Absorbed water in the cork structure. A study by thermally stimulated currents, dielectric relaxation spectroscopy, isothermal depolarization experiments and differential scanning calorimetry

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This paper reports on a modification of the dielectric properties of cork which occurs as a consequence of heating above 60° C or evacuation for several days. This phenomenon was observed using different experimental techniques (thermally stimulated currents, dielectric relaxation spectroscopy, isothermal depolarization experiments and differential scanning calorimetry), and the corresponding kinetics were analysed. It was observed that the original properties of cork were recovered if the sample was exposed to room air for several weeks. It is suggested that the reported modification of the dielectric properties arises from desorption, induced by heating or evacuation, of water molecules absorbed in the cork structure.

1. Introduction

Cork is a natural material whose remarkable properties are at the origin of its diversified applications. The most widespread use of cork is in the production of stoppers for wine bottles. The cellular structure of cork makes it, on the other hand, a very good thermal and acoustic insulator (it is used to provide insulation in refrigerators and houses through the lining of walls and floors). The cellular structure of cork also explains its ability to absorb energy which is used in packaging and manufacturing of shoe soles. Since cork is a dielectric material it is also used as an electric insulator.

In previous work [1] the dielectric relaxation behaviour of cork was studied using the technique of thermally stimulated discharge currents (TSDC). The samples were annealed ("annealed" is used here as a synonym of "previously heated") at 90° C for 10 min before the experiments were performed. When submitted to static electric fields, annealed cork exhibits a very complex pattern of relaxation mechanisms. The detailed analysis of the complex TSDC spectra of cork showed that at least three different relaxation mechanisms must be distinguished: (1) a low temperature relaxation observed between − 100 and − 50 °C, which was attributed to local motions arising from slightly hindered internal rotations of polar groups in the polymeric chains constituting the walls of the cork cells; (2) a relaxation mechanism showing a compensation behaviour

(indicative of a high degree of cooperativity) which was attributed to a glass transition-like relaxation process; (3) a higher temperature discharge observed between 30 and 80° C which is probably due to the melting of waxen substances present in cork.

More recently, we observed that the TSDC spectrum of cork was significantly different if the sample was not previously annealed at 90° C. In fact, the TSDC spectrum of non-annealed cork shows a huge peak with maximum intensity at ca. − 5 °C, which is superposed to the TSDC spectrum of the annealed sample and disappears on heating. The aim of the present work was to understand the nature of this discharge observed for non-annealed cork and the reasons for the observed changes in the dielectric properties of cork on heating. Different experimental techniques were used in order to detect and monitor this effect, namely the TSDC technique, dielectric relaxation (DR) spectroscopy, isothermal depolarization (ID) and differential scanning calorimetry (DSC). Anticipating the conclusions of this work it can be said that the discharge peak observed for non-annealed cork, which is not present in annealed cork, is presumably due to the rotation, under influence of the electric field, of water molecules absorbed in the cork structure. Furthermore, the disappearance of this discharge upon heating or evacuation probably arises from desorption of these water molecules.

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2. Experimental procedure

2.1. Thermally stimulated discharge current (TSDC)

These experiments were carried out with a TSC/RMA Spectrometer (Solomat Instruments, Stamford, CT, USA) covering the temperature range of -170–400° C. A Faraday cage shielded the sample and prior to the experiments the sample was evacuated to 10^{-2} Pa and flushed several times with 1.1×10^5 Pa of high purity He. In order to analyse specific regions of the TSDC spectrum, different methods of polarizing the sample were used, namely the so-called TSDC global and the thermal windowing (or cleaning) experiments [1–3]. In both types of experiment the sample was polarized by applying a static electric field in a given temperature range (with the field applied between T_p and $T'_p < T_p$), the polarization was frozen in by cooling down to T_0 and the depolarization current was then measured as the polarized sample was heated up to T_f, at a constant rate. The difference between the two types of experiment is that in a TSDC global experiment $T'_p = T_0$, whereas in a thermal windowing experiment $T_p - T'_p$ ca. 4° C and $T_0 \ll T_p$ or T'_p. Since the sample is polarized in a narrow temperature range in a thermal windowing experiment, this technique allows the identification of the individual components of a complex relaxation process.

2.2. Dielectric relaxation (DR)

These experiments were done in the frequency range of 20–10^6 Hz and were performed on a Hewlett–Packard 4284 A precision LCR meter. The sample was placed between the electrodes of a three-terminal parallel plate capacitor, described elsewhere [4]. The complex permittivity, $\varepsilon^*(\omega)$, is expressed in terms of its real part, $\varepsilon'(\omega)$ (or dielectric constant), and its imaginary part, $\varepsilon''(\omega)$ (or dielectric loss). The dielectric loss is the quantity most often used in studies of dielectric relaxation [5]. In the present work the results are expressed as $\varepsilon''(\omega)$ C_0 (units of pF), where C_0 is the geometric capacitance of the cell. Since we are concerned with the variation of the loss intensity with temperature and frequency, all the useful information can be obtained from ε'' C_0 and C_0 does not need to be known accurately.

2.3. Isothermal depolarization (ID)

These experiments were carried out with the TSC/RMA spectrometer used for the TSDC experiments, but the experiment is now described as follows. The sample is polarized with a step voltage, V, during time t_p at a given temperature T; the field is then removed and the depolarization current is measured isothermally as a function of time. The intensity of the transient current, $I(t)$, is a complicated decay function of time and its treatment enables us, as discussed later, to calculate the complex permittivity as a function of frequency in the ultra-low frequency range of 10^{-1}–10^{-4} Hz [5]. As in the case of DR experiments, ID results are expressed as $\varepsilon'' C_0$.
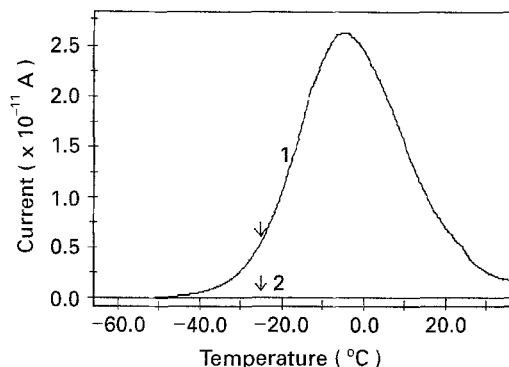

Figure 1 TSDC spectra of cork obtained on the same sample in two successive identical experiments. Experimental conditions for both experiments: electric field strength, $350\ \mathrm{V\ mm^{-1}}$; T_p, $-25\,^\circ$C; T'_p, $-28\,^\circ$C; T_0, $-80\,^\circ$C; T_f, $75\,^\circ$C. Curve 1 corresponds to the non-annealed sample and curve 2 to the annealed sample. Note that in the first experiment the sample was heated up to 75° C.

2.4. Differential scanning calorimetry (DSC)

These experiments were performed using a Setaram DSC-121 calorimeter. The samples were analysed between -70 and 100° C. Prismatic cork samples were encapsulated in aluminium pans and heated at 5° C min^{-1}. The low temperatures were achieved using liquid N_2 and He was used as a purge gas. Since no transitions were detected below room temperature, most experiments were performed between 20 and 100° C. At these higher temperatures no purge gas was used.

In a first experiment the heat flow was measured while the sample was heated to 100° C and it was kept at this temperature for 1 h. After being cooled down to room temperature the sample was consecutively heated and cooled (six cycles) between 20 and 100° C.

In another experiment a sample of cork was rapidly heated to 60° C. The heat flow was registered at this temperature for 1 h.

First quality cork is characterized by low porosity, and all our measurements were carried out on such material. After boiling in water for 1 h and air drying, the cork was cut with a razor blade into slices with ca. 0.5 mm thickness perpendicular to the tangential direction (the direction perpendicular to the axis of the tree and to the radial direction). This section was chosen because it offers larger surface areas free of defects. Different cork samples were studied by the different techniques and the results showed a very good reproducibility.

3. Results and discussion
3.1. TSDC

At the origin of this work is the observation that cork samples which are annealed at temperatures higher than ca. 60° C, exihibit TSDC spectra remarkably different from the ones obtained with non-annealed samples. Fig. 1 shows the reported difference: curve 1 was obtained from a TSDC experiment on a non-annealed sample whereas curve 2 was obtained in
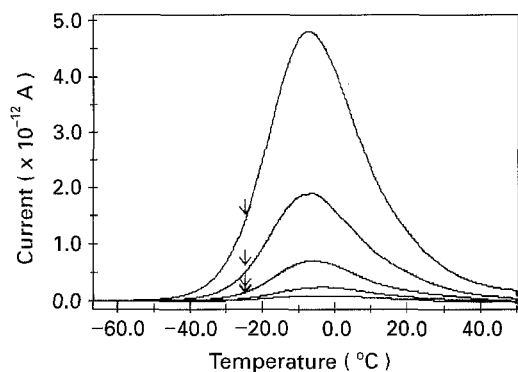
Figure 2 TSDC spectra of cork obtained on the same sample in a series of successive identical experiments. The experimental conditions for all the experiments were: electric field strength, $350 \, V \, mm^{-1}$; T_p, $-25\,°C$; T'_p, $-28\,°C$; T_0, $-80\,°C$; T_f, $50\,°C$. Note that in each experiment the sample is heated up to $50°\,C$. Under such conditions it is possible to monitor the disappearance of the peak. In Fig. 1, on the contrary, the sample was heated up to $75°\,C$ and the TSDC peak disappeared more quickly.

Figure 3 Intensity of the TSDC peaks obtained in a series of successive identical experiments on the same sample with different T_f. The experimental conditions for all experiments were: T_p, $-25°C$; T'_p, $-28\,°C$; T_0, $-80\,°C$. The final temperature, T_f, for the different series are (°C) : ●, 40; ■, 50; ▲, 55; ▼, 65. The rate of disappearance of the peak increases when T_f increases.

a similar experiment on the same sample carried out immediately after expt. 1 (note that in expt. 1 the sample was heated up to $75°$ C). The huge discharge observed in the non-annealed sample (curve 1) is now completely absent. In order to monitor the disappearance of this discharge a series of TSDC thermal windowing experiments with different final temperatures, T_f (the maximum temperature of the experiment), were performed. Fig. 2 is an example of the results obtained for $T_f = 50\,°C$; the disappearance of the peak as the experiments are successively repeated, can be observed.

Different series of experiments with different T_f were carried out in order to analyse the influence of T_f on the rate of disappearance of this discharge. It was observed that the rate of disappearance of the peak increased with increasing T_f. This behaviour is evident from Fig. 3, where the intensities of the peaks obtained in several series of experiments with different T_f values are shown. It is clear that the peak disappears slowly when the temperature of each experiment does not exceed $40°$ C, but it disappears rapidly when the sample is heated up to $65°$ C in each experiment.

The detailed analysis of this TSDC discharge shows several interesting features. First of all, it can be concluded from TSDC global experiments that Arrhenian behaviour is exhibited. Otherwise stated, the representation of the decimal logarithm of the relaxation time, $\log \tau(T)$, as a function of $1/T$ (shown in Fig. 4), presents an apparent linearity. This behaviour suggests that the observed process does not involve a distribution of activation energies but, on the contrary, it is characterized by well-defined activation parameters.

The calculated activation enthalpy is ca. $46 \, kJ \, mol^{-1}$ (ca. $11 \, kcal \, mol^{-1}$). This value suggests that the process corresponds to a local non-cooperative molecular mechanism. On the other hand, it was observed that the discharge under study was absent if the sample was previously evacuated, at
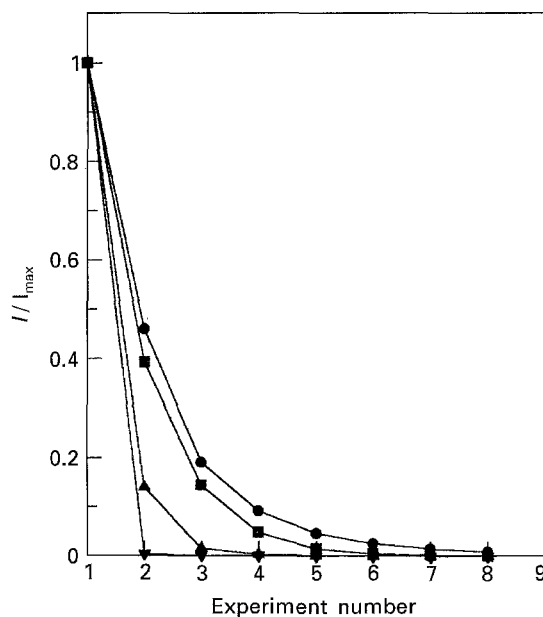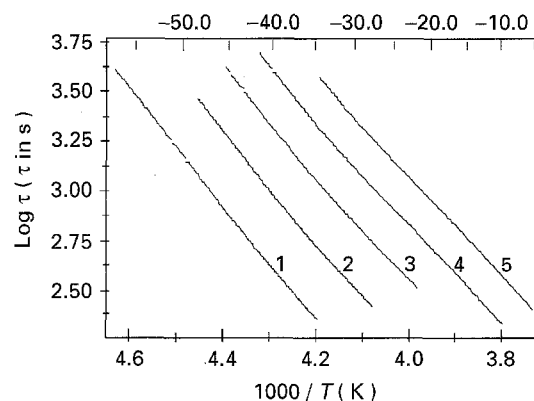

Figure 4 Arrhenius plots of $\log \tau$ versus $1/T$ obtained from different TSDC global experiments. The experimental conditions were: polarization temperature, T_p (°C) : 1, -40; 2, -30; 3, -20; 4, -10; 5, 0; electric field strength, $350 \, V \, mm^{-1}$; T_0, $-100\,°C$; T_f, $30\,°C$.

room temperature, in a vacuum oven for several days (after 4 days the discharge was completely absent). Interestingly, if the evacuated sample or that annealed at $T > 65\,°C$ (where the peak has disappeared) were left in air at room temperature for several weeks, they would recover the discharge (partially recovered after one week and totally recovered after three weeks). These observations lead us to believe that this discharge may be attributed to dipolar relaxation of water molecules absorbed in the cork structure, and that its disappearance corresponds to desorption induced by heating and/or evacuation. In order to verify the presence of this relaxation in cork and the way it behaves upon heating, we carried out the analysis of cork by DR spectroscopy in the frequency range 20–10^6 Hz.
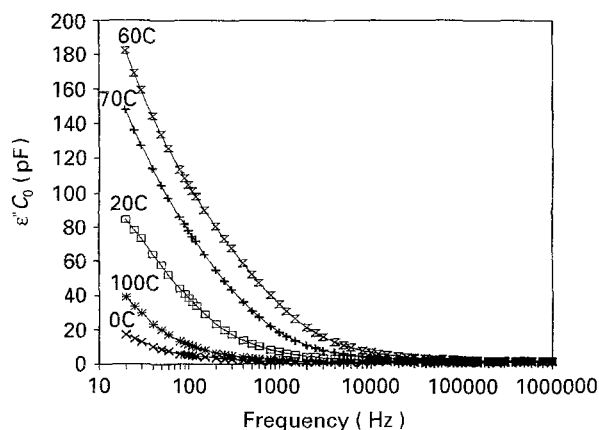
Figure 5 Loss factor as a function of the frequency for cork at different temperatures. The dielectric loss at a given frequency is not a monotonic increasing function of the temperature.

3.2. DR spectroscopy

DR spectroscopy is a very widely used technique to study molecular motions [5]. In this technique the *stimulus* is an oscillating electric field of small amplitude (typically 1 or 2 V). As a consequence of the friction from the surroundings, polar molecules or polar groups are not able to follow instantaneously the direction of the electric field vector, i.e. the polarization is delayed. The relation between the stimulus (electric field) and the answer (polarization) is described by the complex permittivity, and the imaginary part of this quantity, also called loss factor, $\varepsilon''(\omega)$, is the experimental quantity most often used to study dipolar relaxation mechanisms [5, 6]. When such a mechanism is present in the experimentally available frequency range, the function $\varepsilon''(\omega)$ is a peak which presents a maximum whose location in the frequency axis indicates the relaxation time, τ, of the process. With increasing temperature the peak moves to higher frequencies (shorter relaxation times) and the rate at which it moves is related to the activation energy of the process.

In the present work the dielectric properties of cork samples were measured in the frequency range of 20–10^6 Hz, at temperatures between -40 and $140°$ C. No loss peak was observed under these frequency and temperature conditions. However, there is an answer from the system which appears as a decrease of $\varepsilon''(\omega)$ with increasing frequency in the low frequency side. Fig. 5, which shows different loss curves obtained at different temperatures, illustrates this behaviour. Without further examination, those curves could be ascribed to a d.c. conductivity phenomenon. In fact, a d.c. conductivity is usually displayed in the loss curves as a tail in the low frequency side, similar to the ones present in Fig. 5. Nevertheless, a more careful examination leads us to discard this hypothesis. The loss curves in Fig. 5 show an increase in intensity with increasing temperature, up to $60°$ C, followed by a decrease as the temperature rises to $100°$ C. This behaviour rules out the hypothesis that the curves could be ascribed to a d.c. conductivity phenomenon whose intensity always increases with temperature. It is our belief that the obtained $\varepsilon''(\omega)$ curves correspond to the high frequency part of a loss peak which is located
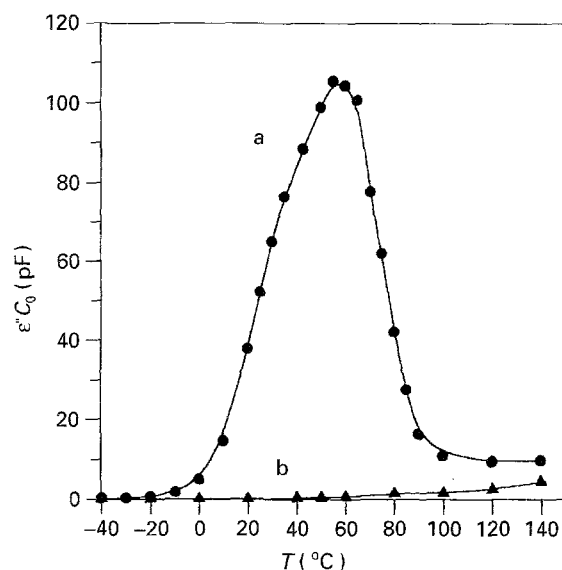

Figure 6 Variation of the loss factor for a given frequency (100 Hz) as a function of temperature. Curve a was obtained with a non-annealed sample (first run). Curve b was obtained with the same sample in a second run. The fact that the sample was heated up to $140°$ C in the series of experiments in curve a leads to the suppression of the loss mechanism in curve b.

outside our available frequency range. The increase in the intensity of the curves observed at temperatures up to $60°$ C (see Fig. 5) would thus correspond to the shift of the loss peak to higher frequencies, as the temperature increases. On the other hand, the decrease observed for higher temperatures would correspond to the suppression of the relaxation mechanism as a consequence of heating. These observations are compatible with those previously reported from TSDC experiments. Fig. 6 (curve a) shows the variation of the loss factor at a fixed frequency (in this case 100 Hz) as a function of the temperature. The disappearance of the peak which was attributed to the relaxation of absorbed water molecules begins at ca. $45°$ C and, at $100°$ C, it is completely suppressed. The same cork sample was submitted to a second series of experiments and the results are shown in curve b of Fig. 6. It is clear that the observed loss is now completely suppressed so that the cork now behaves as an insulating material without any observable dielectric relaxation mechanism.

To have some insight on the kinetics of the desorption process a series of experiments were carried out at a given temperature as a function of time. Fig. 7 shows some results: the normalized loss factor at 100 Hz (ratio between the loss factor and the maximum loss factor at 100 Hz) is plotted versus time for different temperatures. It can be concluded from these results that the desorption process is fast at $75°$ C and slow, although significant, at $50°$ C. It should be pointed out that processing the data from Fig. 7, in order to obtain the rate constant at different temperatures, led us to obtain an activation energy for the desorption process of ca. 58 kJ mol^{-1} (ca. 14 kcal mol^{-1}). The fact that the DR results correspond to a dielectric relaxation mechanism and not to a conductivity tail, associated with the fact that this relaxation mechanism is suppressed on heating or evacuating, suggests that the
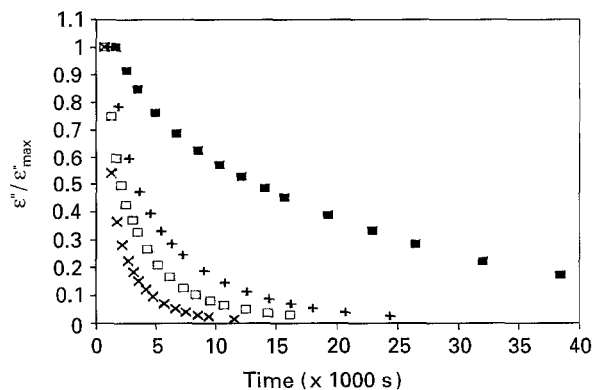
Figure 7 Normalized loss factor, $\varepsilon''/\varepsilon''_{max}$, at 100 Hz as a function of the time for different temperatures (°C): ■, 50; +, 60; □, 70; ×, 75. The disappearance of the loss mechanism is slow at 50° C and fast at 75° C.

Figure 8 Transient current obtained in an isothermal depolarization experiment on non-annealed cork at 30° C (curve 1) and on annealed cork at the same temperature (curve 2). The polarizing electric field strength was 200 V mm^{-1}.

3.3. ID experiments

It was previously pointed out that the results obtained with DR spectroscopy in the frequency range of $20\text{–}10^6$ Hz did not correspond to a charge carrier conductivity tail. We thus believe that the curves (tails) shown in Fig. 5 correspond to a dipolar loss process whose maximum occurs at lower frequencies. The impossibility of observing the whole loss peak in the frequency range available in our DR equipment should be due to the fact that the corresponding relaxation mechanism disappears upon heating above 55–60° C. In order to confirm this point of view we carried out measurements of d.c. transient currents on cork. The experiments include the measurement, as a function of time, of the transient current resulting from the isothermal depolarization of the sample which was previously polarized with a step voltage V. The $I(t)$ curve (the transient behaviour) can be processed by a Laplace transform to obtain the $\varepsilon''(\omega)$ values in the frequency range of $10^{-1}\text{–}10^{-4}$ Hz (steady-state behaviour) [5,6]. Since $I(t)$ may be a complicated function of time, the Laplace transform cannot be performed analytically. There are two methods for the approximate calculation of $\varepsilon''(\omega)$ from $I(t)$: the Brather method [7,8], which is a Fourier transform approximation, and the Hamon method [5,6,9], a less satisfactory procedure, which avoids numerical integration. The Hamon method has been widely used in practice and it will be used in the present work since it is sufficient for our purposes. The method assumes the Hopkinson decay function

$$\phi(t) = \frac{I(t)}{C_0 V} = Kt^{-m} \tag{1}$$

($m = 0.3\text{–}1.2$) for a dielectric at a given temperature and relates the frequency with time according to $f = 0.1/t$. In Equation 1 V is the applied step voltage and C_0 the geometrical capacitance of the cell. The
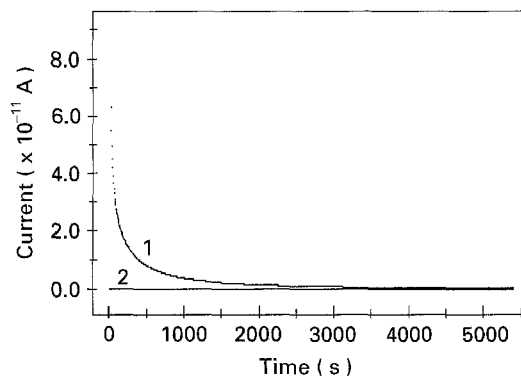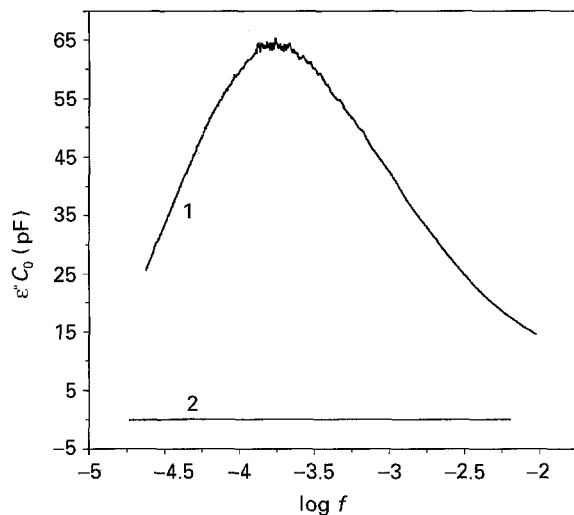

Figure 9 Dielectric loss peak (curve 1) obtained from curve 1 of Fig. 8 using the Hamon approximation. The dielectric loss mechanism disappears if the sample is previously heated to above 60° C or evacuated for several days in a vacuum oven (curve 2).

equation obtained for the dielectric loss, $\varepsilon''(\omega)$, is:

$$\varepsilon''(\omega) = \frac{I(0.63/\omega)}{V\omega C_0} \tag{2}$$

or

$$\varepsilon''(\omega)C_0 = \frac{5tI(t)}{\pi V} \tag{3}$$

where ω is the angular frequency. This equation allows calculation of the dielectric loss as a function of frequency $\varepsilon''(\omega)$, from the $I(t)$ data obtained in an ID experiment. Fig. 8 shows a typical $I(t)$ experimental curve and Fig. 9 (curve 1) shows the corresponding dielectric loss peak obtained using the Hamon approximation.

These results, which were obtained for cork at 30° C, are a clear confirmation of our previous hypothesis that the tails obtained by DR spectroscopy are not conductivity tails but that they in fact correspond to the higher frequency part of a dielectric loss peak. ID experiments similar to that shown in Fig. 8 were performed at different temperatures between 0 and 40° C and it was observed that the location of

the loss peak is displaced, as expected, to higher frequencies as the temperature increases.

Another important finding is the observation that the loss peaks obtained from ID experiments disappeared for samples which were previously heated above 60° C or previously evacuated for several days in a vacuum oven at room temperature (see curve 2 of Fig. 9). This behaviour, which also occurred in the TSDC and DR experiments, constitutes an elegant confirmation of the fact that the same molecular process is being observed by different experimental techniques, and strengthens the idea that this molecular process is related to the dipolar relaxation of water molecules absorbed on the cork structure.

Finally, it should be noted that the intensity of the loss peaks obtained with ID experiments decreases in successive experiments at the same temperature. Since the intensity of these peaks is proportional to the total relaxed dipole moment (i.e. to the number density of the relaxed dipoles), this result suggests that the application of a d.c. voltage to the cork samples induces the desorption of the water molecules.

3.4. DSC

As previously mentioned in the experimental section, the samples of cork were analysed by DSC between 20 and 100° C. This technique allows the detection of any transition involving absorption or release of heat upon heating or cooling the sample at a controlled rate. When the samples are heated for the first time the thermogram obtained shows a broad endothermic peak with an onset temperature ca. 48° C and a maximum at ca. 77° C (Fig. 10, curve 1). The total energy associated with this endothermic peak is, on average, $10.0 \pm 1 \, J \, g^{-1}$.

In order to understand the nature of this peak the sample was kept at 100° C for 1 h, cooled to room temperature and heated again to 100° C. One can still observe an endothermic peak, sharper than the first one, showing an onset temperature at 60° C and a maximum at 75° C (Fig. 10, curve 2). The energy absorbed decreased to an average value of $5.5 \pm 1 \, J \, g^{-1}$. The area of the peak remains constant as the sample is consecutively submitted to thermal cycles between 20 and 100° C.

This result suggests that the endothermic peak observed when the sample was heated for the first time is a composite peak resulting from two distinct transitions, one reversible and the other irreversible. The reversible one, which was also detected in the TSDC spectra, probably results from the melting of waxen substances which are present in the cellular structure of cork [1]. The irreversible one may be attributed to desorption of physisorbed water from the cork structure. The irreversible transition is consistent with the results obtained with the techniques previously described.

Fig. 11 shows the thermogram obtained under isothermal conditions, at $T = 60$ °C. As soon as the temperature reaches 60° C an endothermic transition occurs which lasts for 4 min. After the sample has been kept at 60° C for 1 h it was cooled to room
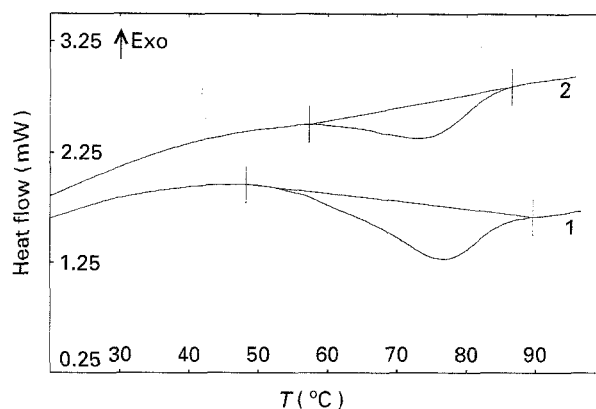

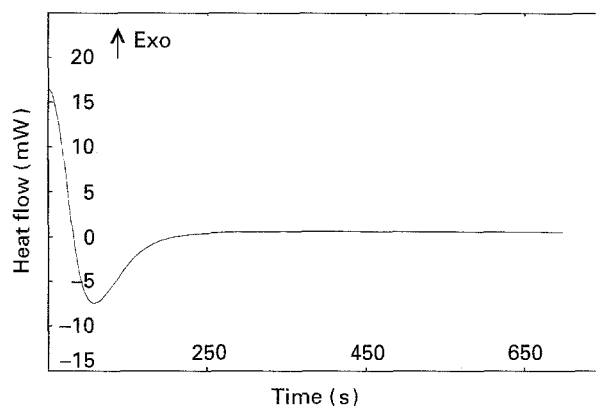*Figure 10* DSC thermograms of cork. 1, First run; 2, second heating, after being at 100° C for 1 h.

Figure 11 Isothermal DSC thermogram of cork at $T = 60$° C.

temperature and heated again at 5° C min^{-1} to 100° C. The enthalpy associated with the observed endothermic peak is of the same order of magnitude as the enthalpy of the peak in curve 2 of Fig. 10. This result suggests that the amount of water released when cork is kept at $T = 60$ °C for a period of time > 4 min, is of the same order of magnitude as the amount of water released on heating the sample to 100° C.

4. Conclusions

In this work we report a modification of the dielectric properties of cork as a consequence of being heated at temperatures slightly above room temperature. This modification was detected through the disappearance, upon heating, of a huge discharge in the TSDC spectrum of cork. The rate at which this relaxation peak disappears in successive TSDC experiments is an increasing function of T_f, the final (maximum) temperature at which the sample is submitted in the TSDC experiment. It was also observed that this relaxation peak is completely absent if the sample is previously heated at 80° C for 15 min, or if it is evacuated for some days in a vacuum oven at room temperature. Interestingly, if the sample is left in air, at room temperature, for three weeks the peak is completely recovered. These observations led us to attribute this TSDC peak to a relaxation mechanism associated with the water molecules absorbed in the cork struc-

ture. The disappearance of the peak, on the other hand, is attributed to the desorption of the water molecules induced by heating or evacuation.

The reported modification upon heating of the dielectric properties of cork was also observed by DR spectroscopy. Since the DR experiments are isothermal (which is not the case for TSDC experiments) this technique could be used to monitor the water desorption process as a function of time at different temperatures. In this context, it was found that the water desorption process became rapid at temperatures $> 60\,^{\circ}C$, with an activation energy close to $58\,kJ\,mol^{-1}$. The existence of a dielectric relaxation mechanism in cork, probably associated with absorbed water molecules, which disappears by heating or evacuating the sample, was confirmed by ID experiments. This technique showed the existence of a dielectric loss process occuring at low frequencies which probably arises from the dipolar relaxation of the absorbed molecules. The experiments performed at different temperatures confirmed that the observed process is characterized by a low Arrhenius activation energy.

The desorption process previously reported was also detected by DSC. The endothermic peak associated with the desorption of water was partially superposed by the peak having a maximum at $T = 75\,^{\circ}C$, which was attributed to the melting of waxen substances [1]. In spite of this, it was possible to separate the two phenomena based on the fact that desorption of water is an irreversible process in the timescale of the experiment and under the conditions of the experiments, while the melting of the waxen substances is a reversible one. The results obtained with the DSC showed that heating and cooling the sample between 20 and 100° C several times is equiva-lent to keeping the sample at $T = 60\,^{\circ}C$ for a period of time $> 4\,min$.

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