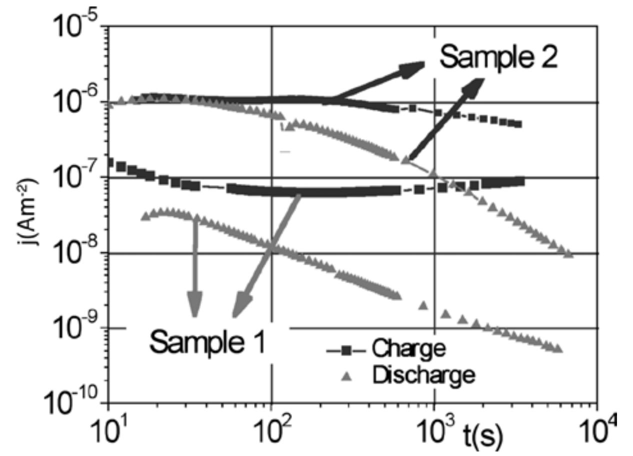


**Fig. 3.** ICC and IDC (2 kV/mm, 25°C, air) for cork/TetraPak®/paraffin composite for sample 1 stored in air at 70ºC and sample 2 stored in a $P_2O_5$-loaded desiccator.

As can be seen the current density for the sample stored in $P_2O_5$ is nearly two orders of magnitude higher than the one for the sample stored in the oven at higher temperature. This trend is the same for all the ICC/IDC measurements made. There is less water in the sample that suffered the thermal treatment by being stored at 70°C than in the ones that were stored in dry atmosphere. Examining the current around 10 s, IDC and ICC are coincident in sample 2 but not in sample 1 and the slope is higher for IDC in sample 2. This indicates higher water content in sample 2 and consequently the presence of more water dipoles giving rise to a faster decrease.

### 3.3. Electrical conductivity

Electrical conductivity was measured for natural cork with samples cut along the different plans referred in 2.1. Results were compared for dried and non-dried samples. The derivative materials were also studied but all measurements were performed in air and no drying procedure was made to the samples. The results are shown in Table 2. The values were calculated by measuring the charge current at the end of 1h after applying the voltage ($\sigma = j/E$, $\sigma$ is the electrical conductivity, $j$ is the current density and $E$ is the applied electric field). Previous work reports values for natural cork in air at ambient RH and RT for non-dried material of $1.2 \times 10^{-10}$ Sm$^{-1}$ and for a dried samples (four months in vacuum) an intrinsic value for the cork conductivity of $2.9 \times 10^{-15}$ Sm$^{-1}$ [12]. The last value is similar to the one present in the table for natural cork dried 14 day in vacuum. However the result in air is higher by 2 orders of magnitude. Ambient RH can change significantly over time, so it is reasonable to assume that the value of ambient RH for natural cork was higher for the measurements presented in [12] than the ones in Table 2. The influence of small changes of the humidity gives rise to significant changes in the electrical conductivity in natural cork. Moreover similar behavior was observed for the derivatives.

**Table 2.** Electrical conductivity after 1h charging at 2 kV/mm and 25°C for natural cork (different cuts) and cork derivatives.

| Cork material | Measurement atmosphere | $\sigma$(Sm$^{-1}$) | Cork material | Measurement atmosphere | $\sigma$(Sm$^{-1}$) |
|---|---|---|---|---|---|
| **Natural cork (axial)** | **Air<br>(6 days)** | **$2.7 \times 10^{-12}$** | **Natural cork (radial)** | **Air<br>(5 days)** | **$6.7 \times 10^{-12}$** |
| **Natural cork (axial)** | **Vacuum<br>(14 days)** | **$1.7 \times 10^{-15}$** | **Commercial cork agglomerate** | **Air<br>(5 days)** | **$1.7 \times 10^{-9}$** |
| **Natural cork (tangential)** | **Air<br>(6 days)** | **$5.4 \times 10^{-12}$** | **Cork/TetraPak®** | **Air<br>(5 days)** | **$4.2 \times 10^{-10}$** |
| **Natural cork (tangential)** | **Dry air<br>(6 days)** | **$1.8 \times 10^{-14}$** | | | |

The current-voltage characteristic was obtained for different temperatures (25 to 100°C) for natural cork (radial cut) for electric fields of $10^4$ to $10^6$ V/m in vacuum. Also at 25°C in air at ambient RH, the characteristic was obtained for the composite and the agglomerate and compared with natural cork (tangential cut). From fitting to the equation

$$j \propto E^n \tag{1}$$

were obtained the results in Table 3.

**Table 3.** Current-voltage characteristic results from fittings using equation (1) for natural cork at different temperatures and at RT for the natural cork (tangential cut), the composite and the agglomerate.

| T(ºC) | *n* | $\sigma \times 10^{-14}$ (Sm$^{-1}$) | Cork material | *n* | $\sigma$(Sm$^{-1}$) |
|---|---|---|---|---|---|
| **25** | **1.2** | **0.2** | **Natural cork (tangential)** | **1.2** | **$4.4 \times 10^{-12}$** |
| **50** | **1.1** | **1.0** | **Commercial cork agglomerate** | **1.3** | **$4.2 \times 10^{-10}$** |
| **75** | **1.0** | **6.4** | **Cork/TetraPak®** | **1.0** | **$1.7 \times 10^{-9}$** |
| **100** | **1.0** | **76.8** | | | |

The current-voltage characteristic reveals that samples not dried show an ohmic behavior and the mechanism of conduction changes for dried samples.

The charge transport is strongly influenced by the charge stored in the sample that is correlated with the structural disorder and the inhomogeneity of the conducting paths. Even in dried cork the low-field conductivity is ohmic but as the field increases the conduction mechanism changes. The long time measurements demonstrate that the space-charge-controlled conductivity mechanism dominates the charge transfer [13]. A careful examination of the data in Figure 1 for longer times in curve 2 shows that the current does not vary smoothly because of the competition between the charge injection process and the constraint imposed by the trapped charge on the injection process.

### 3.4. Dielectric relaxation spectroscopy

Figure 4 shows the imaginary part ε" of the dielectric permittivity at different temperatures 50, 80 and 85°C to follow the effect of drying. For a sample measured in air at ambient RH, above 60 – 70°C, ε" decreases. This range of temperature agrees with the temperature found for melting of the waxes present in cork [4, 5]. Water will be able to diffuse faster in cork above the wax melting temperature and, has a result of water desorption, the imaginary component of permittivity is reduced. At 85°C the sample was kept for 12 hours in dry nitrogen and the measurement was continued. It can be observed that there is a significant decrease of ε" and this drop is faster at lower frequencies, in good agreement with the observation that the behavior at low frequencies is dominated by water (see the Figures 5 and 6). At high frequencies a small peak can be observed which might be related to the intrinsic properties of cork and hidden by the presence of water before the drying process.

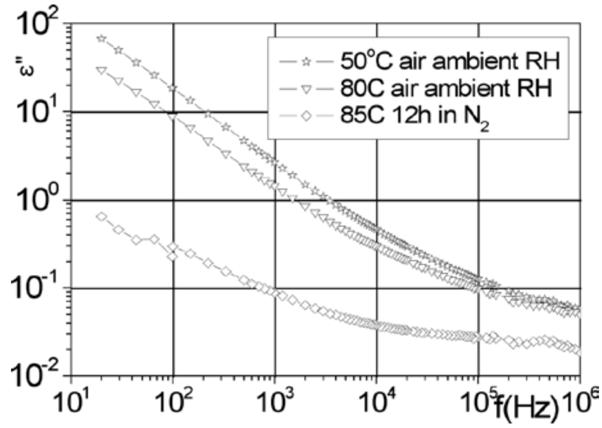
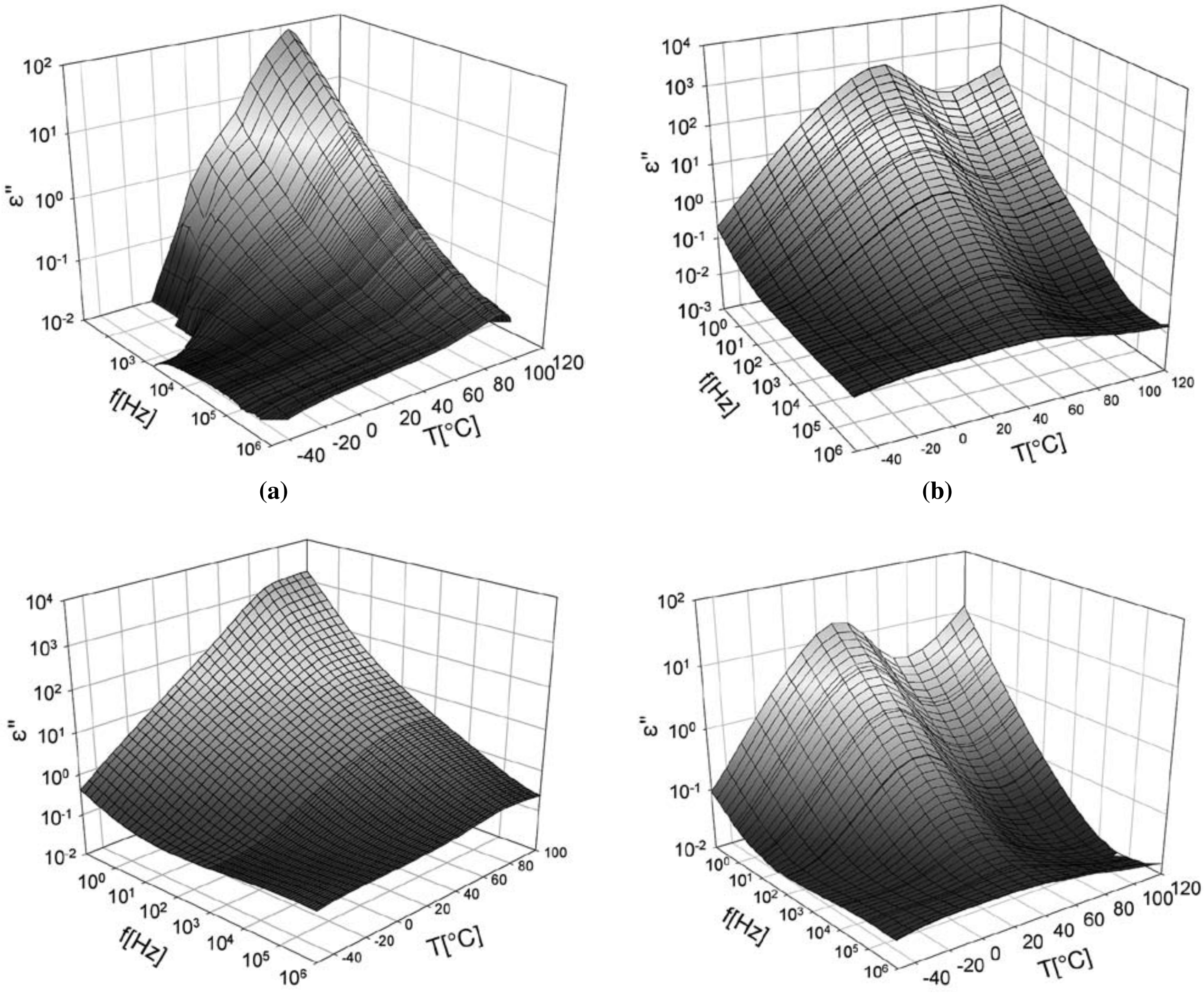


**Fig. 4.** The imaginary part ε" of the dielectric permittivity before (normal) and after drying in a Nitrogen atmosphere for 12h (12 h in $N_2$).



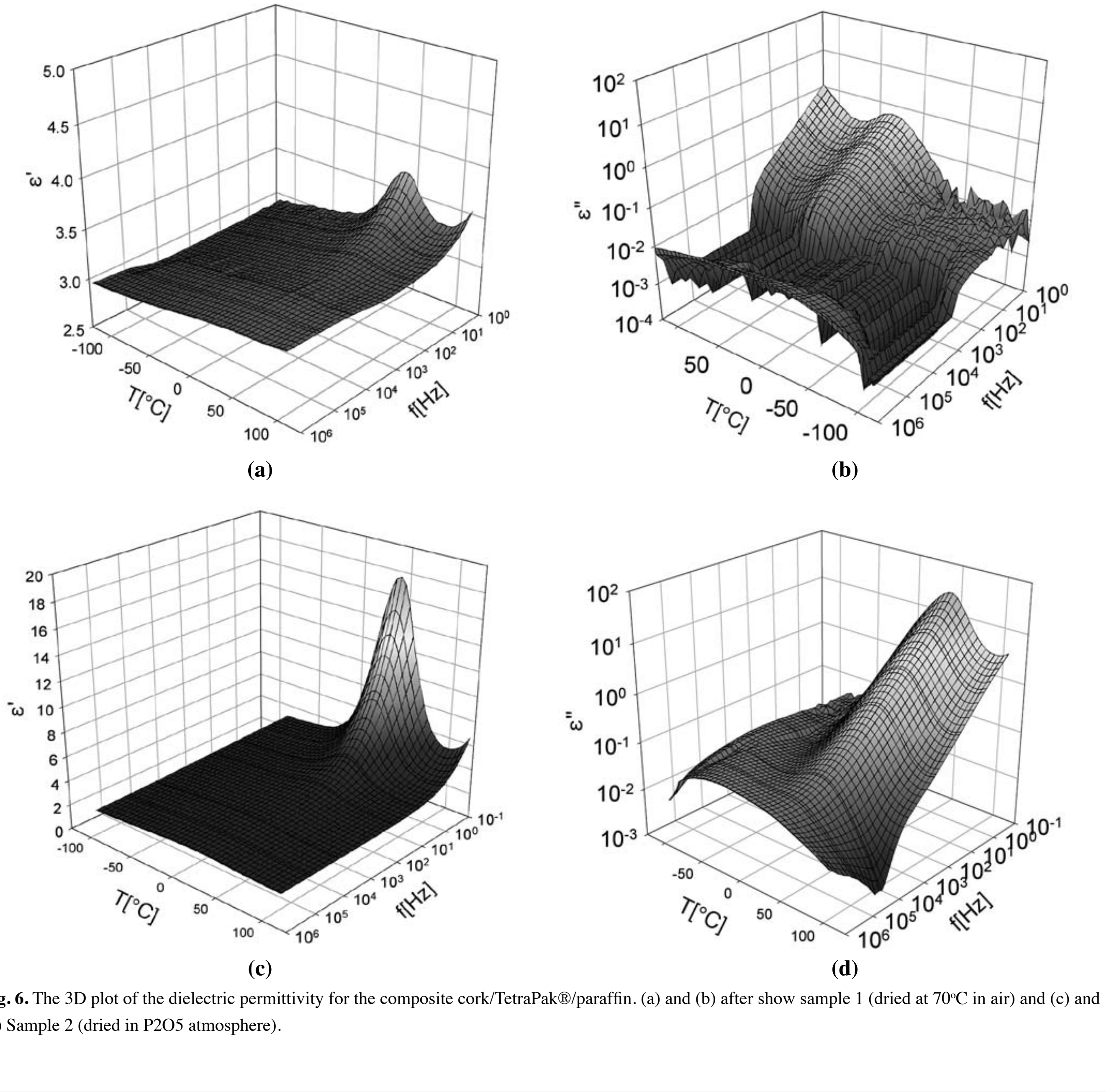
**(a)** **(b)**

**(c)** **(d)**

**Fig. 5.** The 3D plot of imaginary part of the dielectric permittivity for natural cork (a); composite cork/TetraPak® (b); commercial cork agglomerate (c) and composite cork/TetraPak®/paraffin (d).

The imaginary part of permittivity compared for the different cork materials was studied in ambient air for samples not dried. In Figure 5 are plotted the permittivities (imaginary part) for the four different cork materials. No thermal or drying treatment was made on the samples after pressing and prior to the DRS measurements. In natural cork a relaxation peak is observed with temperature around 80°C and with ε'' maxima decreasing with increasing frequency. The peak temperature does not shift with frequency. The other cork materials show a peak with maxima at a temperature around 40 to 60°C (not shifting with frequency,) but also with maxima increasing as frequency decreases. For these derivative materials a peak with similar behavior is also observed for the real component of permittivity. Furthermore these peaks in real and imaginary component of permittivity decrease and disappear with successive measurements (each corresponding to a thermal cycle up to +120ºC, consequently with sample drying). This kind of behavior is attributed to relatively free water [14, 15] that is removed from sample by drying. In natural cork the maxima values for ε'' are of the same order of magnitude but lower that for the composite with paraffin. The commercial agglomerate and the cork composite with paraffin show a value one order of magnitude higher in agreement with ICC/IDC results.

The cork/TetraPak®/paraffin composite, as the samples in ICC/IDC plots in Figure 3, was stored under different conditions. The results of DRS are shown in Figure 6. The real permittivity is plotted in the graphs on the right ((a) and (c)) and it is about four times lower for the sample kept at 70ºC (sample 1) than for the one at RT (sample 2). For the imaginary component of the permittivity, seen on the left side of Figure 6-(b) and (d), a relaxation around 50ºC is observed (similar characteristics as the ones reported for the peak in Figures 5-(b), (c) and (d)). The peak, as for the results in Figure 5, decreases with drying of the samples and it is also attributed to relatively free water. For this relaxation, sample 1 has values one order of magnitude lower than sample 2. In addition in Figure 6-(b) it can be observed an increase of ε'' towards low frequency and low temperature which was not visible before because of the water relaxation peak.



(a) (b)

(c) (d)

**Fig. 6.** The 3D plot of the dielectric permittivity for the composite cork/TetraPak®/paraffin. (a) and (b) after show sample 1 (dried at 70ºC in air) and (c) and (d) Sample 2 (dried in P2O5 atmosphere).

It is clear from the results in Figure 6 (and in Figure 3) that the thermal treatment is more efficient at removing water from the sample. It was also observed that the process of water reabsorption is much slower in sample 1 than in sample 2.

## 4. CONCLUSIONS

The electrical and dielectric properties of cork are strongly dependent on the amount of water present in the material. So processes of drying the cork derivatives and avoiding water reabsorption are essential to ensure dielectric character and stability of the properties in order to be able to have reliable applications as a dielectric. Addition of hydropohobic material, such as paraffin, may be essential to achieve the control of water amount. Higher temperature insures better desorption of the water pre-existing in the composite (may be by increasing the mobility of water in the material and making diffusion faster). Also water absorption and re-absorption is slower in the samples that where stored at higher temperature. The paraffin may have formed a hydrophobic layer around the grains of the composite reducing water re-absorption. At 70°C the paraffin has melted and diffuses out of the samples faster. When returning to RT the paraffin layer solidifies again and is formed again protective layer of paraffin around the grains reappears and water re-absorption is slower. However if the material is too dry the mechanical, acoustic and thermal properties will change. Hence a careful balance between electrical/dielectric and mechanical/acoustic/thermal properties as to be also maintained.

## ACKNOWLEDGMENTS

The authors would like to acknowledge the financial support of the Portuguese Ministry of Science and Technology (FCT-MCTES PEst-C/CTM/LA0025/2011 – Strategic Project – LA 25 – 2011-2012). The authors would also like to thank Prof. Madalena Dionísio of FCT/UNL and her group for making available the DRS measurement setup and the helpful discussions of the DRS results.

## REFERENCES

[1] L.J. Gibson and M.F. Ashby, “Cellular Solids-Structure and Properties”, Cambridge Univ. Press, Cambridge, 1997.

[2] L. Gil, “Cortiça-Produção, Tecnologia e Aplicação”, INETI, Lisboa, 1998.

[3] S.P. Silva, M.A. Sabino, E.M. Fernandes, V.M. Correlo, L.F. Boesel and R.L. Reis, Int. Mat. Rev. 50 (2005) 345-365.

[4] J.F. Mano, N.T. Correia, J.J. Moura-Ramos and B. Saramago, J. Mat. Sci. 30 (1995) 2035-2041.

[5] M.S.C. Dionísio, N.T. Correia, J.F. Mano, J.J. Moura-Ramos, A.C. Fernandes and B. Saramago, J. Mat. Sci. 30 (1995) 4394-4400.

[6] J.N. Marat-Mendes, E.R. Neagu, Ferroelectrics 294 (2003) 123-131.

[7] M. Carmo Lança, W.Wirges, E.R. Neagu, R. Gerhard-Multhaupt, J. Marat-Mendes, J. Non-Crystalline Solids, 353 (2007), 4501-4505.

[8] M.C. Lança, M. Brandt, E.R. Neagu, C.J. Dias, J.N. Marat-Mendes, J. Non-Crystalline Solids, 356 (2010), 763-767.

[9] E.R. Neagu, M.R. Neagu, Phys. Status Solidi A, 144 (1994), 429-438.

[10] J. Crank, The Mathematics of Diffusion, Clarendon Press, Oxford, 1975.

[11] M. E. Rosa and M. A. Fortes, Wood and Fiber Sci. 25, (1993), 339-348.

[12] J.N. Marat-Mendes, E.R. Neagu, Mat. Sci. Forum, Vol. 455-456 (2004), 446-450.

[13] E. R. Neagu and J.N. Marat Mendes, Appl. Phys. Lett., Vol. 82 (12), (2003), 1920-1926.

[14] F. Kremer, A. Schönals, Broadband dielectric spectroscopy, Springer-Verlag, Berlin, 2002.

[15] J. Banys, M. Kinka, G. Völkell, W. Böhlmann, A. Pöppl, Dielectric response of water confined in metal-organic frameworks, Appl. Phys. A, 96 (2009), 537-541.