

The viscoelastic properties of cork

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The viscoelastic properties of cork (from *Quercus suber*) have been investigated in the temperature range -40 to 120°C using the technique of Dynamic Mechanical Analysis (DMA). The results were compared with dielectric data previously reported. A relaxation was detected with a maximum in $\tan \delta$ at ca 20°C ($f = 1$ Hz) and with a mean activation energy of $140 \text{ kJ} \cdot \text{mol}^{-1}$. A decrease in the intensity of the relaxation and an increase of the storage modulus is observed when cork is previously subjected to an annealing process above 60°C . This result is in agreement with previously reported dielectric data. Thermogravimetric experiments seem to confirm that such effect could be caused by the desorption of water molecules. Specimens oriented along the prismatic direction presented higher storage modulus than the ones oriented along the transverse prismatic direction. The rheological properties of cork also showed a dependence upon the mechanical mode used during measurements: for example, the stiffness is the highest for the tensile mode and the lowest for the compression mode. © 2002 Kluwer Academic Publishers

1. Introduction

The remarkable combination of properties in cork has been exploited by man since pre-Christian times. It has been mainly used in fishing floats, soles of shoes and to seal wine flasks and bottles. For the later application, no better material is known, even today, due to the junction of the particular elastic properties, and chemical stability of cork, which is also impermeable to liquids and mostly unaffected by microbial activity.

Commercial cork is the bark of *Quercus suber*, an oak that grows mainly in the Mediterranean countries. Cork has great economical importance in Portugal, with 30% of the total values of portuguese exports being cork-bases. The extraction of cork in Portugal corresponds to more than half of the total world production.

The composition of the cork cells are made up mainly of suberin and lignin (40% and 22%, respectively), and 9% cellulose [1]. Other compositions have been reported, for example: suberin (45%), lignin (27%), polysaccharides (12%), waxes (6%) and tannins (6%) [2]. The cellular walls are composed of a lignin- and cellulose-rich middle lamellae and a thicker secondary layer with alternate lamellae of suberin and waxes [3]. Suberin is a copolymer of aromatic and long chain (18–30 carbon atoms) ester monomers. Lignin is a crosslinked polymer, partially aromatic and composed by alcohols derived from 1-phenylpropane.

Robert Hooke first examined sections of cork using a compound microscope, being such experiences a mark in the History of Science. He published drawings of what he saw in his book *Micrographia* [4], in which he illustrated the walled cavities of what he termed “cells”, after the Latin *cella*, for small room or cubicle. Cork has been more recently described as a homogeneous

tissue of thin-walled closed cells, regularly arranged without intercellular spaces [5]. Such closed rectangular prismatic cells (mostly pentagonal or hexagonal) are packed in columns parallel to the radial direction of the tree. The cell dimensions depend on the season in which they were generated: whereas spring cells are 30–40 μm long with thin walls, the height of the autumn cells decreases to 10–15 μm and show thicker walls. The cellular structure of cork makes it a very good thermal and acoustic insulator. It is used as insulator in refrigerators and houses through the lining of walls and floors. Moreover, cork has a high damping capacity and a high coefficient of friction; that is why cork is used as soles for shoes, packaging and as handles of tools. Such properties are intimately related to the anelastic properties of the material. In fact, during a complete cycle of deformation in a cork piece there is a component of the work that is never recovered. This is due to the activation of molecular motions in the polymeric component of the material that are partially dissipated as heat.

In spite of the early studies on the mechanical properties of cork from *Quercus suber*, many issues relating to its viscoelastic properties have been scarcely reported. Dynamic mechanical analysis (DMA) is a suitable technique that enables the individualisation and characterisation of the elastic and viscous components of solids [6], and will be used to study the solid rheological behaviour of cork. This work is part of a larger project that attempts to correlate mechanical relaxation results with the structure and processing conditions of natural and synthetic polymeric based systems.

DMA experiments were carried out with different mechanical modes (tensile, compression and flexural);

this information ensemble could be useful to predict the mechanical behaviour in more complex stress fields or to have a better perception on the damping properties of cork. Moreover, the anisotropic structure of cork suggests that the viscoelastic properties could depend on the direction of the mechanical excitation; therefore experiments are performed at suitable directions relative to the cells geometry.

2. Materials and methods

Cork specimens were cut with a razor blade from a plank, with a minimum of 9 years of age (this age corresponds to the minimum period legally allowed between cork extractions [7]). For the compression experiments cork plaques were obtained in three orthogonal directions: radial (R), axial (A) and tangential (T), with respect to a cylinder obtained by a transversal cut from the original tree (see Fig. 1). Flexural and tensile tests were carried out with T and R specimens. Virgin and annealed cork samples were investigated. The annealing was achieved by placing the samples in a vacuum oven at 90°C during 3 hours.

The dynamic mechanical measurements were carried out using a DMA7e Perkin-Elmer apparatus with controlled cooling accessory in the temperature range from -30 to +120°C. High purity helium was used to improve heat transfer to the sample environment during the experiments. All experiments were run under isochronal conditions at 4°C · min⁻¹. The typical calibration routines of the apparatus were carried out.

Using DMA the sample undergoes repeated small-amplitude strains in a cyclic manner. Molecules perturbed in this way store portion of the imparted energy elastically and dissipate a portion in the form of heat. The modulus acquires in this case a complex form, $E^* = E' + iE''$. The quantity E' , the storage modulus, is a measure of the energy stored elastically, whereas E'' , the loss modulus is a measure of the energy lost as heat. The loss factor is defined as $\tan \delta = E''/E'$, δ being the angle between the in-phase and out-of-phase components in the cyclic motion.

For the compression experiments, cylindrical samples with the same diameter of the parallel plates (5 mm) were obtained from circular cuts of the original plaques (~2.5 mm thickness). The top plate imposed a static stress of 1.2×10^4 Pa and a 1 Hz dynamic stress with amplitude of 1.0×10^4 Pa.

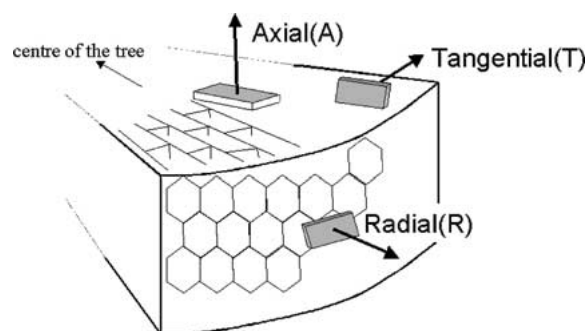


Figure 1 Scheme of cork showing the cells structure and the three kind of samples studied in this work.

For the three point bending and tensile experiments rectangular specimens with typical dimensions of 5.1×2.2 mm were cut from the original cork plaques and tested at 1 Hz. In the first case, the samples were placed over a 20-mm bending platform and a 5-mm knife-edge probe tip provided the mechanical excitation. In all flexural experiments a static stress of 1.2×10^4 Pa and a dynamic stress of 1.0×10^4 Pa were imposed on the sample. In the tensile tests the samples are fixed vertically by means of two clamps. Such experiments were performed under a static stress of 1.2×10^5 Pa and a dynamic stress of 1.0×10^5 Pa. In that case, experiments were carried out at different frequencies, from 0.6 to 30 Hz. In all experiments the strain amplitudes were small enough to ensure the measurements in the linear viscoelastic regime.

Differential Scanning Calorimetry tests (DSC) were performed in a Perkin-Elmer DSC7 calorimeter, with N₂ purge gas. The samples, with weights around 7 mg and encapsulated in aluminium pans, were analysed in the temperature range from 25 to 100°C at 20°C · min⁻¹. The temperature of the equipment was calibrated with indium and lead standards at 20°C · min⁻¹ and for the heat flow calibration only the same indium sample was used.

A thermogravimetric experiment (TGA) was carried out in a Perkin Elmer TGA apparatus. The initial weigh of the cork sample was of 5.246 mg. The temperature varied between 25 and 120°C at 0.2°C · min⁻¹.

3. Results

The tensile DMA results are shown in Figs 2 and 3 for the R and T samples, respectively. For each type of sample the storage modulus (E') and loss factor ($\tan \delta$) are presented. Moreover, the results of experiments for a virgin and for a previously annealed sample are shown in each figure.

Figs 2 and 3 shows that the storage modulus decreases with increasing temperature due to the softening of the material. In the early stages of the experiments (ca -10°C) a strong decrease of E' is detected. This inflection of the E' vs T plots is related with the

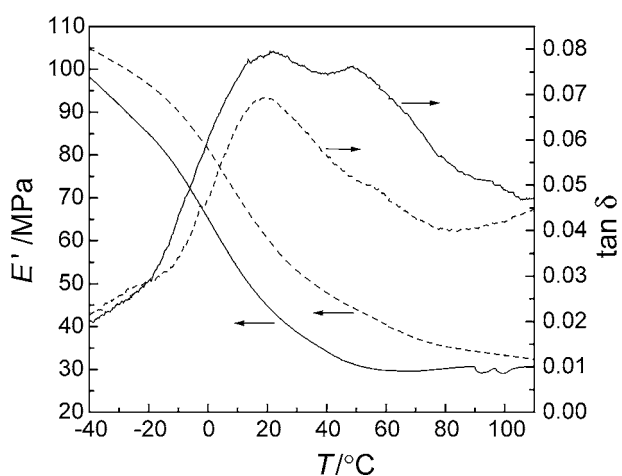


Figure 2 Tensile DMA spectra of a R sample obtained at 1 Hz. Solid line: virgin sample; Dashed line: annealed sample.

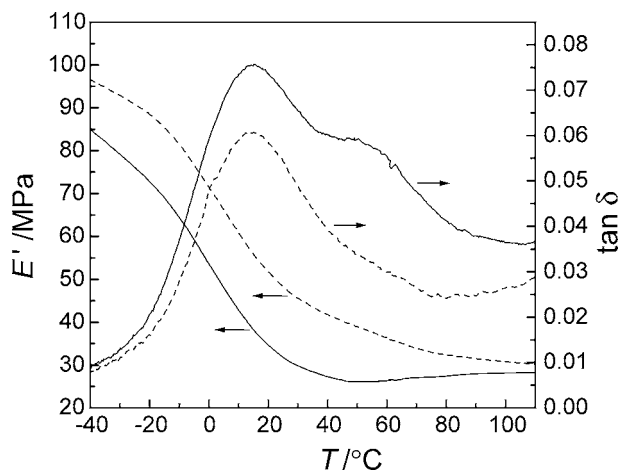


Figure 3 Tensile DMA spectra of a T sample obtained at 1 Hz. Solid line: virgin sample; Dashed line: annealed sample.

occurrence of a relaxational process. This relaxation is also observed in the $\tan \delta$ plot, where a broad peak covers the studied temperature region. This relaxation presents a complex shape. In fact Figs 2 and 3 suggest the existence of two processes: a more intense one at $\sim 20^\circ\text{C}$ and a second one at $\sim 50^\circ\text{C}$ more clearly observed in the R sample. It is interesting to observe such relaxation process in the room temperature region: it may have practical importance for the tree that may absorb mechanical energy when subjected to external periodic loads such as cyclic blasts of wind.

The effect of annealing in the viscoelastic properties of cork is also shown in Figs 2 and 3. After 3 hours at 90°C the flexural modulus of cork increases significantly. Moreover, the intensity of the $\tan \delta$ peak decreases, mainly the component at $\sim 50^\circ\text{C}$ that almost disappear. The location in the temperature axis of the component at $\sim 20^\circ\text{C}$ maintains but the peak at $\sim 50^\circ\text{C}$ shifts to higher temperatures. This result strengthens the idea that the complex peak in the $\tan \delta$ plots may be assigned to two independent processes.

In order to better understand the underlying process associated to the observed annealing effect the thermal properties of the cork were investigated. Thermogravimetry analysis (TGA) could provide evidence for any desorption or thermal degradation processes. Some results showing the effect of heating cork in air and water vapour were already reported for treatments from 100°C to 300°C (see [8] and references therein). In this work the mass loss was measured in a virgin sample heated at $0.2^\circ\text{C} \cdot \text{min}^{-1}$ from room temperature up to 120°C (Fig. 4). The slow heating rate used in the experiment would detect more precisely any mass loss process in the temperature axis. Fig. 4 shows that the decrease of mass is smooth between 30 and 110°C and of about 4% relatively to the initial mass.

Differential scanning calorimetry (DSC) was used in this work in order to investigate if the annealing of cork induces any kind of irreversible exothermal or endothermic process such as chemical reactions or phase transitions. Several DSC were carried out at different samples. Fig. 5 shows representative DSC scans for the same sample. The solid line is for the first run whereas the dashed line is for the sample after being annealed

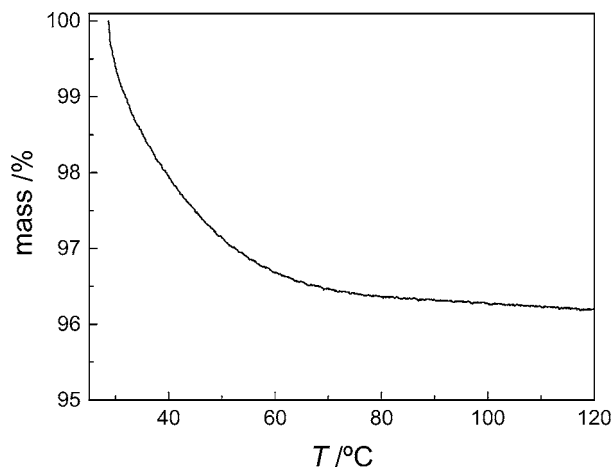


Figure 4 TGA result for a virgin sample (initial mass 5.246 mg) obtained at a scanning rate of $0.2^\circ\text{C} \cdot \text{min}^{-1}$.

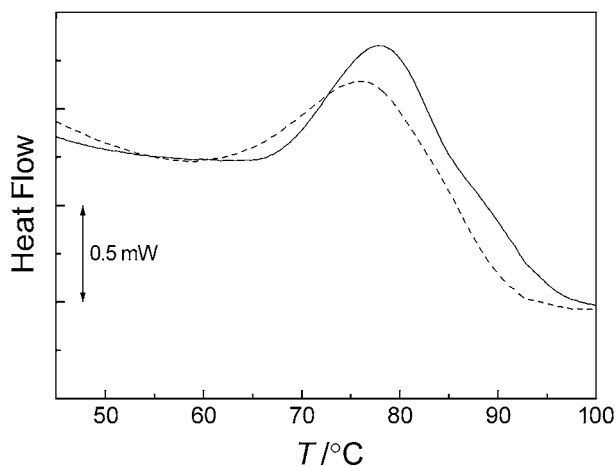


Figure 5 DSC results obtained at $20^\circ\text{C} \cdot \text{min}^{-1}$ on virgin cork (solid line) with 7.579 mg and on the same sample after an annealing period at 100°C for 1 h (dashed line). The former trace presented an onset temperature for the endothermic peak of 66.2°C and a melting enthalpy of $5.5 \text{ J} \cdot \text{g}^{-1}$ and the same parameters of the later trace presented the values of, respectively, 62.5°C and $5.2 \text{ J} \cdot \text{g}^{-1}$.

at 100°C for 1 hour. Apparently no glass transition process exists in the studied temperature range. Only an endothermic peak is observed that shows a lower onset temperature for the annealed sample. The difference of the onsets temperatures is less than 4°C and therefore not significant, taking into account differences in the thermal resistance of the sample that may arise during the different scans. The enthalpy of the process is 5.5 and $5.2 \text{ J} \cdot \text{g}^{-1}$ for the virgin and annealed sample, respectively. This difference is very small, being within the experimental error.

The effect of the mechanical mode used in the DMA experiments on cork was also investigated. Flexural results at 1 Hz are shown in Fig. 6 for virgin R and T samples. The data is more scattered than for the tensile results (Figs 2 and 3) due, probably, to the friction of the ends of the rectangular samples on the flexural platform edges. However, the same relaxational process is easily detected because of the presence of the $\tan \delta$ peak and the intense decrease of the storage modulus. The maximum of $\tan \delta$ occurs at $\sim 10^\circ\text{C}$, that is in accordance with results reported elsewhere [9]. Note that the bimodal character of the peak that is observed in

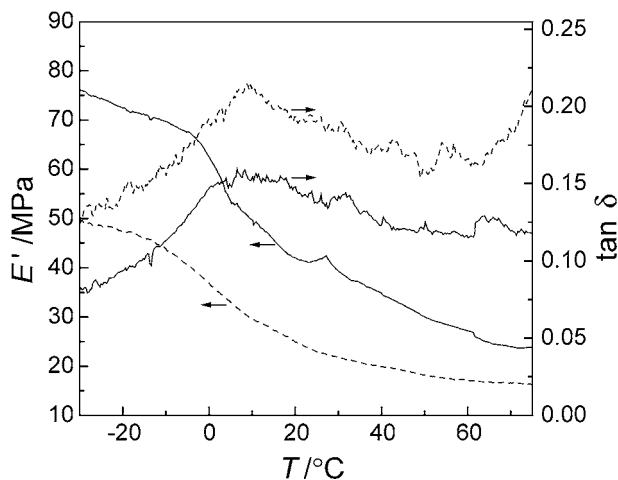


Figure 6 Flexural DMA spectra of a R sample (solid line) and a T sample (dashed line) obtained at 1 Hz.

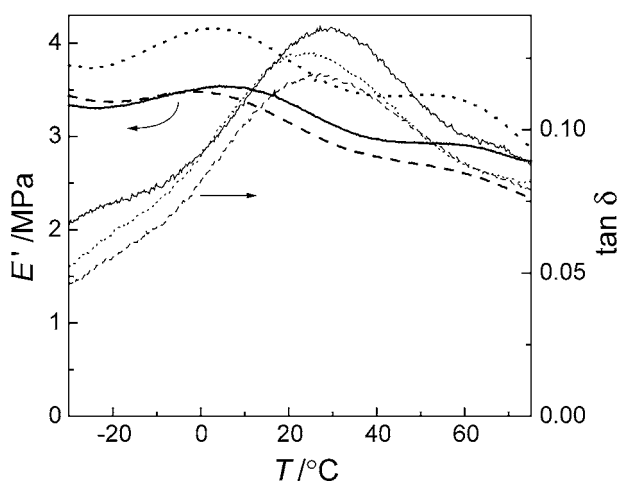


Figure 7 Compression DMA spectra obtained at 1 Hz over the three directions: solid line: R sample; dotted line: T sample; dashed line: A sample. The thicker lines are for E' and the thinner lines are for $\tan \delta$.

the tensile tests is not well distinct in the flexural case; only a shoulder is apparent in the right hand-side of the $\tan \delta$ peaks.

Fig. 7 presents the compression DMA results in the three directions: R, T and A. An unexpected behaviour is observed in the E' traces, where a peak is present in the temperature range 0–10°C. This apparent stiffening with the increase of temperature could be an artefact caused by geometrical changes due, for example, to the melting of the water component in cork. As in the tensile and flexural results the relaxation process is also visible in the $\tan \delta$ vs T curves. However, in this case only one component, with a maximum at $\sim 25^\circ\text{C}$ is observed.

4. Discussion

4.1. Origin of the relaxation process

The study of the broad relaxation process observed in the DMA spectra may be important in the understanding of the impact resistance, sound-absorption and the frictional properties of cork [10, 11]. Other mechanical tests can be performed to follow the viscoelastic character of cork. For example, stress-strain loops se-

ries enable to obtain the energy that is dissipated during cyclic loads [10]. These experiments at room temperature measured values of loss coefficient (proportional to $\tan \delta$) at frequencies between 10^{-2} Hz and 4 kHz, showing a maximum at 2 kHz [10, 12]. The relatively high values of $\tan \delta$ observed by DMA in the present work as well as its position in the temperature axis at 1 Hz and its broadness are in agreement with such results.

The comparison between the mechanical results obtained in this work with previously published dielectric results could be also interesting. Dielectric active processes are also usually observed by mechanical spectroscopic techniques, because the same kind of molecular mobility is activated [13]. The difference is that whereas in dielectric processes the stimulus is an electric field and the response is a polarization, in mechanical processes the stimulus is a stress (or a strain) and the response of the material is a strain (or a stress). There are exceptions when dielectric relaxations are not observed by mechanical techniques and vice versa. For example, rotations of nearly symmetrical or small groups with large dipole moments (for example hydroxyl groups) are dielectrically active but not mechanically. Oppositely, molecular mobility of non-polar groups is only mechanically active. Thus the combination of mechanical and dielectric spectroscopies may be useful when one requires a complete characterisation of the relaxational processes of materials.

A relaxation was detected below 30°C by thermally stimulated depolarisation currents (TSDC) [14], a dielectric sensitive technique. The activation energies of the individual components of this complex process presented a maximum at 5°C . The TSDC technique has a low equivalent frequency (around 10^{-2} Hz [15]) and therefore the same process should be observed a lower temperatures than from DMA, that uses higher frequencies. A relaxation process is visible by dielectric relaxation spectroscopy as a broad peak, from 0 to 100°C (centred at 60°C) for a frequency of 100 Hz [16]. The processes observed by these two dielectric techniques should be the same, taking into account the associated frequencies. Moreover, this relaxation should also be related with the one observed by DMA in this work at a frequency of 1 Hz, that appears at intermediate temperatures. To confirm this it should be interesting to compare the activation energies obtained by the dielectric and mechanical methods.

Dynamic experiments performed at different frequencies allow for the characterisation of the relaxational processes in terms of their kinetic behaviour. Different DMA isochronal experiments performed at different frequencies were carried out in R samples using the tensile mechanical mode. The dependence of the relaxation time upon the temperature of the maximum of E'' is shown in Fig. 8, in a typical Arrhenius plot. The original E'' vs T data is also shown in the inset graphics. The relaxation time for each experiment was calculated as $\tau = 1/(2\pi f)$, where f is the experimental frequency. The linear fitting allows for the estimation of the mean activation energy of the process. In this case we obtained $E_a = 143 \text{ kJ} \cdot \text{mol}^{-1}$. This parameter

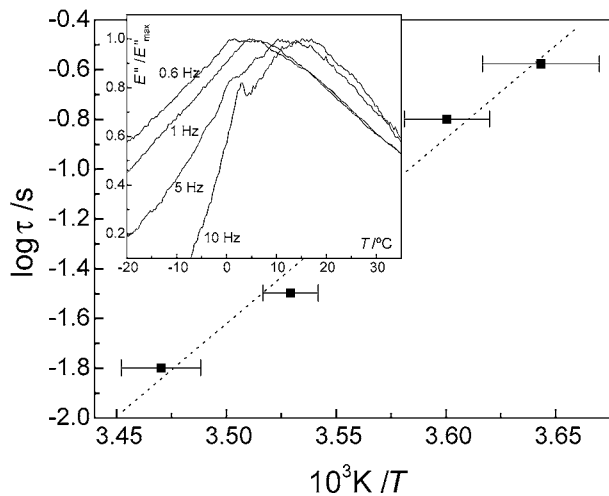


Figure 8 Arrhenius plot ($\log \tau$ vs $1/T$, where $\tau = 1/(2\pi f)$ being f the used frequency and T the temperature of maximum loss modulus) for the tensile DMA results obtained at different frequencies on a R sample. The inset graphics shows the temperature dependence of the normalised loss modulus of such sample for the studied frequencies.

corresponds to the energy barrier that must be jumped during the conformational transition involved in the relaxation and may be used to predict the position in the temperature axis of the process at other frequency.

The individual components of the previously discussed complex relaxation observed by TSDC between -10 and 30°C presented activation energies between 100 and $160 \text{ kJ} \cdot \text{mol}^{-1}$ [14]. Thus, the relaxation studied in this work by mechanical methods and this dielectric process should have the same underlying nature.

The origin of this relaxational process at the molecular level is not yet fully understood. From the TSDC results it was suggested that a glass-transition like process should occur near 18°C due to the existence of a so-called compensation phenomenon and due the increase of the activation energy of the individual components in this temperature region [14]. However, the relatively small drop of stiffness during this process (Figs 2 and 3) seems to not corroborate this thesis, at least for a glass transition of the entire fraction of the material. Moreover, as seen in Fig. 5, no apparent glass transition is observed by DSC. Therefore, one should attribute the observed relaxation to a glass-transition like process within a component in cork. It must be pointed out that the observed activation energies for the studied process are too high to be secondary processes, at least for a β or δ relaxational process seen in polymeric systems [13].

One possibility is to assign the observed relaxation to the conformational mobility within a major fraction cork component, such as lignin, cellulose or suberin. The assessment to dielectric or mechanical spectroscopy data on wood could be valuable because this material has the two first components. Dielectric results did not find any relaxational process in wood in this temperature region [17]. Tensile and flexural DMA experiments on pine wood samples were carried out in our laboratory in the temperature range from -25 to 100°C at a frequency of 1 Hz . A relaxation was found below 25°C , beginning below the initial temperature

of the experiment. This process is probably associated with the β relaxation of cellulose that appears with a maximum intensity at ca. -50°C at 1 Hz and is assigned to localised motions within the cellulose main chains [18]. Therefore the relaxation observed in cork could not, in principle, be related to the molecular mobility in the cellulose fraction but rather to other cork constituent. No mechanical relaxation processes were observed in wood in the temperature region also studied in cork. Therefore one can conclude that the relaxation in cork should not be attributed to lignin. Thus the observed relaxation could be assigned to the presence of suberin. However, more experimental work should be carried out in order to confirm this affirmation without ambiguity.

4.2. Effect of annealing

The effect of the annealing on the DMA results was shown for the tensile experiments in Figs 2 and 3. An increase of E' was also detected in flexural experiments after an annealing process (not shown). This effect was systematically studied by dielectric techniques [16]. The dielectric relaxation intensity strongly decreases as a consequence of heating cork at temperatures slightly above room temperature. The relaxation peak is, in fact, 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. These effects are reversible and the relaxation recovers if the sample is left in air at room temperature for three weeks. Thus the effect of annealing on cork is much stronger in the dielectric response of the material than in the mechanical one. It was proposed from the dielectric results that the effects of the annealing should be related with the desorption of water molecules in the cork structure. This water desorption could explain the stiffening of the annealed samples observed in this work, detected by the increase of the storage modulus, E' . The higher temperature component of the DMA peak (50°C) in Figs 2 and 3 seems to shift to higher temperatures and decrease its intensity with annealing. This could be caused by an anti-plasticization effect due to this water desorption. The lower temperature component of the peak, with maximum at $\sim 20^\circ\text{C}$ maintains its temperature location with annealing. The decrease of its intensity could be a consequence of the decrease of the strength of the higher temperature component. Thus, it seems that the lower temperature component is not affected by the annealing.

It should be noticed that the desorption of water molecules can occur during the DMA experiment on heating in the virgin samples. This could explain, for example, the slight increase of E' of the virgin sample above 60°C shown in Fig. 3.

DSC results on virgin and annealed cork samples were also previously reported [16]. As in the DSC scans performed in this work (Fig. 5) the results in ref. 16 presented an endothermic peak. This phase transition should correspond, at least partially, to the melting of wax substances present in the cellular structure of cork. A peculiar feature of this endothermic peak is that the

enthalpy of the transformation decreases from 10.0 to 5.5 J · g⁻¹ after the annealing of the sample for 1 hour at 100°C [16]. Simultaneously, the data showed that the onset temperature increases from 48 to 60°C. Such effects were also ascribed to the desorption of water during annealing. However the results obtained in the present work do not confirm such results. In fact neither the onset temperature nor the enthalpy of the endothermic process change significantly. Therefore, one should consider the hypothesis that the transformations upon the dynamic mechanical features occurring during the annealing of cork should not be related with the endothermic process observed above room temperature, that probably may be assigned to the melting of wax compounds.

The TGA experiments showed a continuous and smooth decrease of mass of about 4% between 30 and 110°C (see Fig. 4). A release of water in cork of 6–6.5% at 100°C was also reported [7, 8]. Therefore the main part of the lost mass observed in the TGA trace is due to the release of water. This observation also support the idea of desorption of water molecules as the cause for the observed effects of the annealing. Note, finally, that the changes in the dielectric properties are much larger than in the mechanical ones due probably to the strong polar character of the water molecules.

4.3. Anisotropic behaviour and dependence on the mechanical mode

The anisotropic mechanical properties of cork are evident when one compares the results of virgin cork in Figs 2 and 3. Apparently, the bimodal character of the relaxation observed in the tan δ peak in the DMA spectra is stronger in the R sample than in the T sample. Moreover, the R sample shows higher values of E' , when compared with the T sample. For example at 25°C we have $E' = 40 \times 10^6$ Pa for the R sample and 30×10^6 Pa for the T one. These results are in qualitative agreement with quasi-mechanical results where the compression modulus along the prismatic cells is roughly twice than along the other two directions [10]. The modulus has circular symmetry about the prism axis. In the plane normal to this axis, cork is roughly isotropic [19, 20].

The anisotropic behaviour of cork for flexural experiments is also shown in Fig. 6. As for the tensile results, the R samples present higher flexural E' values than the T sample. However, the compression results did not exhibit this tendency. This experimental mode was used in the three directions: R, T and A. The T sample presented higher modulus. However, taking into account the low absolute values of the storage modulus and the heterogeneous nature of the cork samples, the three results may be considered as indistinguishable within the experimental errors.

The comparison between Figs 2 and 3 and Fig. 6 allows to conclude that for a given sample's orientation, the tensile moduli are higher than the flexural ones. Moreover, the tan δ values are higher for the case of the flexural experiments. These results are due to the fact that the compression modulus of cork is lower and the

compression loss factor is higher than the tensile ones (Fig. 7).

The compression storage modulus of cork at room temperature are between 3.0 and 3.5 MPa depending on the direction of the stress (Fig. 7). The low compression modulus of cork is on the base of its use in stoppers for wine bottles. More important in this context, cork has also a low bulk modulus (K) [10]. Its value of K is one third of the Young modulus [21]. Typical polymeric systems also have low Young moduli above the glass transition temperature but large K , and this is what makes them hard to be adjusted in the bottle. The compression Young moduli reported for cork obtained from stress-strain experiments are 20 ± 7 MPa for R samples and 13 ± 5 MPa for both T and A samples [10]. Such values are higher than the compression storage moduli obtained in this work (see Fig. 8). However, as the two types of tests are based on quite distinct solicitation schemes, one should be carefully compared the results as absolute values [22].

5. Conclusion

Dynamic mechanical analysis was used for characterise the solid rheological properties of cork in the temperature range -40 to 120°C . An anelastic process was detected in this temperature range (maximum of tan δ at $\sim 20^\circ\text{C}$ for a frequency of 1 Hz). This relaxation, with a mean activation energy of $140 \text{ kJ} \cdot \text{mol}^{-1}$, was assigned to a glass transition-like process within a component of cork, presumably suberin. This process takes places trough a large temperature region, where the stiffness decreases by a factor of 3. Tensile, flexural, and compression tests were performed, indicating that the stiffness of cork is the highest for the former mode and the lowest for the later. The viscoelastic behaviour of cork is affected by annealing (heating above 60°C) that increases the storage modulus and decreases the intensity of the observed relaxation process. TGA and previously reported dielectric data support a desorption process of water molecules in the cellular cork structure during annealing. The viscoelastic properties of cork are anisotropic: higher values of the storage modulus are found when the material is oriented along the transverse prismatic direction. This is in agreement with quasi-static mechanical tests previously reported.

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