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# Mechanical behaviour of cork modified by heat treatment at high temperature

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## 1. Introduction

Nowadays, the use of cork as building material is promoted, same materials in developing the industry are the products manufactured from secondary treatment of the ecological and environmentally friendly [1]. As the cork is characterized by an important anisotropy, it is a very complex material. It is also a hygroscopic material: its water content varies with time according to humidity conditions, temperature, environment and the nature of soil (which has an effect on the physical and chemical characteristics) [2]. The improvement of some porous biomaterials characteristics and their preservations are mostly carried out by chemical process [3], even for other materials, which consists in high-temperature heat treatment. With respect to energy savings and environmental protection, thermally activated systems are of a major importance in the areas of thermal and phonic insulation. It is noted that the effects of heat treatment at high temperature on a porous biomaterial (cork) causes physical changes and chemical properties as well. Consequently, these changes yield biological resistance to rot.

First cross-linking in the lignin is demonstrated by a hardening of the material. Then, and according to the same authors [4], the change in the crystallography of cellulose decreases the material bending strength.

Degradation of Hemicellulose and cellulose decreases the water uptake, resulting in increase in durability of the material against the attacks of micro-organisms. The modelling of moisture transfer in cork requires the accurate knowledge of several thermophysical and boundary condition parameters that may appear in the formulation.

In literature, the models describing migration in porous media of water usually in vapor form. The aim of this paper is to present analysis of mass transfer in liquid form before and after heat treatment of Algerian cork.

This work is based on the indirect method of conductimetric measurement for following the kinetics of desorption of the aqueous solution (NaCl “0.2M”). This method has been revealed very simple in its material conception, highly accurate and the results thereof immediately obtainable. The aqueous solution diffuses radially and longitudinally within an anisotropic porous medium (Cork in form of plate before and after treatment) towards an external environment.

As determination of the diffusivity by conventional methods requires long and laborious steps, the conductivity method constitutes infact, a good alternative which requires less effort. In this context, the apparent diffusion coefficient $D_{app}$ of cork has been determined successive assessment starting from a mathematical model.

Indeed, by analysing an impregnated porous material in a aqueous solution, the model key entry is the reduced mass from the experimentally measured conductivity. The experimental database is used to develop a methodology that will be employed to determine the diffusion coefficient by a statistical approach based on Artificial Neural Networks, which will be a future study.

## 2. Materials and methods

### 2.1. Sample preparation

Cork which is used in this study is a porous biomaterial has been obtained from the Berouaguia Region in Algeria. The experiments were conducted on group of plates cut parallel to the direction of the pores (radial direction) and Axial direction with an average size of $4.4\times10^{-2}$ m$^2$ and $1.5\times10^{-3}$ m thick (direction of diffusion).

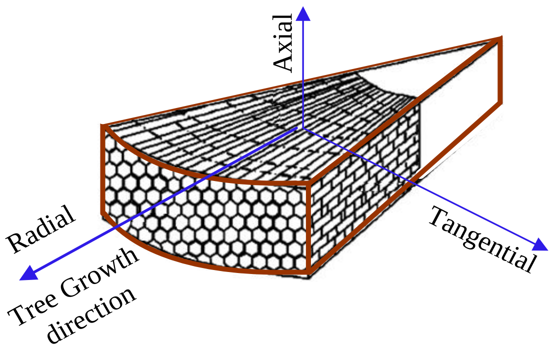


Fig. 1 Illustration of the three main directions of the disposal cell in a section of cork

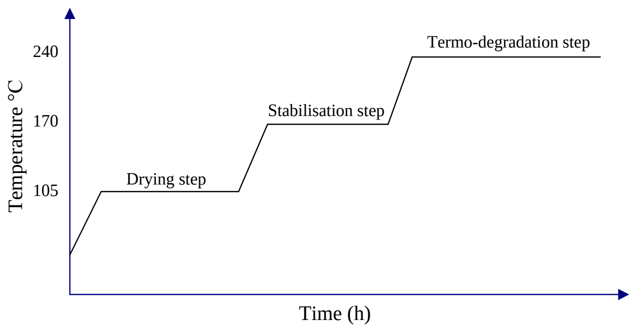


Fig. 2 Typical heat treatment schedule

The samples were dried in an oven at 103°C then divided into two groups *G*1 and *G*2. Given the physical and chemical affinity of the cork with wood, it was considered appropriate to apply the same treatment cycle of the wood used by Thermowood Association [5].

The *G*2 samples were heat treated according to the diagram in Fig. 2.

2.2. Experimental protocol

It consists, firstly, of preparation of shavings according to the geometrical (in form of plate), direction of cutting (radial or axial), drying aspects and according to their masses. The drying, at 105°C, causes significant losses in mass, which gives tremendous decrease in density $\rho$ (kg m$^{-3}$). This phenomenon has been confirmed by Mir [6].

Secondly, the experimental set-up is illustrated in Fig. 3 into two parts, the impregnation of cork in an aqueous solution (NaCl) (Fig. 3, a) and finally, the shavings are introduced into initially distilled and ionized water (Fig. 3, b). As the measurement of the evolution of the concentration represents the image of electric conductivity (Eq. (1)), the experiment is repeated at a number of different temperatures in the radial direction for both untreated and treated group.

The fluid concentration in function of time is attained at through electric conductivity, thus

$$C_{NACL}(mM) = \frac{(\Lambda_{NaCl})_t - (\Lambda_{NaCl})_{t=0}}{\lambda_{Na^+}(T) + \lambda_{Cl^-}(T)}, \quad (1)$$

where $\Lambda_{NaCl}$ the conductivity of the fluid indicated by the conductimeter; $\lambda_i$ the equivalent conductivity of the ion *i* given by the extrapolated value for an infinite dilution.

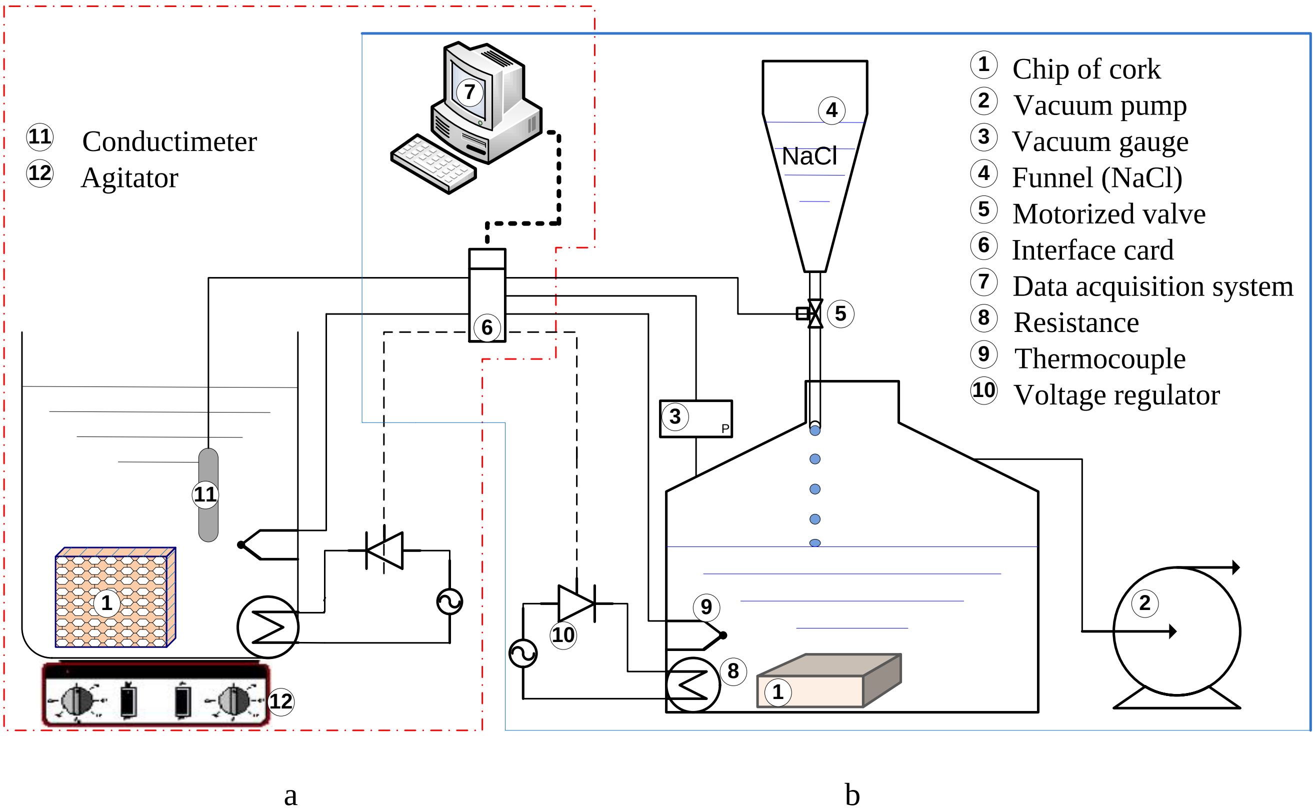


Fig. 3 Illustration of the: a - vacuum impregnation of the sample; b - measurement of concentration of desorption

**3. Modeling**

Our model is based on the mass balance of chemical species diffusing through an elementary volume of the composite. The general equation governs the diffusion mass transfer for different geometries of the composite.

The model is based on the fact that the composite has an initial concentration $c_0$ and remains in a stirred media for a concentration $c_\infty$.

The coefficient of surface mass transfer *k* is considerable as the surface concentration $c_s$ still constant and is equal to $c^*$ while starting the process $c^* = k\, c_\infty$.

One determines the concentration distribution in side the composite for a finite simple geometry during desorption. This consideration can be explained in dimensionless form, as in our case it works in the absence of terms of production and convection, and then we get:

$$\frac{\partial c_i(\zeta,t)}{\partial t} - D_{iapp}\left[\frac{\partial c_i^2(\zeta,t)}{\partial \zeta^2} - \frac{\beta}{\zeta}\frac{\partial c_i(\zeta,t)}{\partial \zeta}\right] = 0. \quad (2)$$

Since the chip has a plate shape, $\beta = 0$ [7].

According to the simplifying assumptions, to the boundary conditions and to the initial condition the system to be solved takes the following form of model:

$$\frac{c_i(x,t)-c_{i0}}{c_{ip}-c_{i0}}=\sum_{n=0}^{\infty}(-1)^n\left\{erfc\left[\frac{(2n+1)\left(\frac{l}{2}\right)-x}{2\sqrt{D_{iapp}\,t}}\right]+erfc\left[\frac{(2n+1)\left(\frac{l}{2}\right)+x}{2\sqrt{D_{iapp}\,t}}\right]\right\}, \tag{3}$$

or

$$\frac{m_t}{m_f}=1-\frac{8}{\pi^2}\sum_{n=0}^{\infty}\left\{\frac{1}{(2n+1)^2}\,exp\left[-\frac{(2n+1)^2\pi^2 D_{iapp}}{l^2}\,t\right]\right\}. \tag{4}$$

Similarly, it will be possible to reach the quantity of the substance released experimentally at time $t$ $(m_t)_{exp}$ from the instantaneous concentration $(c_t)_{exp}$ measured by the conductivity:

$$(m_t)_{exp}=(c_t)_{exp}\,v_{sol}\,, \tag{5}$$

where $c_i$ concentration of the chemical species ($i$) diffusing (mol/m$^3$); $D_{iapp}$ the diffusivity of species ($i$) apparent, $m_t$ mass of the substance released at time $t$:

$$m_t=\int_0^t J_0\,dt \tag{6}$$

and $m_f$ mass substance transferred after total desorption from the shaving after an infinite time:

$$m_t=\int_0^{\infty} J_0\,dt\,, \tag{7}$$

$C_i$ reduced concentration $C_i=\frac{c_i-c_{i0}}{c_{ip}-c_{i0}}$ and $l$ is the thickness of the sample; $J_0$ flux density of the interfacial material:

$$J_0=D_{iapp}\left.\frac{\partial c_i}{\partial x}\right|_{x=\pm\frac{l}{2}}. \tag{8}$$

We recall here: $ierfc(x)$ is the integral of the complementary error function $x$.

## 4. Results and discussions

Fig. 4 illustrates the tremendous increasing of the coefficient of diffusion with temperature. It is also seen that the experimental results and those of numerical modeling are in perfect agreement.

This is confirmed by the Arrhenius law and the Nernst-Einstein relationship (Eq. (9)) [8], which enable us to determine, the $D_{app}$ along with the tortuosity $\tau$ and porosity $\varepsilon$ after the computation of $D_A$ (effective diffusivity for NaCl).

$$D_{app}=D_A\frac{\varepsilon}{\tau^2}\,, \tag{9}$$

with $D_A=D_{Na^+Cl^-/H_2O}=5.4033\times10^{-8}T$ .

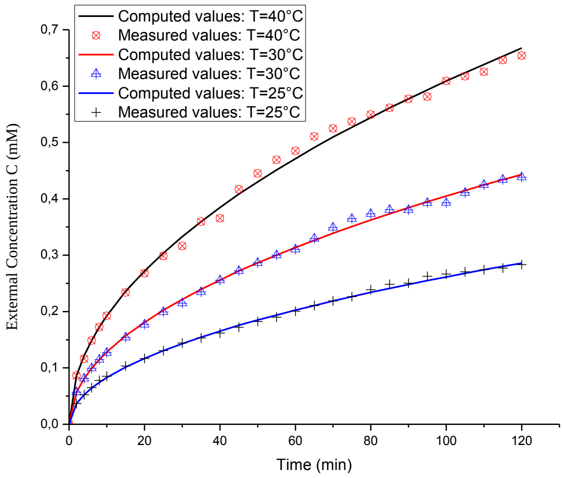


Fig. 4 Model validation ($G1$ samples and radial direction)

Table

Diffusion coefficients of cork in isothermal conditions (radial direction)

| Sample | Temperature | 25°C | 35°C | 40°C |
|---|---|---|---|---|
| $G1$ | $D_{app}\times10^{11}$ (m$^2$s$^{-1}$) | 2.95 | 4.47 | 6.04 |
| $G2$ | $D_{app}\times10^{12}$ (m$^2$s$^{-1}$) | 5.02 | 6.46 | 9.01 |

Note that this coefficient is about $10^{-11}$ in order for the untreated cork and $10^{-12}$ for the treated cork (Table) which is in perfect accordance with the experimental results [8].

Furthermore this coefficient increases with temperature, which induces dilation of the pores of our material and an increase in the water entropy: these two factors contribute to strong mass diffusion.

Fig. 5 shows the influence of high temperature treatment. Indeed, it gives a decrease of the Released mass released (apparent diffusion coefficient $D_{app}$). This phenomenon is due to chemical modifications confer with the new Cork properties, involves several reactions of polymer degradation and synthesis giving numerous reaction products as the study of wood [9, 10], such as, the polysaccharides are the most heat sensitive components: at 200°C, hemicelluloses disappear and cellulose is degraded to a considerable extent.

The lignin polymer structure is modified [11, 12], the ratio between the amorphous and the crystalline cellulose is also changed [13], hemicelluloses are strongly decomposed [14, 15].

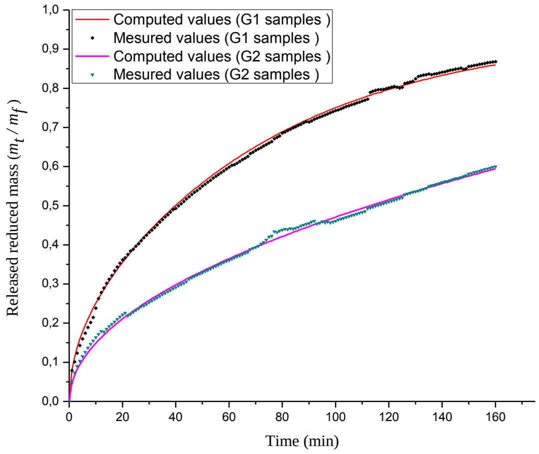


Fig. 5 Model validation (radial direction)

These changes increase the tortuosity of the cork which is inversely related to the mass diffusion coefficient as shown in Fig. 5.

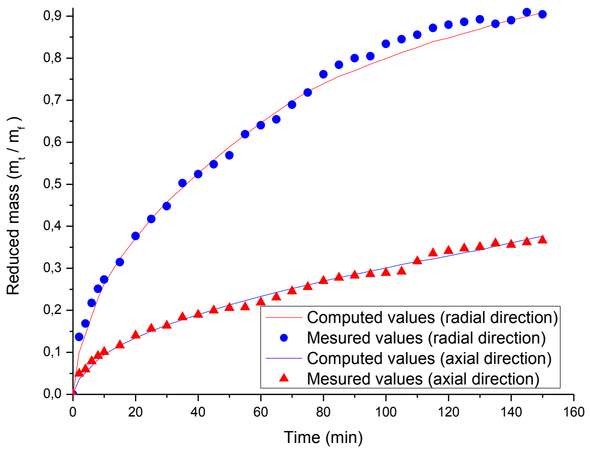


Fig. 6 Effect of direction on the reduced mass

Fig. 6 shows the evolution of the reduced mass in function of time for both radial and axial direction. Firstly, it is clearly seen that this is a good agreement between model results and those determined experimentally. Secondly, $D_{app}$ increased as we shift from axial to radial direction.

## 5. Conclusion

These structural changes, together with the chemical alteration of the cell wall material, explain the observed effects on the mechanical properties.

A study of morphologic transformations of cork during heat treatments was made using diffusion coefficient variation.

The effect of pyrolysis of cork was studied under experimental protocol described conductimetric and by applying the mathematical model of the kinetics of the chemical species (NaCl). The coefficient of mass diffusion in the radial direction of the cork has been determined, it is of the order of $10^{-11}$ in their natural state and decreases by a factor of 6 in the treated state. It increases with temperature in the same configuration. This confirms the Arrhenius relationship. This finding, in a forthcoming study shows that further studies are still needed to precisely define the appropriate treatment, in terms of temperature and duration of treatment.

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AUKŠTOSE TEMPERATŪROSE TERMIŠKAI MODIFIKUOTO KAMŠČIO MECHANINĖ ELGSENA

R e z i u m ė

Apdorojimas karščiu dažnai naudojamas kamštyje vykstančių šilumos ir masės mainų charakteristikoms pagerinti. Šioje studijoje laidumo matavimo metodu ištirtas terminio apdorojimo poveikis kamščio (alžyrietiško kamštmedžio) difuzijos koeficientui ($D_{app}$) ir cheminei struktūrai. Terminiškai apdorotas kamštis, palyginti su atitinkamu gamtiniu kamščiu, įgavo didesnį pasipriešinimą difuzijos kryptimi. Izoterminėmis sąlygomis gauti rezultatai tiksliai atitinka Arenijaus priklausomybę.

T. Kermezli, K. Amokrane, A. Bensmaili, A. Gacemi

MECHANICAL BEHAVIOR OF CORK MODIFIED BY HEAT TREATMENT AT HIGH TEMPERATURE

S u m m a r y

Heat treatment is often used for improving the characteristics of heat and mass transfer of cork. In this study the effects of heat treatment on diffusion coefficient ($D_{app}$) of Cork (Algeria cork) were examined, by the conductimetric method, and the influence on the treated chemical structure gave a decrease in this coefficient, this heat treatment offers more resistance to the mass diffusivity when compared with the corresponding natural cork in the direction of diffusion. The results found in isothermal conditions, faithfully represent the Arrhenius relationship.

**Keywords:** cork, heat treatment, diffusion coefficient, conductimetric.

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