

THE WATER VAPOUR SORPTION
BEHAVIOUR OF WOOD

BY

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award of Doctor of Philosophy

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DECLARATION

This is to certify that the thesis comprises of only my original work towards the PhD except where indicated. This thesis contains no material which has been accepted for the award of any other degree or diploma in any University and is less than 100,000 words in length exclusive of tables, figures and references. Based on my knowledge, this thesis contains no material previously published or written by another person, except where due reference has been made. My contribution towards this work included all of the experimental work, sample preparation, data gathering and data analysis.

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ABSTRACT

The water vapour sorption properties of several commercial tropical hardwoods and temperate softwood species as well as thermally modified wood and acetylated wood has been studied. A dynamic vapour sorption apparatus was used for this investigation to give data on the sorption isotherms under equilibrium conditions as well as sorption kinetic behaviour. Small differences in the sorption isotherms were found between the wood species, but modification resulted in substantial changes to the sorption isotherms. The sorption isotherms were analysed using the Hailwood-Horrobin model. Sorption kinetics behaviour was found to be accurately described using the parallel exponential kinetics (PEK) model. This model has only recently been applied to wood and this work represents a much more comprehensive study of the applicability of the model. Until now the favoured approach has been based upon Fickian models. The conventional interpretation of the PEK model relies upon the idea of different types of sorption sites, but his work has shown (partly based upon Hailwood-Horrobin analyses of the isotherms) that this interpretation is not applicable. Instead, an interpretation based upon relaxation limited kinetics has been adopted. These ideas are commonly employed in the polymer science literature, but have hardly been used in wood science. The model employed was that involving two Kelvin-Voigt elements in series, from which cell wall moduli and viscosities have been determined. The values of the moduli appear sensible, but the model is only tentative at this stage. The kinetic data has also been used to determine activation energies, entropies and Gibbs free energy of sorption. This is the first time that the entropy and Gibbs free energy of sorption have been studied. The purpose of this work was to understand the phenomenon of sorption hysteresis and in particular to examine if there was a link between sorption hysteresis and sorption kinetics.

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LIST OF ABBREVIATIONS

BET	Brunauer-Emmett-Teller
K-V	Kelvin-Voigt
H-H	Hailwood and Horrobin
GAB	Guggenheim-Anderson-de Boer
p-FSP	projection fibre saturation point
IUPAC	International union of pure and applied chemistry
W	molecular weight
Mh	monolayer
Ms	polylayer
RH	relative humidity
EMC	equilibrium moisture content
DVS	dynamic vapour sorption
OH	hydroxyl groups
R ²	regression coefficient
PEK	parallel exponential kinetics
X _o	number of moles of unhydrated polymer
X _h	number of moles of hydrated polymer
X _s	number of moles of dissolved water
H	hydrogen
A/D	adsorption/desorption
IUPAC	International Union of Pure and Applied Chemistry
NMR	nuclear magnetic resonance
DTA	differential thermal analysis
<i>T_g</i>	glass transition temperature
TMW	thermally modified wood
AH	absolute hysteresis
R	the universal gas constant
T	the absolute temperature
ε	strain

φ	time constant
Π	swelling pressure
σ_0	stress
p	water vapour pressure
p_i	water vapour pressure (initial)
p_f	water vapour pressure (final)
M	molecular weight of water
E	modulus
η	viscosity
n	Avogadro's number
k	the rate constant
A	the collision factor
h	Planck constant
h	hour
min	minute
HR	hysteresis ratio
k_1	rate constant for fast process
k_2	rate constant for slow process
E_a	activation energy
ΔS_a	entropy of activation
ΔG_a	Gibbs free energy of activation