Water sorption thermodynamics and transport in polymer matrices

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OUTLINE

- General framework and motivation
- Overview of modelling approach for water sorption thermodynamics in glassy and rubbery polymers accounting for Hydrogen Bonding (HB)
- Overview of experimental strategy: combining gravimetry with FTIR spectroscopy
- Analysis of water sorption thermodynamics and mass transport in selected glassy polymer/water and rubbery polymer/water systems
General framework and motivation: effects of absorption of water in polymers

✓ **Plasticization**: different mechanisms and efficiency related to the type of interactions penetrant molecules establish with the matrix. Penetrant can also act as an “antiplasticizer”.

✓ **Changes of physical properties**: $T_g$ depression, decrease of mechanical moduli, decrease of yield strength, change of yield/deformation mechanisms.

✓ **Hygrothermal and chemical degradation**: microcrazes and microcracks, aging, chain scission through hydrolysis and other reactions, degradation of fiber/matrix interface in composites.

✓ **Swelling stresses**
Schematic illustration of possible moisture sorption locations and mechanisms in composites

Main features of low m.w. solute sorption thermodynamics in polymers

- Molecular dispersion of the penetrant with **no specific interaction**
- Polymer-polymer, polymer-solute and solute-solute **specific interactions** (e.g. HB)
- **Excess free volume** (glassy polymers)
- Polymer **sub-T_g relaxation** (glassy polymers)
Goals

- Understanding and modelling sorption thermodynamics and mass transport of water in rubbery and glassy polymers

- Quantitative prediction of the amount of different water species as well as of self and cross H-bonding interactions

- Validation of theoretical approach by comparison with combined gravimetric and in situ FTIR spectroscopy measurements
Strategy

Combine:
- gravimetric analysis
- difference FTIR spectroscopy with curve resolving analysis
- 2D-FTIR correlation spectroscopy

to gather experimental information in terms of interactions sites and water populations to be used for development and validation of a model for water sorption and transport
Modelling:
Water sorption thermodynamics in rubbery polymers with Lattice Fluid theories
Non Random Hydrogen Bonding (NRHB) model
EOS Lattice Fluid (LF) theories grounded on statistical thermodynamics

**Equation of state (EOS)**

\[
\tilde{P} + T \left[ \ln(1 - \tilde{\rho}) - \tilde{\rho} \left( \sum_{i=1}^{2} \phi_i \frac{l_i}{r_i} - v_H \right) - \frac{z}{2} \ln \left( 1 - \tilde{\rho} + \frac{q}{r} \tilde{\rho} \right) + \frac{z}{2} \ln \Gamma_{00} \right] = 0
\]

**Chemical potential of penetrant**

\[
\frac{\mu_1}{RT} = \ln \frac{\phi_1}{\omega_1 \tilde{r}_1} - r_1 \sum_{j=1}^{2} \frac{\phi_{1,j} l_j}{r_j} + \ln \tilde{\rho} + r_1 (\bar{v} - 1) \ln (1 - \tilde{\rho}) - \frac{z}{2} r_1 \left[ \bar{v} - 1 + \frac{q_1}{r_1} \right] \ln \left[ 1 - \tilde{\rho} + \frac{q}{r} \tilde{\rho} \right]
\]

\[
+ \frac{z q_1}{2} \left[ \ln \Gamma_{11} + \frac{r_1}{q_1} (\bar{v} - 1) \ln \Gamma_{00} \right] + r_1 \frac{\tilde{P} \tilde{\nu}}{\nu_1} - \frac{q_1}{q_1} + \frac{\mu_{1,H}}{RT}
\]

with

\[
\frac{\mu_{1,H}}{RT} = r_1 v_H - \sum_{i}^{m} d_i^1 \ln \left( \frac{V_i^d}{V_{i0}} \right) - \sum_{j}^{n} a_j^1 \ln \left( \frac{V_j^a}{V_{0,j}} \right)
\]

Non random lattice fluid contribution

Hydrogen Bonding contribution
Non Random Hydrogen Bonding (NRHB) model

Model parameters:

\( \psi \): mean field interaction parameter

\( E_{0ij}, S_{0ij} \): Energy and entropy of formation of HB between a proton acceptor of type ‘i’ and a proton donor of type ‘j’.

Types and number of proton acceptors and proton donors is suggested by IR spectroscopic analysis
Modelling: Water sorption thermodynamics in glassy polymers
Extension of equilibrium EOS theories to nonequilibrium glassy polymer – solute mixtures

**NETGP (Non Equilibrium Theory Glassy Polymers)**


**Mixtures with an internal state variables**

The glassy polymer – solute mixture is considered a thermodynamic system endowed with an internal state variable(s).

Nonequilibrium expression of Gibbs free energy is coupled with the evolution laws of the internal state variables:

\[
\begin{align*}
\bar{G} &= g(T, p, \omega_1, z) \\
\frac{\partial z}{\partial t} &= f(T, p, \omega_1, z)
\end{align*}
\]
NELF (Non Equilibrium Lattice Fluid)

Polymer density taken as an order parameter and is thermodynamically treated as an internal state variable. The non equilibrium state of the glassy polymer mixture is hence defined by

\[ T, \rho, \omega_1, \rho_2 \]

PSEUDO-EQUILIBRIUM HYPOTHESIS

It is assumed that the mixture volume reaches a pseudo-equilibrium value which appears to be asymptotically stable over the time scale of the experiments, although it does not represent the true final equilibrium value.

\[ \bar{G} \] is taken from LF-EOS theory with no HB contribution. The actual density of the mixture is used and not its equilibrium value.

\[ z = \rho_2 \]
\[ f(T, p, \rho_{2,\infty}, \omega_1) \cong 0 \]
\[ \rho_2 = \rho_{2,\infty} \neq \rho_{2,\text{EQ}} \]

\[
\begin{align*}
\bar{G} & = g(T, p, \omega_1, \rho_{2,\infty}) \\
\frac{\partial \rho_2}{\partial t} & = f(T, p, \omega_1, \rho_{2,\infty}) \cong 0
\end{align*}
\]
NELF: extension of simple LF theories with no HB to glassy systems

Sorption pseudo-equilibrium condition

\[ \alpha = \left( \frac{\partial G}{\partial \rho_2} \right)_{T, p, n_1, n_2} \neq 0; \quad \rho = \frac{\rho_{2,\infty}}{\omega_2} \]

\[ \alpha \equiv \text{affinity to the internal state variable } \rho_2 \]

\[ \mu_{1,\text{GAS}}(T, p) = \mu_{1,\text{POL}}(T, p, \omega_1, \rho_2 = \rho_{2,\infty}) = \left( \frac{\partial G}{\partial n_1} \right)_{T, p, n_2, \rho_{2,\infty}} = \]

\[ RT \{ \ln(\bar{\rho} \phi) - \left[ r_1^0 + (r_1 - r_1^0) / \bar{\rho} \right] \ln(1 - \bar{\rho}) - r_1 - \bar{\rho} \left[ r_1^0 v_1^*(p_1^* + p^* - \phi_2^2 \Delta p^*) \right] \} \]
Extension of NRHB to glassy system: 
**NETGP-NRHB**


There are now three sets of order parameters: \( \rho_2, \Gamma_{ij}, N_{ij} \)

\( \rho_2 \)

As in the case of NELF \( \rho_2 = \rho_{2,\infty} \neq \rho_{2,eq} \) - **pseudo eq. hypothesis**

\( N_{ij} \)

The **HB interactions instantaneously** follow the density change according to the equations valid for equilibrium systems

\( \Gamma_{ij} \)

The **nonrandomness factors instantaneously** follow the density change according to the equations valid for equilibrium systems
Extension of NRHB to NE glassy system: \textbf{NETGP-NRHB}

Expression of ‘pseudo-equilibrium’ chemical potential of penetrant

\[
\frac{\mu_1}{RT} = \ln \frac{\phi}{\delta r_1} - r_i \sum_{j=1}^{2} \frac{\phi_j l_j}{r_j} + \ln \tilde{\rho} + r_i (\tilde{v} - 1) \ln(1 - \tilde{\rho}) - \frac{\tilde{v}}{2} \ln \left( 1 - \frac{q_1}{r_1} \right) \ln \left[ 1 - \frac{q}{r} \tilde{\rho} \right] + \frac{\tilde{v}}{2} \ln \left( 1 - \frac{r_1}{q_1} (\tilde{v} - 1) \ln \Gamma_0 \right)
\]

\[
\frac{-q_1}{T_1} + \tilde{T} \left[ \ln(1 - \tilde{\rho}) - \tilde{\rho} \left( \sum_i \phi_i l_i \right) - \frac{\tilde{v}}{2} \ln \left( 1 - \frac{q}{r} \tilde{\rho} \right) + \frac{\tilde{v}}{2} \ln \Gamma_0 \right] \frac{r x_2}{\pi x_1} \frac{\partial \tilde{v}}{\partial x_1} \left|_{p,T,\rho_2,N_{ij}^{IE,HB},N_{irs}^{IE,NR}} \right.
\]

\[\frac{\mu_{1,H}}{RT} = r_i v_H - \sum_i d_i \ln \left( \frac{v_i^j}{v_{i0}} \right) - \sum_j a_j \ln \left( \frac{v_j^a}{v_{0,j}} \right) + \frac{\partial \ln \tilde{v}}{\partial x_1} \left|_{p,T,\rho_2,N_{ij}^{IE,HB},N_{irs}^{IE,NR}} \right. x_2 r
\]

with

Non-equilibrium Non random lattice fluid contribution
Model parameters:

\( \psi \): mean field interaction parameter

\( E_{ij}^0, S_{ij}^0 \): Energy and entropy of formation of HB between a proton acceptor of type ‘i’ and a proton donor of type ‘j’.

\( \rho_2 \): density of dry polymer or determined from dilation data on polymer/water mixture

Types and number of proton acceptors and proton donors is suggested by IR spectroscopic analysis
Use of mixture thermodynamics models for glassy and rubbery polymers (NRHB and NETGP-NRHB)

**Fitting** of gravimetric sorption isotherm

**Model parameters**

**Prediction** of amount of each HB established

Information on PA and PD groups from IR spectroscopy
Use of lattice based theories to evaluate $T_g$ of polymer-penetrant mixtures

$T_g$ is evaluated according to in the Gibbs – Di Marzio procedure, i.e. by equating the entropy of the system to zero

Expression for entropy:

$$S_{tot} = S_{random} + S_{non \ random} + S_{HB} = 0$$

$$+$$

EOS:

$$\widetilde{P} + \tilde{T} \left[ \ln(1 - \tilde{\rho}) - \tilde{\rho} \left( \sum_{i=1}^{2} \phi_i \frac{l_i}{r_i} - v_H \right) - \frac{z}{2} \ln \left( 1 - \tilde{\rho} + \frac{q}{r} \tilde{\rho} \right) + \frac{z}{2} \ln \Gamma_0 \right] = 0$$
Experimental: Gravimetric analysis
Experimental:
FTIR vibrational spectroscopy analysis
In-situ FTIR time-resolved transmission spectroscopy

PMDA-ODA

‘wet’

‘dry’

\[ \text{Assorbance} \]

\[ \text{Wavenumbers (cm}^{-1}\text{)} \]

\[ 4000 \quad 3200 \quad 2400 \quad 1800 \quad 1400 \quad 1000 \quad 600 \]

\[ \nu_{\text{OH}} \quad 3562 \quad 3639 \quad 3486 \quad 3075 \quad 1776 \quad 1116 \quad 1093 \quad 823 \quad 726 \quad 605 \quad 519 \quad 428 \]

\[ \delta_{\text{HOH}} \quad 1615 \quad 1597 \quad 1014 \]

\[ \text{LIB}_{\text{H}_2\text{O}} \]
Information on the polymer-water system

Information on interaction sites on polymer backbone:
*shift of carbonyl peak*

Information on interactions of water molecules and on sorption kinetics:
*difference spectroscopy in $\nu_{OH}$ region*
A series of perturbation induced dynamic spectra are collected first in a systematic manner, e.g., in a sequential order during the process. Such a set of dynamic spectra is then transformed into a set of 2D correlation spectra by cross-correlation analysis of spectral intensities.

In the case at hand, a relatively slow ‘external’ perturbation consists in the step change of external water vapour activity.
Main advantages of the 2D correlation spectroscopy:  
**Asynchronous correlation spectrum**

[Isao Noda and Yukihiro Ozaki *Two-dimensional Correlation Spectroscopy – Applications in Vibrational and Optical Spectroscopy*, 2004, John Wiley & Sons]

It identifies dynamical processes having different rates: a non-zero value is present only if the rate constants of the dynamical processes at the two wavenumbers are different. This effect is responsible for the resolution enhancement of the asynchronous spectrum.

The intensity of an asynchronous peak increases as the difference between the rate of change of the relative signals increases.

Additional information supplied:

a) simplification of complex spectra (overlapped peaks)
b) enhancement of spectral resolution
c) unambiguous assignments through correlation analysis of bands selectively coupled by various interaction mechanisms
d) information about dynamics (asynchronous spectral information).
Unambiguous assignments through correlation of bands

3616-3470 cm\(^{-1}\)
3616: vibration associated to ‘free’ H; 3470: vibration associated with ‘interacting’ H

3660-3570 cm\(^{-1}\)
3660: out-of-phase stretching mode 3570: in-phase stretching mode

Optimized geometry of N-phenylphthalamide-H\(_2\)O complex
Quantitative assessment of concentration of each water species based on gravimetric data and spectral deconvolution
Polyimides-H$_2$O system


Investigated polyimide-water systems

PMDA-ODA

\[ T_g = 383^\circ C \]

6FDA-ODA

\[ T_g = 308^\circ C \]

6FDA-6pDA

\[ T_g = 315^\circ C \]
Water vapour sorption at $T=303K$

FTIR difference spectroscopy: water spectra in the OH stretching region

Water sorption isotherms (gravimetrically)

FTIR difference spectroscopy: water spectra in the OH stretching region

P/P_0=0.6
Polyimide-H$_2$O system
Outcomes of FTIR analysis

Cross-associated water molecules
(first shell)

Self-associated water molecules
(second shell)

Results: 2 water ‘species’
Quantitative assessment of each ‘species’ of water
4 identical PA groups (carbonyls) per repeating unit
Quantitative evaluation of concentration of cross- HB formed by water molecules

The possibility exists for a single water molecule to form two H-bonding interactions with two distinct carbonyls, i.e a 1:2 stoichiometry. Each H$_2$O would still produce two peaks (a symmetric and an antisymmetric ν(OH) vibration).

It is not possible at present to discriminate between 1:1 and 1:2 stoichiometry.

Stoichiometry of the adduct will certainly be reflected in the total amount of established cross H-bonding. Thus we may introduce an ‘upper bound’ experimental (1:2 stoichiometry) and a ‘lower bound’ (1:1 stoichiometry).
Quantitative evaluation of concentration of cross- and self-HB formed by water molecules as a function of $a_w$ (1.1. stoichiometry)
Ratio of concentration of first and second (and possibly higher) shell water species as a function of water content (from combined gravimetric and FTIR experiments)

First shell corresponds to **cross-H bonded** water
Second shell corresponds to **self-H bonded** water
Fitting of water vapour sorption isotherms: **NETGP-NRHB model**

![Graph 1: NETGP-NRHB vs 6FDA-ODA](image1)

- **X-axis:** Pressure of water vapour [MPa]
- **Y-axis:** Water mass fraction

![Graph 2: NETGP-NRHB vs 6FDA-6FpDA](image2)

- **X-axis:** Pressure of water vapour [MPa]
- **Y-axis:** Water mass fraction
Prediction of concentration of self-HB and cross-formed by water molecules: \textbf{NETGP-NRHB}
WATER TRANSPORT MECHANISM

Hypothesis of instantaneous non-linear equilibrium among different water species ruled by double layer BET eq. and of concentration dependent diffusivities

Mass balance on sorbed water

\[
\frac{\partial C_w}{\partial t} = \frac{\partial}{\partial x} \left( D_1 \frac{\partial C_{R_1}}{\partial x} \right) + 2 \cdot \frac{\partial}{\partial x} \left( D_2 \frac{\partial C_{R_2}}{\partial x} \right)
\]

\[D_i = D_i^0 \exp[kC_w] = D_i^0 \exp[k(C_{R_1} + 2f(C_{R_1}))]\]

\[C_{R_2} = f_{EQ}(C_{R_1}); \quad C_w = C_{R_1} + 2C_{R_2} = C_{R_1} + 2f_{EQ}(C_{R_1})\]

\[f_{EQ}'(C_1) = \frac{\partial f_{EQ}}{\partial C_{R_1}}; \quad f_{EQ}''(C_1) = \frac{\partial^2 f_{EQ}}{\partial C_{R_1}^2}\]
WATER TRANSPORT MECHANISM

Concentration dependent diffusivities model:
\[ D_{0,1} = 4.5 \cdot 10^{-9} \text{cm}^2/\text{s}; \quad D_{0,2} = 1.7 \cdot 10^{-9} \text{cm}^2/\text{s}; \quad k = 1.55 \text{ cm}^3/\text{mmol} \]
Epoxies-H$_2$O system


**TGDDM-DDS** ($T_g = 278^\circ$C)

\[
\begin{align*}
\text{TGDDM} & + \text{DDS} \\
\end{align*}
\]

**TGDDM-HHPPA** ($T_g = 160^\circ$C)

\[
\begin{align*}
\text{TGDDM} & + \text{HHPPA} \\
\end{align*}
\]

(HesaHydroPhthalicAnhydride)
Spectra of “dry” sample and “wet” sample for epoxy resin at sorption equilibrium at a specific water vapor activity ($a_w=0.4$). $T = 24^\circ C$. 

![Spectra of epoxy resin at sorption equilibrium](image)

- Absorbance vs. Wavenumbers (cm$^{-1}$)
Time resolved difference spectroscopy in the OH stretching frequency range

\( (T = 24^\circ C, a_w=0.4) \)

- **Non-interacting water molecules**
- **H-bonded water molecules**

**Absorbance vs. Wavenumbers (cm\(^{-1}\))**

**TGDDM-DDS**
Simplified association model for water with proton acceptor (PA) groups (simplified 2-D representation).

Proton acceptor groups are **sulphone** group and **amino-alcohol** groups.
TGDDM-DDS

Possible specific interactions of “$S_2$” water molecules with epoxy backbone

$S''_2$: Interaction of $H_2O$ with amino-alcohol group

$S'_2$: Interaction of $H_2O$ with sulphone group
Quantitative assessment of concentration of each water species.

Indication of **instantaneous linear equilibrium** among the different species.

![Graph showing concentration of water species](image-url)
Comparison of TGDDM-DDS and TGDDM-HHPA: difference spectroscopy ($\nu_{OH}$ region), gravimetric isotherms and concentration of each water species
Comparison of TGDDM-DDS and TGDDM-HHPA: different distribution of water species

Proton acceptor groups in TGDDM-HHPA are **ester carbonyls**
Sorption kinetics evaluated spectroscopically and gravimetrically at $a_w = 0.2$ and $T = 24^\circ C$

Same dynamics for all water species

\[ \frac{M_t}{M_\infty}, \frac{A_t}{A_\infty} \]

Graph showing the relationship between $M_t/M_\infty$ and $t$ for TGDDM-DDS, with peak $S_0$, $S_1 + S_2$, gravimetry, and Fick's law indicated.
Diffusion coefficients vs total water concentration

\[ D_{\text{eff}}(C_{\text{TOT}}) = D(C_{\text{TOT}}) \cdot \phi \]

\( D_{\text{eff}}(C_{\text{TOT}}) \): characterizes the overall sorption kinetics

\( D(C_{\text{TOT}}) \): accounts for free volume changes and would characterize transport through the material in the absence of the ‘sticking’ effect due to the molecular interactions

\( \phi \): an ‘interaction’ factor which accounts for the molecular interactions with specific sites (0.35 for TGDDM-DDS, 0.45 for TGDDM-HHPA)
PCL-H$_2$O system

G. Scherillo, L. Sanguigno, L. Sansone, E. Di Maio, M. Galizia and G. Mensitieri,
*Fluid Phase Equilibria.* (2012), 313, 127
PCL-H$_2$O system: Outcomes of FTIR analysis

Difference spectroscopy

Comparison of PCL-H$_2$O (blue) and PMDA-ODA systems

Shift of the carbonyl stretching peak
PCL-H$_2$O system: Outcomes of FTIR analysis

2D correlation spectroscopy
Result: 2 water ‘species’
1 PA group (C=O) per repeating unit
PCL-H₂O system
Sorption isotherms

**NRHB model** (1 PA per r.u.)
PCL-H$_2$O system

*Self- and cross-hydrogen bonds*

![Graph showing PCL-H$_2$O system with NRHB model at T=30°C](image)
CONCLUSIONS

1. **EoS LF theories containing HB contribution** are needed to interpret sorption behavior in *rubbery polymer-water systems exhibiting HB*. They supply **quantitative predictions** on the amount of *self- and cross- HB* in the system.

2. Available equilibrium **EoS LF theories for HB interacting systems** can be successfully extended to model sorption thermodynamics in *glassy polymers exhibiting HB interactions*, by using an approach based on thermodynamics with internal state variables.

3. On-line in-situ FTIR spectroscopy coupled with analysis of 2D correlation spectra, is a valuable tool to gather important information on i) the **type of molecular interactions**; (ii) **the interaction site(s)** on the polymer backbone (iii) the **nature** and the **number** of the **penetrant species** and, above all, iv) a method to **quantitatively estimate the population of the different species** present in the system.

4. A reliable assessment of thermodynamic **consistency of sorption thermodynamics model for systems exhibiting HB interactions** can be performed by comparing model predictions with outcomes of FITR in situ spectroscopy.