

COMPARATIVE STUDY OF THE 35°C SORPTION ISOTHERMS OF CORK STRIPPED FROM THE TREE IN 1968 AND 2006

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A study was made of the hygroscopicity of two samples of cork with the same characteristics, taken from trees of the same age but with a 38-year gap between debarking. This was achieved by plotting the 35°C sorption-desorption isotherms and fitting them using the GAB model. Infrared spectra were used to determine any chemical changes in the cell wall. Extended exposure to controlled relative humidity and temperature did not cause hygroscopic changes to the cork. The equilibrium moisture content values were not significantly different in the two samples, but the monolayer saturation moisture content values were significantly lower in the older cork. This may be due to partial saturation of the moisture sorptive sites in the cell wall over time.

Keywords: Cork; Desorption; FTIR; Isotherm; Sorption

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INTRODUCTION

Quercus suber L. has a total area of extent of around 2.3 million hectares and is found in western Mediterranean countries: Portugal has 750,000 ha, Spain 500,000 ha, Algeria 410,000, Morocco 340,000 ha, France 100,000 ha, Tunisia 99,000, and Italy 90,000 ha (FAO 2002). The bark of this member of the Fagaceae is extracted as cork, a light, compressible material impermeable to liquids and gases with many applications in several areas. One of its best known uses is as bottle stoppers for quality wines.

Total world cork production is around 340,000 tonnes a year. The major cork-producing countries are Portugal (135,000 t) and Spain (110,000 t) (IPROCOR 2004).

The cell wall structure in cork and wood is similar except for the secondary wall, which has a different chemical composition. The secondary cell wall in wood is composed mainly of cellulose, whereas in cork it is made up of alternate layers of suberin and wax. The primary wall comprises mostly lignin and is responsible for providing mechanical stiffness to cork cells. The very thin outer layer of the cell wall consists of cellulose and hemicellulose.

Suberin is the principal cell wall component in cork and is 38.6% of its dry weight. The other components are lignin (21.7%), polysaccharides (18.2%), total extractives (15.3%), and ash (0.7%) (Pereira 1988).

As in wood, the physical properties of cork are closely associated with water content (Lequin et al. 2010). Although many studies have been made of the hygroscopic behaviour of wood using its isotherms (e.g. Kollmann 1951; Skaar 1988; Wang and Cho 1993; Siau 1995; Esteban et al. 2004; 2005), cork-water relations have been little studied, particularly through the sorption-desorption isotherms (González-Adrados and Haro 1994; Gil and Cortiço 1998; González-Adrados et al. 2008; Abdulla et al. 2009; Lequin et al. 2010).

Isotherms have been used to study how wood hygroscopicity is affected by a range of temperature and relative humidity cycles (Esteban et al. 2005); the passage of time in dry environments (Esteban et al. 2006; 2008a); prolonged immersion for more than 100 years (Esteban et al. 2008b); and burial for 1170 years (Esteban et al. 2009) and for nearly 6000 years (Esteban et al. 2010). However, studies of this type in relation to cork have not been documented. Such studies would increase knowledge of the hygroscopic response of cork and thus explain its behaviour in relation to the passage of time in more or less homogeneous conditions when used as stoppers for wine bottles.

This study compares the hygroscopicity of two batches of cork with the same characteristics but with a 38-year gap between debarking, using the 35°C sorption-desorption isotherms.

EXPERIMENTAL

Samples were chosen from two batches of circular cork pieces in the cork collection of the *Instituto Nacional de Investigación y Tecnología Agraria y Alimentaria* (INIA), held under controlled conditions of relative humidity and temperature. These pieces are normally used to manufacture stoppers for sparkling wine and have a nominal size of 24 mm (diameter) and 6 mm (height).

The batches were from trees of the same age, although one lot of cork had been stripped in 1968 and the other in 2006. Both batches had similar densities. The pieces were chosen so that their commercial quality would be similar (extra, i.e., minimum porosity) and were sliced with a cutting blade into strips around 1 mm thick. The test piece dimensions were 15x10x1 mm. A total of 15 test pieces were placed in each of the controlled humidity environments (above different saturated salt solutions), divided over three flasks (five per flask). Before plotting the first isotherm (desorption), the test pieces were submerged in water for one month to reach cell wall saturation.

The sorption isotherms were plotted following the COST Action E8 saturated salt method (Themelin et al. 1997). The thermostatic baths were verified with micro-crystalline cellulose, following the COST Action E8 protocol (Jowitt and Wagstaffe 1989).

The isotherms were plotted using 10 salts, which resulted in the corresponding equilibrium points (Table 1). The samples were considered to have reached equilibrium moisture content (*EMC*) above each saturated salt solution when their weight differed by

no more than 0.1% after they were weighed in an interval of 24 hours. It took four months to plot the desorption isotherm, after which the wet weight of the samples was obtained. The samples were then dried to anhydrous state in a desiccator with phosphorous pentoxide for 40 days so that the EMC could be calculated by means of Eq. (1):

$$EMC(\%) = \frac{W_w - W_0}{W_0} \cdot 100 \quad \begin{array}{l} W_w: \text{Wet weight (g)} \\ W_0: \text{Anhydrous weight (g)} \end{array} \quad (1)$$

The term ‘wet weight’ will be used in this article when referring the weight of material for a certain relative humidity of the air.

Immediately afterwards, the adsorption isotherms were plotted using the same criteria as for desorption, in a process which took 90 days. The Guggenheim, Anderson, and de Boer (GAB) model was used, as it is particularly appropriate when relative humidities (*RH*) higher than 90% are included (Viollaz and Rovedo 1999) (Eq. 2). It is also the model best suited to this type of material (Lequin et al. 2010):

$$X = \frac{KC_g a_w}{(1 - Ka_w)(1 - Ka_w + C_g Ka_w)} X_m \quad \begin{array}{l} X: \text{emc (\%)} \\ X_m: \text{monolayer saturation moisture content (\%)} \\ C_g: \text{Guggenheim constant (dimensionless)} \\ K: \text{constant (dimensionless)} \\ a_w: \text{RH or water activity on a scale of zero to one (dimensionless)} \end{array} \quad (2)$$

The isotherm fits were considered valid if the correlation coefficient (*R*) was greater than 0.990 and the root mean square error (*RMSE*) was less than 4% (Esteban et al. 2004). The *EMC* of the recently stripped and older cork were compared using the hysteresis coefficients (Eq. (3)):

$$C_H = \frac{EMC_a}{EMC_d} \quad \begin{array}{l} C_H: \text{Hysteresis coefficient} \\ EMC_a: \text{EMC in adsorption} \\ EMC_d: \text{EMC in desorption} \end{array} \quad (3)$$

The thermostatic baths had air recirculation, a range of 20 to 99°C and 0.1°C precision. The balance had a range of 0 to 200 g and 0.0001 g precision. The oven had a range of 0 to 200°C and 0.1°C precision.

Fourier transform infrared spectroscopy (FTIR) was used as a qualitative tool to identify functional groups. Samples of cork granules were prepared, in addition to a control sample of pure cellulose. All samples were oven dried at 103±2°C for 24 hours to remove the -OH groups that were not part of the chemical composition of the material and then cooled at room temperature in a desiccator with silica gel. Approximately 3 mg was taken from each sample and mixed with around 250 mg of potassium bromide. This transformed the material into finely separated dust, which was compressed into a disc in a vacuum press. Data was obtained from 128 scans with a Nicolet spectrophotometer, model Magna-IR 750 Series II, with a precision of 4 cm⁻¹.

The data were compared by applying ANOVA statistical contrast analysis, except in the case of the hysteresis coefficient, for which the Kruskal-Wallis test (a non-parametric version of the ANOVA test) was used, as the conditions of normality were not met.

RESULTS AND DISCUSSION

Table 1 shows the EMC of the cork samples stripped from the tree in 1968 and 2006.

Table 1. Equilibrium Moisture Content (EMC) in Adsorption (EMC_a) and Desorption (EMC_d) and Hysteresis Coefficients (C_H) for the 35°C Isotherms of Cork Stripped from the Tree in 1968 and 2006

Salt	a_w	2006 cork			1968 cork		
		EMC_a (%)	EMC_d (%)	C_H	EMC_a (%)	EMC_d (%)	C_H
LiCl	0.1117	1.33	1.47	0.91	1.31	1.35	0.97
CH ₃ COOK	0.2137	1.96	2.39	0.82	2.56	2.68	0.95
MgCl ₂	0.3200	2.58	2.92	0.88	2.87	3.06	0.94
K ₂ CO ₃	0.4255	3.61	3.92	0.92	3.49	3.65	0.96
Mg(NO ₃) ₂	0.4972	4.33	4.53	0.96	3.72	4.27	0.87
SrCl ₂	0.6608	5.72	6.02	0.95	5.33	5.42	0.98
NaCl	0.7511	6.44	6.74	0.96	6.61	6.72	0.98
KCl	0.8295	7.43	7.90	0.94	7.82	8.29	0.94
BaCl ₂	0.8940	9.35	9.72	0.96	9.14	9.92	0.92
K ₂ SO ₄	0.9671	10.18	10.43	0.98	10.79	11.29	0.96

In all cases the isotherms fitted to a type II sigmoid (Esteban et al. 2004) (Fig. 1), R was greater than 0.990, and the RMSE was less than 4%.

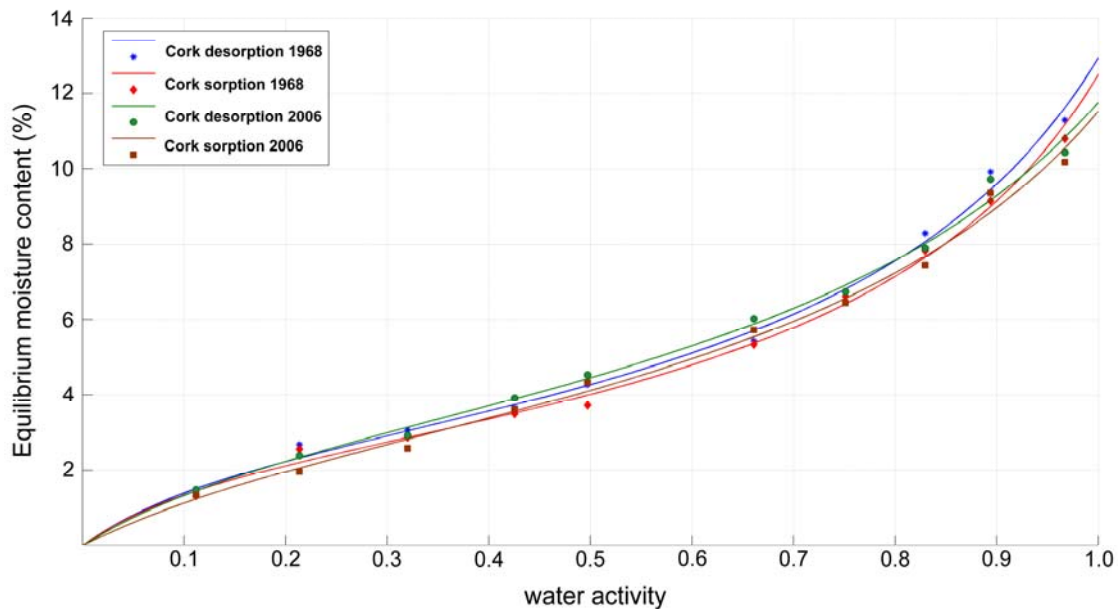


Fig. 1. 35°C sorption isotherms of cork stripped from the tree in 1968 and 2006

The values for the minimum of the *EMC* derivative in relation to *RH*, shown in Table 2, correspond to the points from which multilayer sorption begins to predominate over monolayer sorption (Avramidis 1997) (Fig. 2).

Table 2. Results of the GAB Fit for the 35°C Isotherms of Cork Stripped from the Tree in 1968 and 2006

Isotherm	2006 cork			1968 cork		
	35°C			35°C		
Adsorption	X_m	K	C_g	X_m	K	C_g
	3.51±0.28	0.72±0.40	5.46±0.10	2.90±0.31	0.78±0.64	8.77±0.09
	R		$RMSE(\%)$	R		$RMSE(\%)$
	0.996		0.920	0.997		0.937
	⁽¹⁾ <i>RH</i> (%)	⁽¹⁾ <i>EMC_a</i> (%)	<i>EMC_f</i> (%)	⁽¹⁾ <i>RH</i> (%)	⁽¹⁾ <i>EMC_a</i> (%)	<i>EMC_f</i> (%)
33.4	2.91	0.60	32.3	2.88	0.02	
Desorption	X_m	K	C_g	X_m	K	C_g
	⁽¹⁾ 3.68±0.20	0.71±0.30	6.60±0.06	3.16±0.29	0.76±0.56	8.21±0.08
	R		$RMSE(\%)$	R		$RMSE(\%)$
	0.996		0.433	0.997		0.942
	<i>RH</i> (%)	⁽¹⁾ <i>EMC_a</i> (%)	<i>EMC_f</i> (%)	⁽¹⁾ <i>RH</i> (%)	⁽¹⁾ <i>EMC_a</i> (%)	<i>EMC_f</i> (%)
34.9	3.34	0.34	32.7	3.08	0.08	

⁽¹⁾: Point of inflection of the isotherm. X_m : Monolayer saturation moisture content. K : Constant. C_g : Guggenheim constant. R : Correlation coefficient. $RMSE$: Root Medium Square Error. *RH*: Relative humidity. *EMC_a*: Equilibrium moisture content in adsorption. *EMC_d*: Equilibrium moisture content in desorption. *EMC_f*: Water taken up via monolayer sorption after the point of inflexion

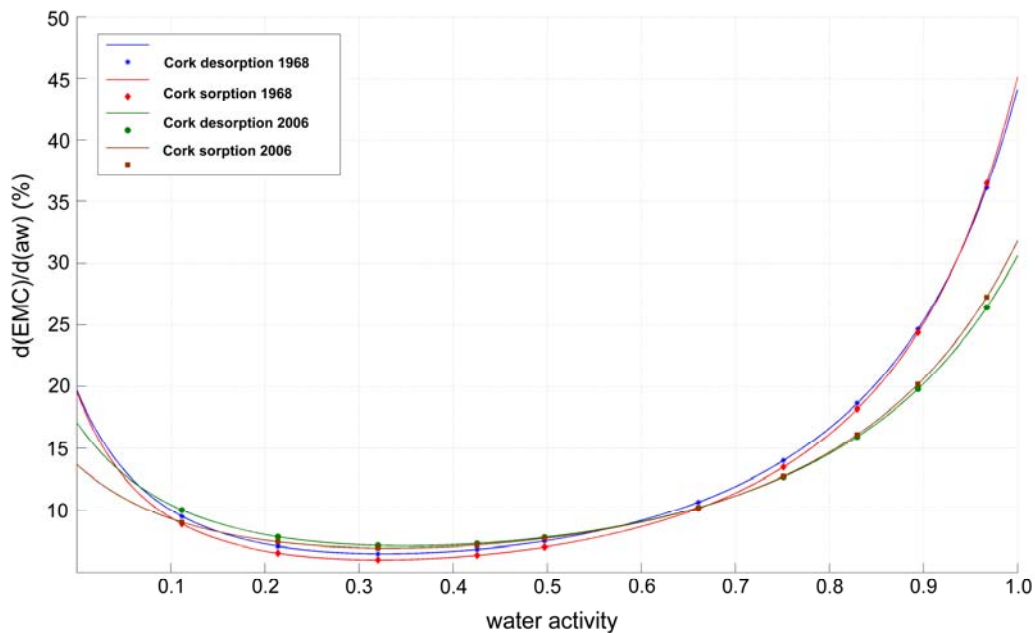


Fig. 2. Derivatives of the 35°C sorption isotherms of cork stripped from the tree in 1968 and 2006

Although both the sorption and adsorption isotherms of the older cork were below those of the recently stripped cork, analysis of variance showed no significant difference in the EMC of the two samples, with a probability of 95%.

The water sorption mechanism in cork appears to be similar to the mechanism in wood, and is divided into three phases: monolayer sorption, multilayer sorption, and capillary condensation (Abdulla et al. 2009). However, some authors (Lequin et al. 2010) have raised doubts about the monolayer sorption phase. This does not seem logical, as the hydrophilic -OH groups belonging to the small amount of cellulose and hemicellulose, in addition to the methoxyl groups mentioned by these authors, have a role in fixing water through hydrogen bonds.

In both isotherms, the EMC values of the two cork samples were lower than the EMC obtained for 35°C in the wood of *Pinus sylvestris* L. (Esteban et al. 2006; 2008a; 2008b; 2009) and *Quercus robur* L. (Esteban et al. 2010). Similarly, the values for the monolayer saturation moisture content X_m in cork were approximately half those obtained in these species of wood. This can be explained by the lower number of hydrophilic groups in the cell wall, caused by the low percentage of cellulose and hemicellulose, and the presence of suberin, which is hydrophobic.

The monolayer saturation moisture content values (X_m) were significantly lower in the older cork. This means that the recent cork had more hydrophilic bonds, which can be explained by the partial saturation of some hydrophilic groups over time.

In the recently stripped cork, the water taken up via monolayer sorption above the point of inflexion (EMC_f), where multilayer sorption predominates over monolayer sorption, was much greater than in the older cork, to the extent that water uptake can be regarded as insignificant in the latter.

Although the water taken up via monolayer sorption is significantly different in the four isotherms, the points of inflexion where multilayer sorption begins to predominate over monolayer sorption remain constant, at around 30% *RH* (Fig. 2). This result is similar to those obtained in other studies on wood using the same isotherm (35°C) (Esteban et al. 2006; 2008a; 2008b; 2009), which seems to indicate that the predominance of multilayer sorption over monolayer sorption is 32 to 35%, regardless of cork age.

The hysteresis coefficients (Table 1) showed no clear pattern that would allow the free energy of the hysteresis loop to be related to cork stability. Earlier studies on wood (Esteban et al. 2008a) showed an obvious narrowing of the hysteresis loop. This feature is common in wood subjected to repeated humidity cycles (Skaar 1988; Esteban et al. 2005), but it was not seen in the present study. A decrease in the isotherm slope corresponding to higher dimensional stability (Skaar 1988; Esteban et al. 2005) was also expected, but the derivatives ($dEMC/da_w$) revealed higher values for the isotherm slopes in the older cork above 65% *RH* (Fig. 2). From this it could be understood that the older cork was less hygroscopically stable, although only an in-depth study of the physical and chemical changes that occur over time in cork cell walls would enable this to be discussed.

FTIR (Table 3, Fig. 3) showed that both cork samples had the same functional groups and their spectra had not changed over time. It is likely that a much longer time or more aggressive environments are required for any of the peaks to be altered, e.g. the

hemicellulose peak. In wood, hemicellulose is the first component to degrade and also shows most degradation (Bardet et al. 2004; Fengel 1991), as cellulose is more resistant because of its crystal structure (Fengel 1991; Yilgör et al. 2005). This degradation may be due to bacterial action, as bacteria degrade selectively, preferring hemicellulose to cellulose (Gelbrich et al. 2008), particularly during the onset of attack in damp environments (Kim 1990). The low percentage of polysaccharides in the cell wall of cork can be an advantage in comparison to the degradation that commonly occurs in wood.

Table 3. Main Functional Groups Present in Cork and Their Absorption Bands (Lopes et al. 2000; Lopes et al. 2001)

	Wavenumber (cm ⁻¹)	2006 cork		1968 cork	
		\bar{x}	σ	\bar{x}	σ
Hydroxyl (-OH)	3400-3500	3410.3	5.7	3406.7	6.1
Suberin ¹ (C-H)	2919-2926	2925.3	1.2	2924.7	1.2
Suberin ¹ (C-H)	2850-2854	2852.0	0.0	2851.3	1.2
Suberin ² (C=O)	1730-1750	1740.7	0.6	1740.7	1.2
Suberin ³	1635	1632.3	0.6	1630.7	2.3
Lignin ⁴ (C=C)	1607	1616.0	0.0	1614.7	2.3
Lignin ⁴ (C=C)	1510	1513.3	1.2	1512.7	1.2
Suberin ³	723	721.7	0.6	721.7	1.2

¹ Suberin aliphatic chains. ² Suberin ester groups. ³ Suberin R₁CH=CHR₂ groups. ⁴ Vibrations of the benzene ring in the lignin.

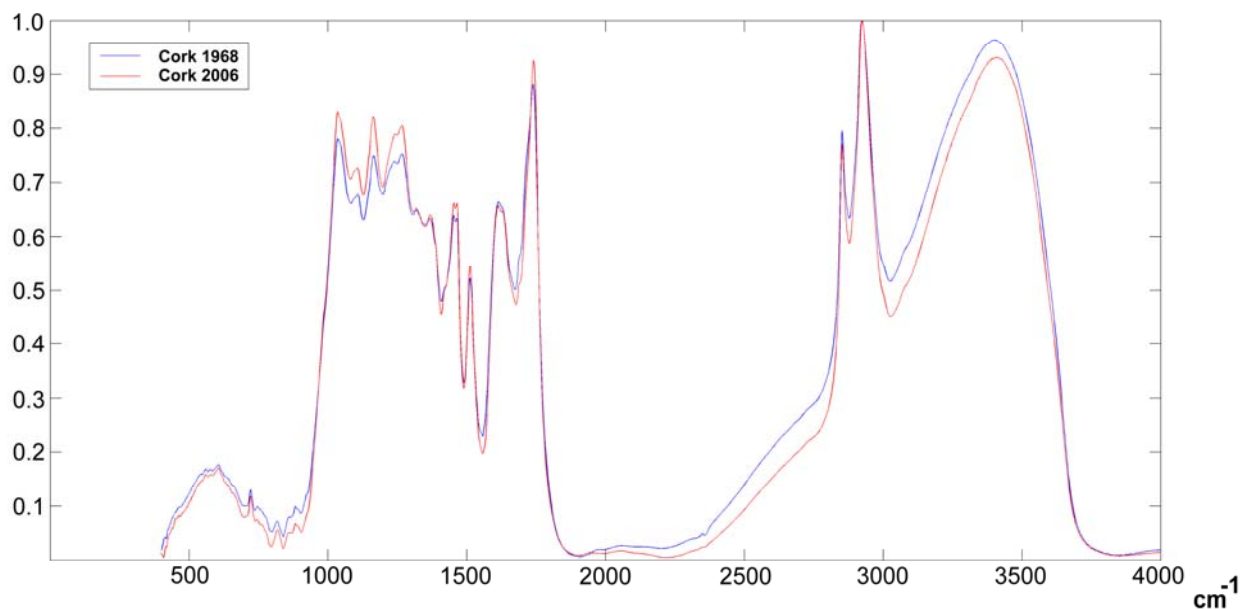


Fig. 3. FTIR spectra of cork stripped from the tree in 1968 and 2006

Further studies on cork exposed to more aggressive conditions will make it possible to determine whether cork changes its cell wall structure and how it responds hygroscopically to this change.

CONCLUSIONS

1. The equilibrium moisture content of both cork samples studied showed similar values, suggesting that their hygroscopic response had not changed over time.
2. The difference between the isotherm slopes of the recently stripped and the older cork did not allow their hygroscopic behaviour to be determined, due to the physical and chemical changes likely to have occurred in the cell wall.
3. In both samples, the points of inflexion where multilayer sorption begins to predominate over monolayer sorption occurred at very similar values, around 32-35% relative humidity.
4. Water taken up via monolayer sorption above the point of inflexion (EMC_f) was greater in the recently stripped cork than in the older cork.

ACKNOWLEDGMENTS

This study is part of the AGL2009-12801 project of the 2008-2011 Spanish National Plan for Scientific Research, Development and Technological Innovation, funded by the Spanish Ministry of Science and Innovation.

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Article submitted: October 8, 2010; Peer review completed: January 15, 2011; Revised version received and accepted: April 25, 2011; Published: April 27, 2011.