Materials and Design 82 (2015) 148–154

Contents lists available at ScienceDirect

Materials and Design

journal homepage: www.elsevier.com/locate/matdes

Mechanical properties of cork: Effect of hydration

Aurélie Lagorce-Tachon [a,b,c], Thomas Karbowiak [a,*], Dominique Champion [a], Régis D. Gougeon [a,b], Jean-Pierre Bellat [c]

[a] UMR PAM, Equipe PAPC, Université Bourgogne Franche-Comté, 1 esplanade Erasme, F-21078 Dijon, France
[b] Institut Universitaire de la Vigne et du Vin, Université Bourgogne Franche-Comté, 1 rue Claude Ladrey, F-21078 Dijon, France
[c] Laboratoire Interdisciplinaire Carnot de Bourgogne, UMR 6303 CNRS, Université Bourgogne Franche-Comté, 9 avenue Alain Savary, B.P. 47870, F-21078 Dijon, France

ARTICLE INFO

Article history:
Received 9 December 2014
Revised 7 May 2015
Accepted 16 May 2015
Available online 18 May 2015

Keywords:
Cork
Mechanical properties
Water
Visco-elasticity
Plasticization
Glass transition

ABSTRACT

Cork is known to exhibit low permeability to liquids and gases, imputrescibility and good mechanical properties, with a remarkable elasticity. These properties make this material particularly interesting for sealing wine. We focused in this study on the compression properties of cork along the radial and tangential direction at 25 °C under atmospheric pressure when cork is stored in various relative humidity environments, from 0% to 100%.

The direction of compression significantly affected the Young's modulus, with a higher value for the radial direction. This corresponds to the orientation of the lenticels which reinforce the rigidity of the material when the strain is applied along their growth direction. More surprising is the effect of water sorption in cork on its mechanical property. Both radial and tangential directions exhibit the same behavior when the relative humidity is increasing. First the Young's modulus is constant up to 50% relative humidity (RH) with mean values around 37 MPa and 22 MPa for radial and tangential directions, respectively. Then, above this point, the increase in water content leads to a decrease in material rigidity which is attributed to water clusters formations. For high moisture contents, the anisotropy of cork is reduced: Young's moduli are of 10.5 MPa and 6.6 MPa for radial and tangential orientations, respectively.

Differential scanning calorimetry and dynamic mechanical thermal analysis (DMTA) allowed to identify a glass transition temperature (T_g) in cork over a broad range of temperatures, depending on the moisture content and giving a T_g-midpoint from −8 °C to 3 °C. Moreover, a secondary transition was observed by DMTA at approximately −80 °C, for 50% RH.

1. Introduction

Cork is the outer bark of cork oak tree *Quercus suber* L. This natural polymer has an alveolar cellular structure with an interesting set of properties: low permeability to gas and liquid [1,2], chemical and microbiological stability [3], low conductivity [4] and remarkable elasticity with dimensional recovery [5–7]. In view of these features, cork is used in many fields such as insulation [8], shoes insole [9], adsorption of pollutants [10] and obviously as stopper to seal wine bottles [11,12].

Due to the geometry of the cells, arranged in a honeycomb alveolar structure, cork is an anisotropic material. Tridimensional cells are empty, but there is no intercellular void space. However, lenticular channels, so called lenticels, crossing cork along the radial direction, constitute a heterogeneous macroporosity. Chemical composition of cork mainly depends on the geographic origin, the age of the tree (virgin or reproduction), the genetic origin and growth conditions [3,13–16]. Nevertheless, the following average composition can be established. The major component is suberin (40–45 wt%) a polyester similar to cutin, composed of long fatty acid chains, hydroxyl fatty acids and phenolic acids linked by ester groups [15,17–19]. Lignin represents 22–27 wt% of the material. It is a rigid and hard polymer, with covalent bonds, known to be responsible for wood resistance to compression [20]. Cellulose and hemicellulose, accounting for 9–12 wt%, are the structural components of the cell walls. Finally, cork contains some other components, such as waxes and tannins, which are not linked to the main structure and thus easily extractable. These extractives represent 10–12 wt% and some of them are known to take part in the organoleptic properties of wine [21].

* Corresponding author at: Agrosup Dijon, 1 esplanade Erasme, F-21078 Dijon, France.
E-mail addresses: aurelie.tachon@u-bourgogne.fr (A. Lagorce-Tachon), thomas.karbowiak@u-bourgogne.fr (T. Karbowiak), d.champion@agrosupdijon.fr (D. Champion), regis.gougeon@u-bourgogne.fr (R.D. Gougeon), jean-pierre.bellat@u-bourgogne.fr (J.-P. Bellat).

http://dx.doi.org/10.1016/j.matdes.2015.05.034
0261-3069/

Although half of cork components are hydrophobic, it can sorb around 10 wt% of water for a relative humidity close to saturation at 25 °C. Sorption of water on cork occurs by a mechanism of physisorption (with clustering), associated to a swelling of the material [22]. Even if a slight hysteresis between sorption and desorption is noticeable, the phenomenon is reversible and associated with a low enthalpy of sorption at low filling, around −60 kJ mol^{-1}.

Surprinsingly, if the interaction of water with wood has been extensively studied [23–27], data related to the effect of water on physical properties of cork are scarce. Mechanical properties of cork have been mostly studied in compression [5–7,11,28]. They have also been determined in tension, but to a lower extent [29,30]. These studies of mechanical properties were essentially focused on the effect of cork quality and density [6,7,29,30], as well as process parameters (boiling treatment) [31,32]. To our knowledge, there is no data in the literature reporting the effect of hydration on the mechanical properties of cork. This study aimed at evaluating the compression properties of cork – when stored under various relative humidity environments, from 0% to 100% at 25 °C – along the radial and tangential directions, which correspond to compression directions in the bottleneck.

2. Material and method

2.1. Cork

Natural raw cork stoppers, from *Quercus suber* L. oak trees in the Mora (Portugal) production area, were supplied by the company Bouchons Trescases S.A. (Boulou, France). The best quality of cork stoppers was chosen (class 0). Stoppers were neither washed nor surface treated (with paraffin or silicone) prior to use. Cork stoppers of 24 mm diameter and 48 mm height were cut with a cutting machine (Mecatome T201 with resinoid cut-off wheels of 180 mm diameter and 0.5 mm thickness, Presi S.A., France).

For unidirectional compression testing, cork was cut into 15 mm edge cubes. For each of the compression direction studied (radial and tangential) and each of the relative humidities (RH), five cubes from five different cork stoppers were prepared and stored until equilibrium under the corresponding controlled humidity before analysis.

For Dynamic Mechanical Thermal Analysis (DMTA), cork stoppers were cut into sheets following the tangential axis. These cork were 1.5 mm thick, 8 mm height and 12 mm long.

2.2. Hydration of cork

Cork samples were equilibrated under various relative humidity environments, from 0% to 100% in air-tight containers over P_2O_5 or various saturated salt solutions (LiCl, $KC_2H_3O_2$, $MgCl_2$, K_2CO_3, $Mg(NO_3)_2$, KI, KBr, K_2SO_4) or water, at 25 °C, in order to fix 0%, 22.6%, 32.7%, 43.8%, 53.5%, 68.7%, 80.7%, 96.9% and 100% RH, respectively. Equilibrium was considered to be achieved when the weight variation did not exceed 0.05 wt% over two weeks.

Sorption isotherm of water vapor on cork was well fitted by the GAB model:

$$\frac{m_a}{m_m} = \frac{CK(p/p_s)}{[1-K(p/p_s)][1-K(p/p_s)+CK(p/p_s)]} \quad (1)$$

where m_a is the amount of water adsorbed by the cork (wt%), m_m is the amount of water adsorbed on the equivalent monolayer (wt%), p/p_s is the relative pressure (RH/100) defined as the ratio between the pressure at equilibrium and the pressure at saturation (for water p_s = 31.66 hPa at 25 °C), C and K are constants related to the adsorption energy for the first and second layers and second and subsequent layers, respectively.

2.3. Mechanical properties of cork

2.3.1. Static measurement

Cork cubes were submitted to a unidirectional compression test using texture analyzer TA-HD + (Swantech, France) with a 100 kg load cell and a P50 probe. The test was performed with constant crosshead speed of 1 mm s^{-1} up to 80% strain. Compression was performed following the radial or the tangential axis. Strain–stress curves were analyzed as follows: Young's modulus was calculated from the slope in the elastic region and stress at 23% and 34% of strain were also noted (Fig. 1). These last two values correspond to the compression of cork in the bottleneck (initial stopper diameter: 24 mm; final diameter in the bottleneck: 18.5 mm) and during the bottling process (compressed diameter before insertion: 15.8 mm) respectively [33].

2.3.2. Dynamic measurement

The viscoelastic properties were measured using a dynamic mechanical analyzer Q800 (TA Instrument, USA) operating between 1 and 18 Hz in compression mode. Samples were submitted to a 0.7% strain which corresponds to the elastic region with 0.3 N preload force in order to prevent any sample fall. The range of temperatures for dynamic mechanical and thermal analysis (DMTA) spreads from −100 °C to 100 °C. Isothermal steps were performed every 10 °C, except in the range of temperatures between −80 °C and −60 °C as well as between 0 and 30 °C, where transitions were identified, in order to achieve higher sensitivity. The viscoelastic behavior was investigated by following the evolution of the storage modulus E', loss modulus E'' and the loss factor $\tan\delta$ ($\tan\delta = E''/E'$) as a function of temperature.

2.4. Cell structure of cork

Some cork samples after the static compression test were observed by scanning electron microscope (SEM), using a Jeol JSM 7600F (15 kV). Prior to observation, 1 mm thick cork samples were cut with a razor blade and coated with carbon (15–20 nm).

2.5. Phase transition of cork

Differential scanning calorimetry (DSC) measurements were carried out using a Q20 calorimeter (TA Instruments, France), calibrated in temperature and energy with the melting of pure indium (T_m = 156.7 °C and ΔH_m = 28.4 J g^{-1}). Around 4 mg of cork were placed in a sealed aluminum pan and scanned at 10 °C min^{-1} in

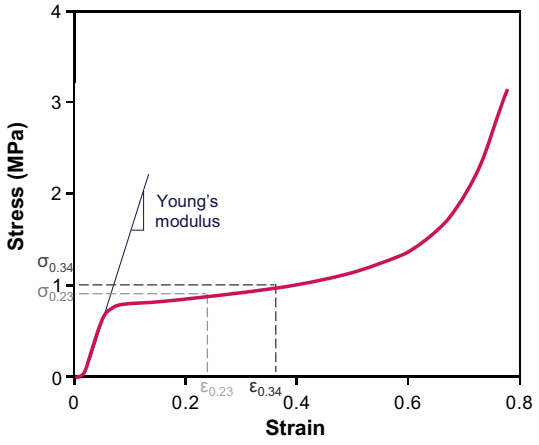

Fig. 1. Typical strain–stress curve of cork obtained by compression in tangential direction on a cork stopper equilibrated at 53% RH (strain is expressed as l/l_0, with l_0 the initial dimension of the sample in the compression direction).