THERMODYNAMIC CHARACTERISATION OF PARTICLEBOARD USING SORPTION ISOTHERMS

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ABSTRACT

The sorption and desorption isotherms of standard particleboard were obtained in this study using the equilibrium moisture contents achieved by applying the gravimetric method of saturated salts at 35°C and 50°C in the water activity range of 0.11 to 0.89. The curves were fitted following the Guggenheim, Anderson and Boer-Dent model, and the isosteric heat of sorption was obtained by means of the Clausius-Clapeyron integration method. The results show that although particleboard has a thermodynamic behaviour which is qualitatively similar to solid wood, its hygroscopic behaviour is nonetheless different, as the monolayer becomes saturated by chemisorption before physisorption starts to prevail over chemisorption.

KEY WORDS: sorption, isotherm, particleboard, isosteric heat, heat of wetting

INTRODUCTION

Very few studies have been made of the thermodynamic properties of wood. While some studies have been made on solid wood (Cao and Kamdem 2004), wood pulp and lignin (Sciban and Klasnja 2004), and even on bamboo (Peralta et al. 1997), none appear to have been made to determine the thermodynamic properties of particleboard through the sorption isotherms.

As with all hygroscopic materials, knowledge of the relation between moisture content and water activity through the sorption isotherms is important for predicting quality, stability and shelf-life (Labuza 1984), particularly in aggressive applications such as formwork, marine environments, roof slopes and external cladding.
Sorption isotherms are commonly used for studying the hygroscopic behaviour of wood and products derived from wood, and for explaining the sorption processes and their relation to the –OH groups in the cell wall (García Esteban et al. 2004, 2005). For the same environmental conditions, particle boards present different equilibrium moisture content (EMC) values from solid wood (Shida 1991, Bader et al. 2007). This is due to the neutralisation of some –OH groups in the cell wall by the adhesives used, which in turn condition different EMC depending on their composition (Sekino and Asakura 1993).

While the fixing of water vapour by the –OH groups in the cell wall is an exothermic process, the loss of the water vapour is endothermic. The heat of adsorption and desorption is a measurement of the energy required to break the intermolecular forces between the water vapour and the substratum (Al-Muhtaseb et al. 2004).

This process can be studied using thermodynamics, by means of the sorption isotherms (Hunter 1991, Avramidis 1992, Aviara et al. 2004). In fact, the isosteric heat of sorption is an indicator of the total number of hydroxyl groups which are accessible to water (Avramidis 1997). It is also an indicator of the state of the water adsorbed by the substratum (McMinn and Magee 2003) and it measures the bond strength between the water molecules and the wood (Avramidis 1997, Quirijns et al. 2005). Knowledge of the isosteric heat of sorption and of the sorption isotherms provides a very important method for characterising a material and studying its interaction with gaseous systems (Wadsö 1997).

The aim of this study was to establish the sorption isotherms of standard particleboard manufactured in Spain and to use the isotherms to determine its thermodynamic properties: net isosteric heat of sorption and total heat of wetting.

MATERIAL AND METHODS

The particleboards used for this study were of the standard type, 19 mm thick with an average density of 633 kg/m³. The samples came from ten boards taken from the same production line at a Spanish factory. The boards are made up of pine wood (*Pinus pinaster* Aiton, *Pinus radiata* D. Don), eucalyptus wood at less than 10% (*Eucalyptus globulus* Labill), and urea-formaldehyde adhesive. A cutting blade was used to obtain samples for the thermostatic baths with the following measurements: 1 mm thick in the dimension parallel to the long dimension of the board, 5 mm wide in the dimension perpendicular to the long dimension of the board and 10 mm long in the thickness dimension of the board.

The isotherms were plotted by using the saturated salt method in thermostatic baths. In order to verify the baths, microcrystalline cellulose was used in accordance with the Community Bureau of Reference protocol, Certified Reference Material CRM 302: “Water content of microcrystalline cellulose (MCC) in equilibrium with the atmosphere above specified aqueous saturated salt solutions at 25ºC”. Once the moisture findings were obtained for each salt, they were compared with the certified values of the Community Bureau of Reference, CRM 302 (Community Bureau of Reference 1989, Jowitt and Wagstaffe 1989).

Ten equilibrium points were obtained for each isotherm, corresponding to the ten salts shown in Tab. 1.

The desorption isotherms were plotted first, by placing the samples in saturation in *K₂SO₄* at 35º and 50º C respectively for one month. It was considered that saturation had been reached when the results of two consecutive weighings taken twenty four hours apart differed by no more than 0.1%. Next, 10g of board was placed in each sorbostat with its corresponding salt. It
took 40 days to reach desorption equilibrium, and it was considered that equilibrium had been reached in each salt, as in the previous case, when the results of two consecutive weighings taken twenty four hours apart showed a difference of no more than 0.1%. Once desorption equilibrium was reached, the samples were placed in a desiccator with phosphorous pentoxide in order to reach the anhydrous state. The EMC were obtained through the equation:

\[
EMC(%) = \frac{W_W - W_0}{W_0} \times 100
\]  
(1)

\(W_W\): wet weight  
\(W_0\): ovendry weight

Once anhydrous weight was reached, the adsorption isotherms were plotted following the same criteria as for desorption. This process took 30 days.

For the plotting of the isotherms, the Guggenheim, Anderson and Boer-Dent (GAB) model was used. This model is particularly appropriate for obtaining a good fit in studies involving relative humidities of more than 90%, when adsorption through capillarity and the multilayer effect play a relevant role (Viollaz and Robedo 1999).

The sigmoid fit for the Guggenheim, Anderson and Boer-Dent model corresponds to the equation:

\[
X = \frac{KC_\infty a_w}{(1 - Ka_w)(1 - Ka_w + C_g Ka_w)} X_m
\]  
(2)

\(X\): equilibrium moisture content  
\(X_m\): monolayer saturation moisture content  
\(C_g\): Guggenheim constant  
\(K\): constant  
\(a_w = RH\): relative humidity or water activity on a scale of zero to one

The fit, both for desorption and adsorption, was considered valid if the regression coefficient \(R\) was higher than 0.990 and the root mean square (RMS%) was lower than 4% (Viollaz and Rovedo 1999, Bacour and Daudin 2000, García Esteban et al. 2004, 2006).

The thermostatic baths used were of the Grant brand, model Y38, with a 38-litre capacity, forced circulation, a range of 20–99°C and a precision of 0.1°C. The scales used for the weighings were of the Sartorius brand, model Handy H110, with a range of 0–100 g and a precision of 0.0001 g. The oven used to reach the anhydrous weight was of the Heraeus brand, model VT6025, with a range of 0–200°C and a precision of 0.1°C. The MATLAB 6.5.0 Release 13 programme was used for fitting the sorption isotherms and for calculating the net isosteric heats and the total heat of wetting.

The thermodynamic parameters obtained through the isotherms were: net isosteric heat of sorption and total heat of wetting.

The total isosteric heat of sorption is obtained by means of Avramidis’s (1997) equation, which relates the three types of energy participating in the sorption process (Fig. 1):

\[
Q_s = q_s + \Delta H_{evap}
\]  
(3)

where,

\(Q_s\): Total isosteric heat of sorption: Energy released when water is absorbed by the
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sorption points in the cell walls, or energy required to evaporate the water from its bound water phase.

$\Delta H_{\text{vap}}$, Latent vaporisation heat: Energy released when the water vapour condenses, or energy required to evaporate the water from its liquid phase.

$q_s$, Net isosteric heat of sorption: Differential energy, differential enthalpy or energy released when the liquid water molecules are absorbed. Also defined as the amount of energy above the latent vaporisation heat of the water associated with the sorption process (McMinn and Magee 2003, Moreira et al. 2005).

Fig. 1: Types of energy participating in the sorption process (Skaar 1988, Avramidis 1997)

For the calculation of the net isosteric heat of sorption the Clausius-Clapeyron integration method was used (Skaar 1988, Kiranoudis et al. 1993, Peralta et al. 1997). This is a widely used method recommended for obtaining the isosteric heat of food products, as the results do not show significant differences in relation to the graphic method (Mulet et al. 2002, Chen 2006).

\[
q_s = -R \cdot \frac{d(\ln(a_w))}{d(1/T)}
\]  

(4)

$q_s$: net isosteric heat

$a_w$: water activity

$T$: absolute temperature

$R$: universal gas constant

This method requires at least two isotherms at close temperatures (Skaar 1988, Peralta et al. 1997, Arslan and Toğrul 2006, Chen 2006) and considers that $q_s$ is independent of the temperature (Kiranoudis et al. 1993, Vazquez et al. 1999, Kaya and Kahyaoglu
This presupposes that the sorption process is reversible, which is not entirely true due to the phenomenon of hysteresis. However, there is experimental evidence indicating that cellulosic materials exposed to successive cycles of adsorption and desorption undergo a reduction in the hysteresis cycle, which means that the sorption process can be considered reversible (Peralta et al. 1997, García Esteban et al. 2005).

The heat involved in the sorption process from the fibre saturation point to oven drying, known as total heat of wetting (Siau 1995), was obtained by integrating the net isosteric heat curve (Avramidis 1997).

\[ W_0 = \int_0^{m_c} q_s \cdot dm \]  

(5)

\( W_0 \): total heat of wetting  
\( q_s \): net isosteric heat of sorption.  
\( m_c \): moisture content of fibre saturation point

RESULTS AND DISCUSSION

The equilibrium moisture contents for plotting the 35°C and 50°C isotherms are shown in Tab. 1.

Tab. 1: Equilibrium moisture contents (EMC) for the 35°C and 50°C isotherms

<table>
<thead>
<tr>
<th>Salt</th>
<th>( a_w )</th>
<th>EMC (%)</th>
<th>( a_w )</th>
<th>EMC (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>adsorption</td>
<td>desorption</td>
<td>adsorption</td>
<td>desorption</td>
</tr>
<tr>
<td>LiCl</td>
<td>0.1117</td>
<td>3.86</td>
<td>4.52</td>
<td>0.1105</td>
</tr>
<tr>
<td>KC(_2)H(_3)O(_2)</td>
<td>0.2137</td>
<td>5.53</td>
<td>6.42</td>
<td>0.2006</td>
</tr>
<tr>
<td>MgCl(_2)·6H(_2)O</td>
<td>0.3200</td>
<td>6.92</td>
<td>7.69</td>
<td>0.3054</td>
</tr>
<tr>
<td>K(_2)CO(_3)</td>
<td>0.4255</td>
<td>8.11</td>
<td>9.06</td>
<td>0.4091</td>
</tr>
<tr>
<td>MgN(_2)O(_6)·6H(_2)O</td>
<td>0.4972</td>
<td>9.13</td>
<td>10.10</td>
<td>0.4544</td>
</tr>
<tr>
<td>BrNa</td>
<td>0.5455</td>
<td>9.83</td>
<td>11.06</td>
<td>0.5093</td>
</tr>
<tr>
<td>SrCl(_2)·6H(_2)O</td>
<td>0.6608</td>
<td>11.81</td>
<td>13.23</td>
<td>0.5746</td>
</tr>
<tr>
<td>NaCl</td>
<td>0.7511</td>
<td>13.83</td>
<td>15.34</td>
<td>0.7484</td>
</tr>
<tr>
<td>KCl</td>
<td>0.8295</td>
<td>15.58</td>
<td>17.14</td>
<td>0.7902</td>
</tr>
<tr>
<td>BaCl(_2)·2H(_2)O</td>
<td>0.8940</td>
<td>19.82</td>
<td>19.49</td>
<td>0.8823</td>
</tr>
</tbody>
</table>

\( a_w \) = RH: relative humidity or water activity on a scale of zero to one

The four isotherms show fits to a type II sigmoid (C>2) (Tab. 2) (Fig. 2 and 3) (Labuza 1984, Singh and Singh 1996). The fits made to the GAB curve present very satisfactory results, as the correlation coefficient is higher than 0.990 in all cases and the root mean square is lower than 4% (Viollaz and Rovedo 1999 Bacour and Daudin 2000, García Esteban et al. 2004, 2006).
Tab. 2: Parameters for fitting the isotherms to the GAB curve. Confidence intervals 95% significant.

<table>
<thead>
<tr>
<th>Isotherm</th>
<th>35°C</th>
<th>50°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$X_m$</td>
<td>$K$</td>
</tr>
<tr>
<td>Adsorption</td>
<td>6.31±0.11</td>
<td>0.75±0.20</td>
</tr>
<tr>
<td>Correlat. coeff</td>
<td>0.99</td>
<td>0.07</td>
</tr>
<tr>
<td>RH(%)</td>
<td>32.3</td>
<td>6.9</td>
</tr>
<tr>
<td>Desorption</td>
<td>7.43±0.06</td>
<td>0.71±0.11</td>
</tr>
<tr>
<td>Correlat. coeff</td>
<td>0.99</td>
<td>0.13</td>
</tr>
<tr>
<td>RH(%)</td>
<td>34.3</td>
<td>8.1</td>
</tr>
</tbody>
</table>

\(^{(1)}\) Point of inflection of the isotherm.

Tab. 2 shows the points from which physisorption or physical adsorption begins to prevail over chemisorption (EMC$_{a,d}$). These points were obtained by using the minimum of the derivative of the equilibrium moisture content in relation to the relative humidity (Avramidis 1997).

![Adsorption isotherms](image)

Fig. 2: Adsorption isotherms
Fig. 3: Desorption isotherms

In the four isotherms the monolayer saturation moisture content $X_m$ is lower than the point of inflection of the isotherm (EMC$_{a,d}$) mentioned above. This means that the saturation of the –OH groups in the monolayer occurs in all cases before physisorption begins to prevail over chemisorption. This behaviour is different from that obtained for new or old non-glued solid wood by García Esteban et al. (2006), where the monolayer remained unsaturated from the point of inflection, although the water vapour taken up never exceeded 1%. This behaviour could be due to the fact that the adhesive of the board may have blocked the –OH groups in the monolayer, as the relative humidity values where the points of inflection are produced are very similar in both particleboard and solid wood.

In reference to the equilibrium moisture content values, for a given $a_w$ these decrease as the temperature increases. This is due to the fact that, on the one hand, the increase in temperature in wood causes a decomposition of the cell wall hemicelluloses (Stamm 1964) and, on the other hand, it provides the water molecules joined to the substratum with enough energy to break their bonds (Hossain et al. 2001, McMinn and Magee 2003, Lahsasni et al. 2004, Yazdani et al. 2006).

In terms of the thermodynamic characterisation of particleboard, the results obtained for the net isosteric heat concur with those obtained by other authors (Tsami 1991, Kaymak-Ertekin and Sultanoğlu 2001, McMinn and Magee 2003, Al-Muhtaseb et al. 2004, Moreira et al. 2005, Yazdani et al. 2006). For values above the fibre saturation point (FSP), the net isosteric heat values are higher in desorption than in adsorption for any given equilibrium moisture content (Tab. 3) (Fig. 4). For this type of particleboard, the maximum value in desorption is 424.49 J/mol as opposed to 228.44 J/mol in adsorption. From the fibre saturation point, 25% EMC, the two curves are virtually parallel. This indicates, on the one hand, that the bond energy is greater in desorption than in adsorption, possibly due
to the number of bonds lost in the hysteresis cycle (Moreira et al. 2005) and, on the other hand, that the energy required in the desorption process is greater than that required in the adsorption process (Kaymak-Ertekin and Sultanoglu 2001; Lahsasni et al. 2004), which is most likely due to the higher presence of active polar groups on the surface of the material during sorption (Tsami 1991).

Tab. 3: Thermodynamic parameters

<table>
<thead>
<tr>
<th></th>
<th>Adsorption</th>
<th>Desorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>FSP (%)</td>
<td>Maximum</td>
<td>Minimum</td>
</tr>
<tr>
<td></td>
<td>Net isosteric heat (J/mol)</td>
<td>Total heat of wetting (J/mol dry wood)</td>
</tr>
<tr>
<td></td>
<td>25.5</td>
<td>228.44</td>
</tr>
</tbody>
</table>

Fig. 4: Comparison of the net isosteric heat of sorption in adsorption and desorption

The fact that the net isosteric heat of sorption increases as the equilibrium moisture content decreases (Fig. 4) is an indication of the high interaction energy existing between the water molecules and the substratum at low equilibrium moisture contents (Maskan and Göğüş 1997, Moreira et al. 2005). This rapid increase may be due to the existence of highly active polar groups on the surface of the material, which would initially form the monolayer (Tsami 1991, McMinn and Magee 2003, Al-Muhtaseb et al. 2004, Lahsasni et al. 2004, Yazdani et al. 2006), followed by polar groups with lower activation energy (McMinn and Magee 2003).
In contrast to this, the fact that the net isosteric heat of sorption decreases the greater the equilibrium moisture contents are indicates a decrease in the bond energy between the water and the substratum (Maskan and Göğüş 1997). This behaviour has been observed in other hygroscopic materials (Kiranoudis et al. 1993, Kaya and Kahyaoglu 2006), including wood (Skaar 1988, Peralta et al. 1997).

Finally, the total heat of wetting is greater in desorption than in adsorption: 3865.0 J/mol as opposed to 1918.1 J/mol. This was to be expected, given that the curve for the net isosteric heat in adsorption is lower than in desorption, which means that the heat involved in the desorption process is greater than in the adsorption process.

CONCLUSIONS

- In standard particleboards the monolayer is saturated by chemisorption before physisorption begins to prevail over chemisorption.
- Qualitatively, the thermodynamic behaviour of particleboard is similar to that of solid wood.
- The net isosteric heat decreases as the water content of the sample increases.
- The net isosteric heat is greater in desorption than in adsorption, which indicates greater bond energy between the water molecules and the substratum during the desorption process.
- The total heat of wetting is greater in desorption than in adsorption, which indicates that the energy involved in the desorption process is greater than in adsorption.

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