# Coupling moisture diffusion and internal mechanical states in composite materials


**[a]F. Jacquemin, [b]A. Célino, [a]S. Fréour**

*[a]Institut de Recherche en Génie Civil et Mécanique,*
*Université de Nantes, UMR CNRS 6183.*
*[b]Institut des sciences analytiques et de physicochimie pour*
*l'Environnement et les Matériaux,*
*Université de Pau et des Pays de l'Adour, UMR CNRS 5254.*

e-mail: frederic.jacquemin@univ-nantes.fr


UNIVERSITÉ DE NANTES

Institut de Recherche en Génie Civil et Mécanique

# Coupling moisture diffusion and internal mechanical states in composite materials



**OBJECTIVE**

**Time-dependent** environmental conditions
temperature and relative humidity

Coupled modelling:
- **stress dependent moisture diffusion**
- **nonlinear hygrothermoelasticity**

*"weak" coupling :* plasticization

*"strong"* stress-diffusion coupling

Decoupled modelling:
- Fourier and **Fick's laws**
- **linear hygrothermoelasticity**

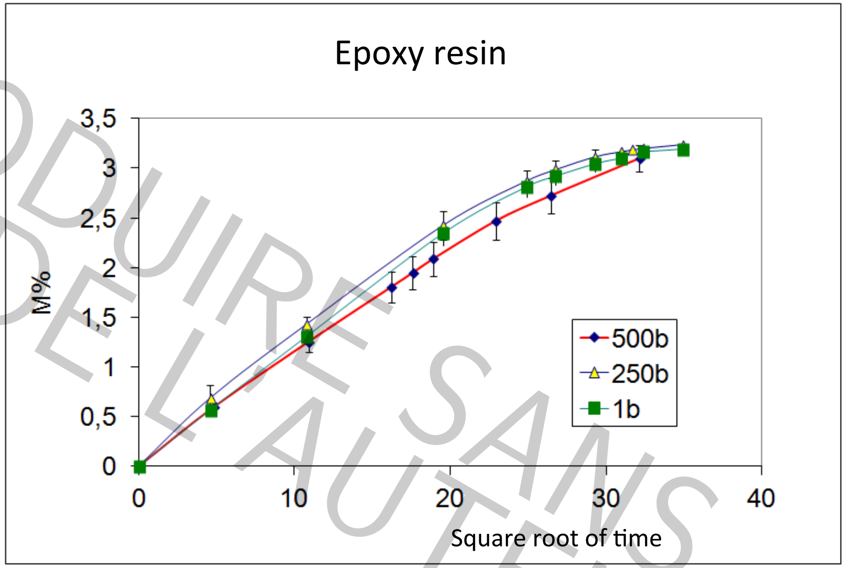
**Time-dependent** moisture content and
**hygrothermal stress** at the micro and macro levels

**Durability of polymer matrix composites**

# Coupling moisture diffusion and internal mechanical states in composite materials



## Stress dependent moisture diffusion




**hyperbaric testing tanks – IFREMER Brest**

**Coupling moisture diffusion and internal mechanical states in composite materials**

**F. Jacquemin, A. Célino, S. Fréour**



**The free volume theory**

The thermodynamical approach

Multi-scale stresses estimations in composite structures submitted to environmental conditions

…and the biocomposites

# DECOUPLED-DIFFUSION MODELS



**Fick's law**

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}$$

- *C, moisture content*
- *D, diffusion coefficient*
- *x, position*
- *t, time*

**Langmuir model**

$$\frac{\partial n}{\partial t} = D \frac{\partial^2 n}{\partial x^2} - \frac{\partial N}{\partial t}$$

$$\frac{\partial N}{\partial t} = \gamma n - \beta N$$

$$\gamma n_\infty = \beta N_\infty$$

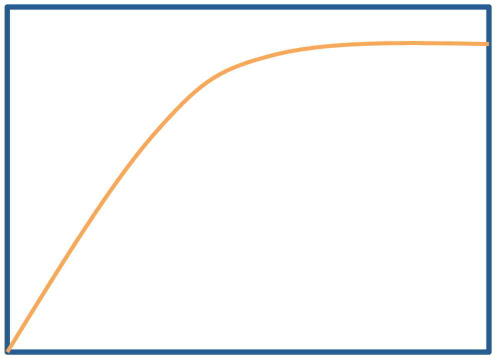
✧ $\gamma$ *and* $\beta$, *probability per unit time that a mobile molecule becomes bound, and probability per unit time that a bound molecule becomes mobile.*

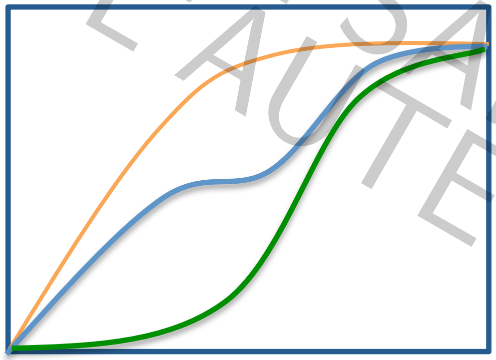
✧ *n and N, number of mobile molecules per unit volume, and number of bound molecules per unit volume.*

# DECOUPLED-DIFFUSION MODELS

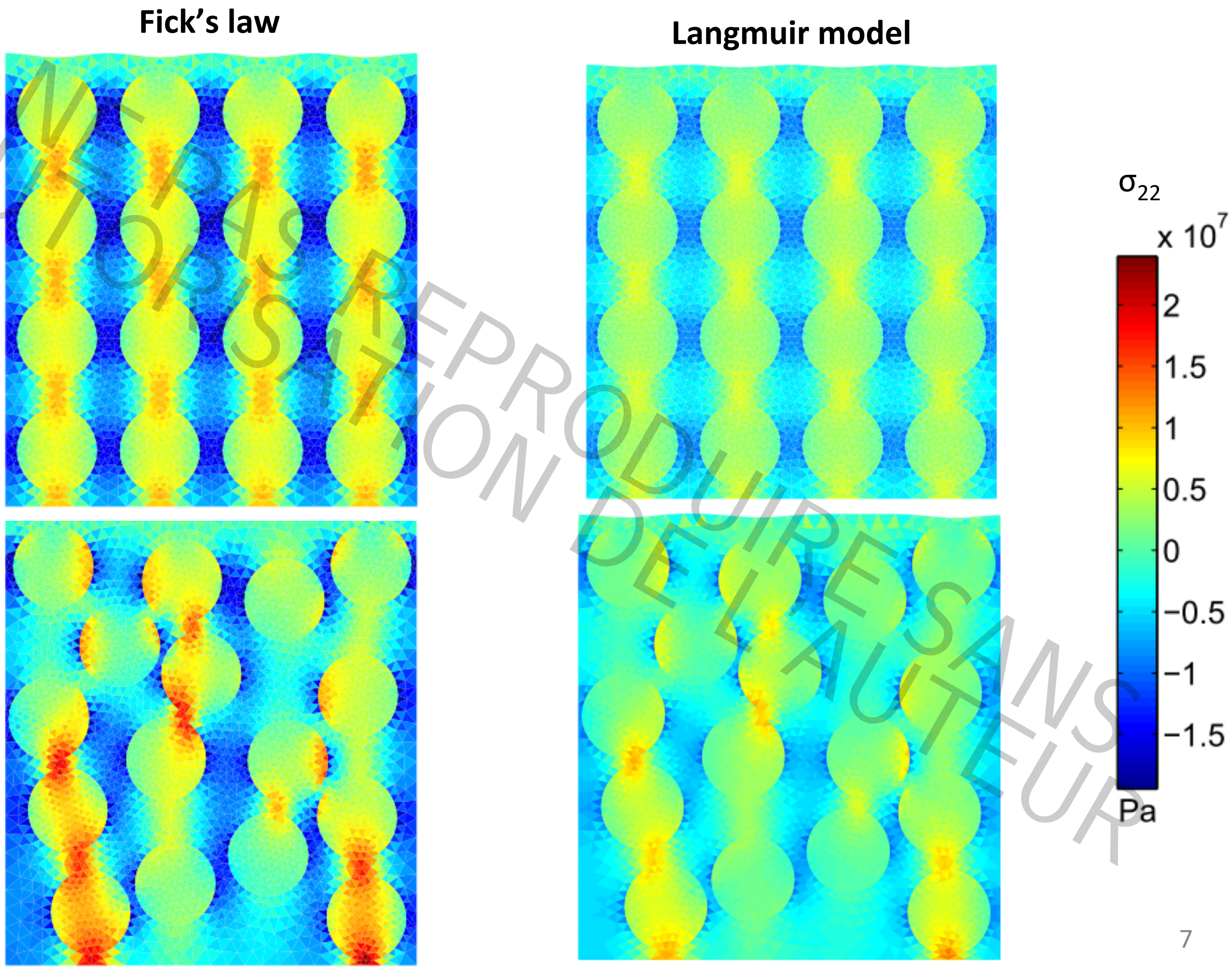


| Fick's law | Langmuir model |
|---|---|
| $\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$ | $\frac{\partial n}{\partial t} = D\frac{\partial^2 n}{\partial x^2} - \frac{\partial N}{\partial t}$ <br> $\frac{\partial N}{\partial t} = \gamma n - \beta N$ <br> $\gamma n_\infty = \beta N_\infty$ |





# DECOUPLED-Modelling (linear hygroelasticity)



## The free volume theory

### Moisture diffusion coefficient

Neumann et Marom[1] have developed a theoretical approach based on the calculation of the free-volume change in the stressed state:

$$\mathrm{Ln}\left(\frac{D_\varepsilon^m}{D_0^m}\right) = \frac{a}{v^m}\left(\frac{1}{v_{f0}^m} - \frac{1}{v_{f\varepsilon}^m}\right)$$

The free-volume fraction for a strained epoxy is related to the corresponding value for the unstrained resin through:

$$v_{f\varepsilon}^m = v_{f0}^m + \frac{\Delta V^m}{V_0^m} = v_{f0}^m + \frac{V_\varepsilon^m - V_0^m}{V_0^m} = v_{f0}^m + \mathrm{Tr}\,\varepsilon^m$$

The moisture diffusion coefficients of the strained/unstrained resins satisfy:

$$\mathrm{Ln}\left(\frac{D_\varepsilon^m}{D_0^m}\right) = \frac{a}{v^m}\mathrm{Tr}\,\varepsilon^m\left\{v_{f0}^m\left[v_{f0}^m + \mathrm{Tr}\,\varepsilon^m\right]\right\}^{-1}$$



[1] **Neumann, S., Marom, G.**, (1986). Free-volume dependent moisture diffusion under stress in composite materials. Journal of Materials Science, 21, 26-30.

## The free volume theory



The general expression enabling to determine the moisture content C according to Fick's diffusion model writes as follows:

$$\frac{\partial C}{\partial t} = \mathrm{div}\left(D\ \overrightarrow{\mathrm{grad}}\ C\right) = D\ \mathrm{div}\ \left(\overrightarrow{\mathrm{grad}}\ C\right) + \overrightarrow{\mathrm{grad}}\ D\ \overrightarrow{\mathrm{grad}}\ C$$

Fick's law

Dependence of the diffusion coefficient upon the mechanical strains

$$\overrightarrow{\mathrm{grad}}\ D = \overrightarrow{\mathrm{grad}}\left(\mathrm{Ln}\left(\frac{D_{\varepsilon}^{m}}{D_{0}^{m}}\right) = \frac{a}{v^{m}}\mathrm{Tr}\ \varepsilon^{m}\left\{v_{f0}^{m}\left[v_{f0}^{m} + \mathrm{Tr}\ \varepsilon^{m}\right]\right\}^{-1}\right)$$

# The free volume theory



**Maximum moisture absorption capacity**

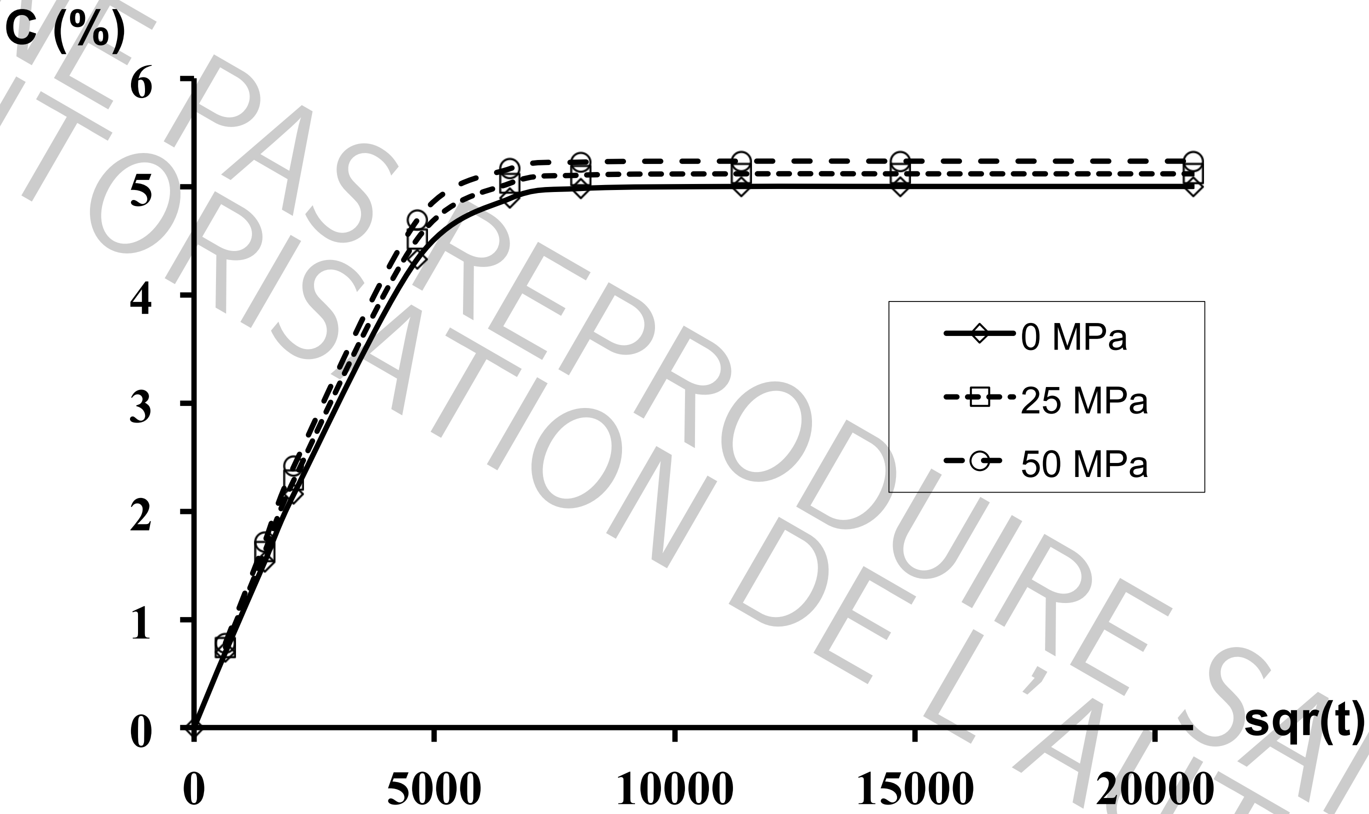
The maximum moisture absorption capacity is defined by:

$M^{m}_{\infty 0} = v^{m}_{f0} \frac{\rho^{w}}{\rho^{m}}$ for the strain-free matrix $M^{m}_{\infty \varepsilon} = v^{m}_{f\varepsilon} \frac{\rho^{w}}{\rho^{m}}$ for the strained matrix

Thus, the equation of the maximum moisture absorption capacity becomes:

$$M^{m}_{\infty \varepsilon} = M^{m}_{\infty 0} + \left(v^{m}_{f\varepsilon} - v^{m}_{f0}\right)\frac{\rho^{w}}{\rho^{m}} = M^{m}_{\infty 0} + \mathrm{Tr}\,\varepsilon^{m} \frac{\rho^{w}}{\rho^{m}}$$

## The free volume theory






➚ UD tensile stress ➔ ➚ Maximum moisture absorption capacity

➔ ➚ Moisture diffusion coefficient

**Coupling moisture diffusion and internal mechanical states in composite materials**

**F. Jacquemin, A. Célino, S. Fréour**

UNIVERSITÉ DE NANTES

Institut de Recherche en Génie Civil et Mécanique

The free volume theory

**The thermodynamical approach**

Multi-scale stresses estimations in composite structures submitted to environmental conditions

…and the biocomposites

## The thermodynamical approach

- Chemical potential of water: $\tilde{\mu}_w(C) = \dfrac{\partial F}{\partial n_w} = \dfrac{\partial F}{\partial C}\dfrac{\partial C}{\partial n_w}$

- Free energy of Helmholtz: $F = F_0 + n\, f_w(C) + V_\varepsilon\, W$

- Hygro-elastic strain energy: $W = \dfrac{1}{2}\boldsymbol{\sigma} : \boldsymbol{\varepsilon}^{el} = \dfrac{k}{2}\left(\mathrm{tr}\,\boldsymbol{\varepsilon} - 3\,\eta\,C\right)^2 + G\,\mathbf{e} : \mathbf{e}$

  where $\eta$, k, coefficient of moisture expansion, and bulk modulus.

- Variation of polymer density: $\dfrac{1}{\rho_p} = \dfrac{1}{\rho_0}(1 + \mathrm{Tr}\varepsilon)$

  where $\rho_p$, $\rho_0$, density of polymer at present and initial states.

- Trace of strain tensor: $\mathrm{Tr}\varepsilon = -\dfrac{Pex + Pis}{k} + 3\eta C$

## The thermodynamical approach

- Chemical potential:

$$\tilde{\mu}_w(C, \mathrm{tr}\,\boldsymbol{\varepsilon}) = \mu_0 + R\,T\ln\frac{C}{C_0} - \frac{3\,\eta\,\omega_w\,k}{\rho_0}(\mathrm{tr}\,\boldsymbol{\varepsilon} - 3\,\eta\,C)(\mathrm{tr}\,\boldsymbol{\varepsilon} + 1) +$$

$$+\frac{\eta\,\omega_w}{A_0\,\rho_0}(3\,A_0\,k - \alpha)(\mathrm{tr}\,\boldsymbol{\varepsilon} - 3\,\eta\,C)(\mathrm{tr}\,\boldsymbol{\varepsilon} + 1) + \frac{\eta\,\omega_w}{A_0\,\rho_0}\frac{3\,A_0\,k - \alpha}{2}(\mathrm{tr}\,\boldsymbol{\varepsilon} - 3\eta\,C)^2$$

where $C_0$ is the reference moisture content.

- The moisture flux is related to the chemical potential:

$$J_i = -\frac{DC}{RT}\nabla\mu_w$$

where D is the diffusion coefficient in [mm²/s], C is the moisture content in [%], R is the ideal gas constant in [kJ/(mol.K)], T is the temperature in [K].

- The law of mass conservation is given by: $\dot{C} + J_{i,i} = 0$

## The thermodynamical approach



**Moisture Flux + Mass Conservation Equation**

$$\dot{C} = D\left[\left(1 + \cancel{V_1 \eta^2 C} + \cancel{V_2 \eta^3 C^2} + \cancel{\xi z_1}\right)\frac{\partial^2 C}{\partial x^2} + \eta^2\left(\cancel{V_3} + \cancel{V_4 C} + \cancel{\xi z_2}\right)\left(\frac{\partial C}{\partial x}\right)^2\right]$$

where:

$$V_1 = -3\,A_0\,k\,\mathrm{tr}\,\boldsymbol{\varepsilon} + 2\alpha\,\mathrm{tr}\,\boldsymbol{\varepsilon} + \alpha \qquad V_2 = 9\,A_0\,k - 3\,\alpha$$

$$V_3 = -3\,A_0\,k\,\mathrm{tr}\,\boldsymbol{\varepsilon} + 2\alpha\,\mathrm{tr}\,\boldsymbol{\varepsilon} + \alpha \qquad V_4 = \eta\,V_2 - \frac{2\,\eta\,\alpha^2}{A_0\,k}$$

$$\xi = \frac{3\,A_0\,k - \alpha}{3}\,\eta$$

**The thermodynamical approach**

- Boundary conditions:

  The boundary condition is obtained by equating the chemical potential of water in humid air:

$$\hat{\mu}_w = \hat{\mu}_0 + RT \ln \frac{p_w}{p_0}$$

Where $\hat{\mu}_0$ is the chemical potential of water in humid air at the reference pressure $p_0$, the partial pressure of water being $p_w$

$$C(x_b, t) = S\, p_w \exp\left[\left(\frac{\eta A_0}{k} - \frac{\eta}{3k^2}(3 A_0 k - \alpha)\right)\left(P^2 - 3\eta C kP - kP\right) - \frac{\eta}{6k^2}(3 A_0 k - \alpha) P^2\right]$$

Solubility (Henry's law)

## The thermodynamical approach



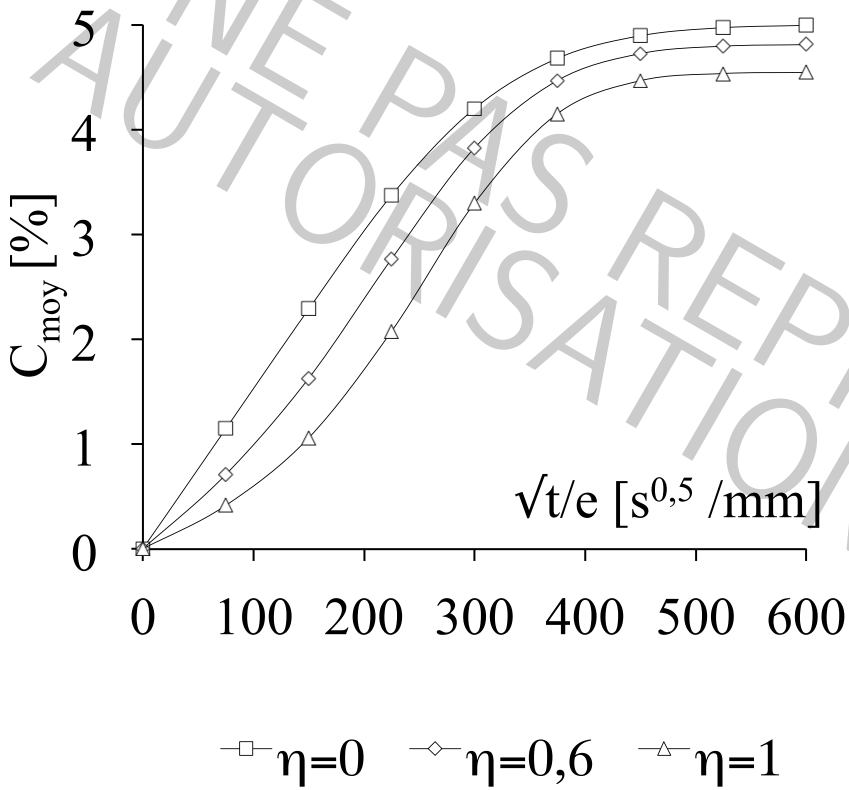



*Figure: Effect of CME on the average moisture content.*

➚ of CME:

- η = 0 : Fick behaviour
- ➘ Maximum moisture absorption capacity
- ➘ Moisture diffusion coefficient
- ➚ Non linear behaviour

## The thermodynamical approach

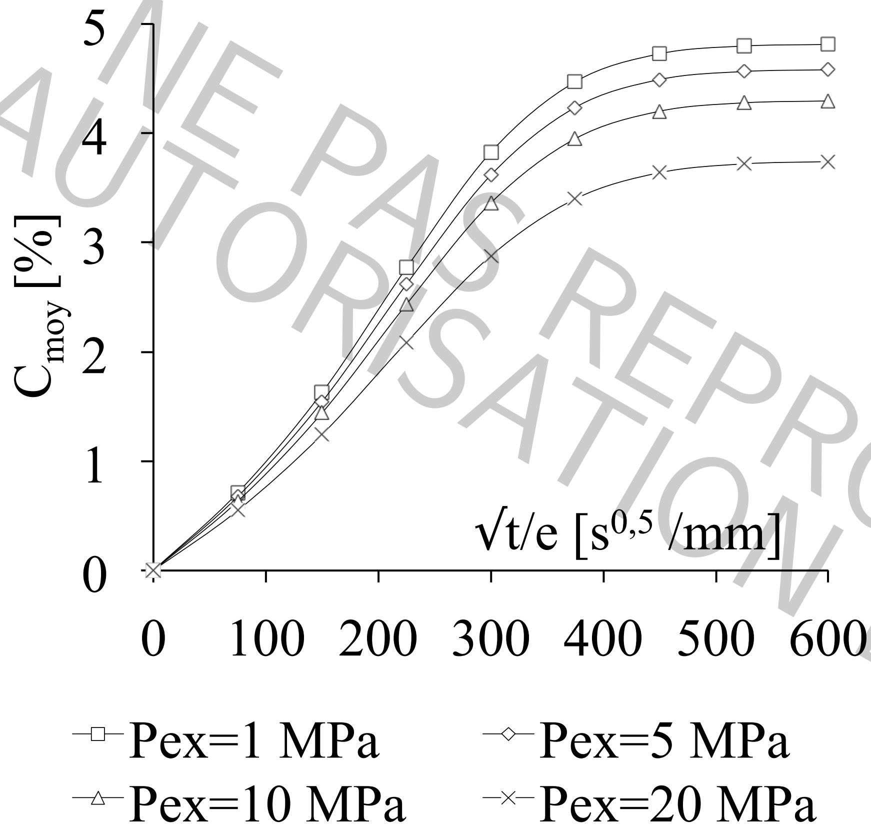



*Figure: Effect of applied pressure on the average moisture content η = 0.6*

➚ of applied pressure:

- ➘ Maximum moisture absorption capacity
- ➘ Moisture diffusion coefficient
- ➚ Non linear behaviour

# The thermodynamical approach

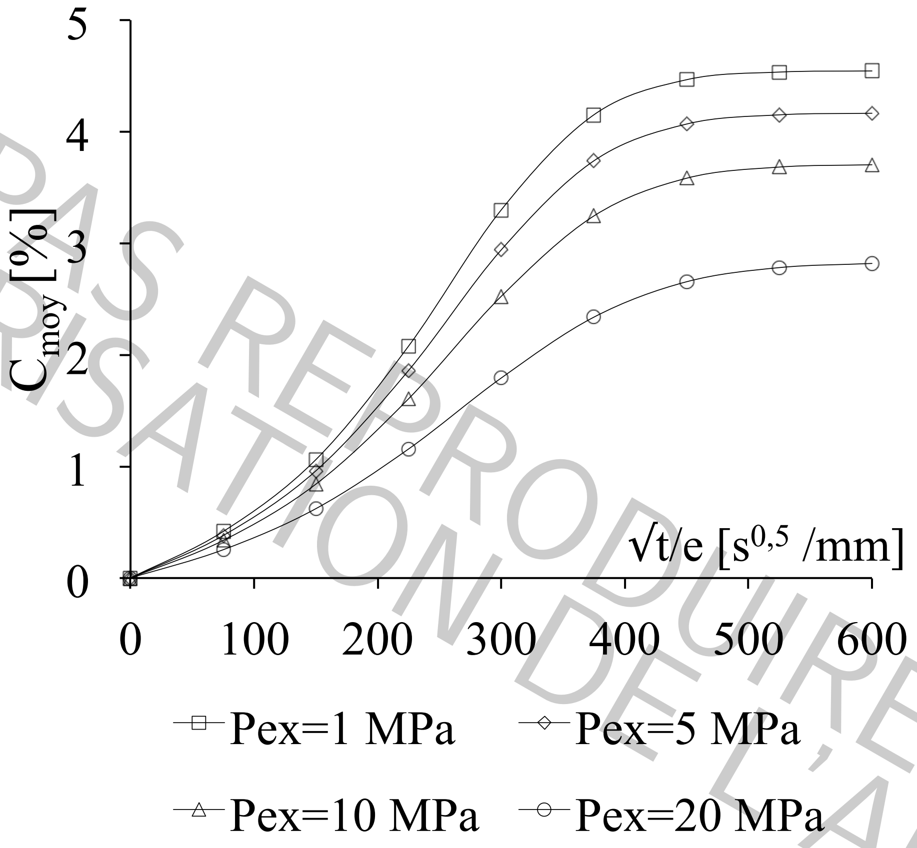



*Figure: Effect of unsymmetrical applied pressure on the average moisture content* $\eta = 0.6$ *and* $P_{int} = 1$ *MPa*

- Differential pressure has a signficant effect on the average moisture content.

# Coupled modelling for the polymers

**The free volume theory**

phenomenological laws

$$\frac{\partial C}{\partial t} = D \operatorname{div}\left(\overrightarrow{\text{grad}}\ C\right) + \overrightarrow{\text{grad}}\ D\ \overrightarrow{\text{grad}}\ C$$

**The thermodynamical approach**

chemical potential of water

$$\dot{C} = D\left[\left(1 + V_1 \eta^2 C + V_2 \eta^3 C^2 + \xi z_1\right)\frac{\partial^2 C}{\partial x^2} + \eta^2\left(V_3 + V_4 C + \xi z_2\right)\left(\frac{\partial C}{\partial x}\right)^2\right]$$

Composite materials ?

UNIVERSITÉ DE NANTES

Institut de Recherche en Génie Civil et Mécanique



**Coupling moisture diffusion and internal mechanical states in composite materials**

**F. Jacquemin, A. Célino, S. Fréour**

The free volume theory

The thermodynamical approach

**Multi-scale stresses estimations in composite structures submitted to environmental conditions**

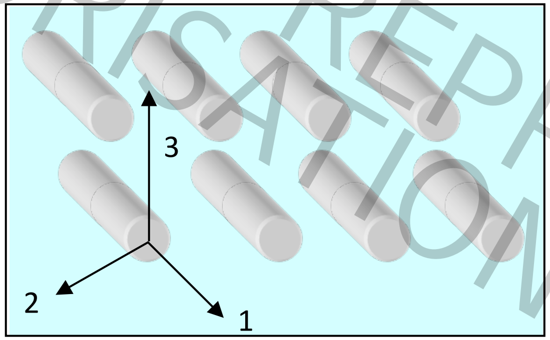
- **Hygro-elastic effective properties**
- **Plasticization effects**
- Stress dependent moisture diffusion

…and the biocomposites

**Multi-scale stresses estimations in composite structures submitted to environmental conditions**



Example of carbon/epoxy composites:




•Moisture contents of the epoxy matrix and carbon fibers are strongly different.

•Carbon fibers are considered not to absorb water.

≠ coefficients of moisture expansion (CME) + hygroscopic environment
⇒ Macroscopic (ply) and local (fiber and matrix) hygro-elastic stresses

**Multi-scale stresses estimations in composite structures submitted to environmental conditions**

## Self-consistent estimates for the hygro-elastic properties

Multi-scale hygroelasic behaviours

$$\boldsymbol{\sigma}^{\alpha} = \mathbf{L}^{\alpha} : \left(\boldsymbol{\varepsilon}^{\alpha} - \boldsymbol{\eta}^{\alpha} \Delta C^{\alpha}\right)$$

Hill's relations on the volume average equations

$$\left\langle \boldsymbol{\sigma}^{\alpha} \right\rangle_{\alpha=f,m} = \boldsymbol{\sigma}^{I}$$
$$\left\langle \boldsymbol{\varepsilon}^{\alpha} \right\rangle_{\alpha=f,m} = \boldsymbol{\varepsilon}^{I}$$

Scale transition relation from Eshelby's formalism

$$\boldsymbol{\sigma}^{\alpha} - \boldsymbol{\sigma}^{I} = -\mathbf{L}^{I} : \mathbf{R}^{I} : \left(\boldsymbol{\varepsilon}^{\alpha} - \boldsymbol{\varepsilon}^{I}\right)$$

$R^{I}$ depends on elastic macroscopic stiffness and morphology of the constituents

**Multi-scale stresses estimations in composite structures submitted to environmental conditions**



## Self-consistent estimates for the hygro-elastic properties

Classical self-consistent estimate for the macroscopic elastic stiffness

$$\mathbf{L}^{\mathbf{I}} = \left\langle \left(\mathbf{L}^{\alpha} + \mathbf{L}^{\mathbf{I}} : \mathbf{R}^{\mathbf{I}}\right)^{-1} : \left(\mathbf{L}^{\mathbf{I}} + \mathbf{L}^{\mathbf{I}} : \mathbf{R}^{\mathbf{I}}\right) : \mathbf{L}^{\alpha} \right\rangle_{\alpha=f,m}$$

Self-consistent estimate for the macroscopic CME

$$\boldsymbol{\eta}^{I} = v^{m} \frac{\Delta C^{m}}{\Delta C^{I}} \mathbf{L}^{I\,-1} \left\langle \left(\mathbf{L}^{\alpha} + \mathbf{L}^{I} : \mathbf{R}^{I}\right)^{-1} \right\rangle_{\alpha=f,m}^{-1} : \left(\mathbf{L}^{m} + \mathbf{L}^{I} : \mathbf{R}^{I}\right)^{-1} : \mathbf{L}^{m} : \boldsymbol{\eta}^{m}$$

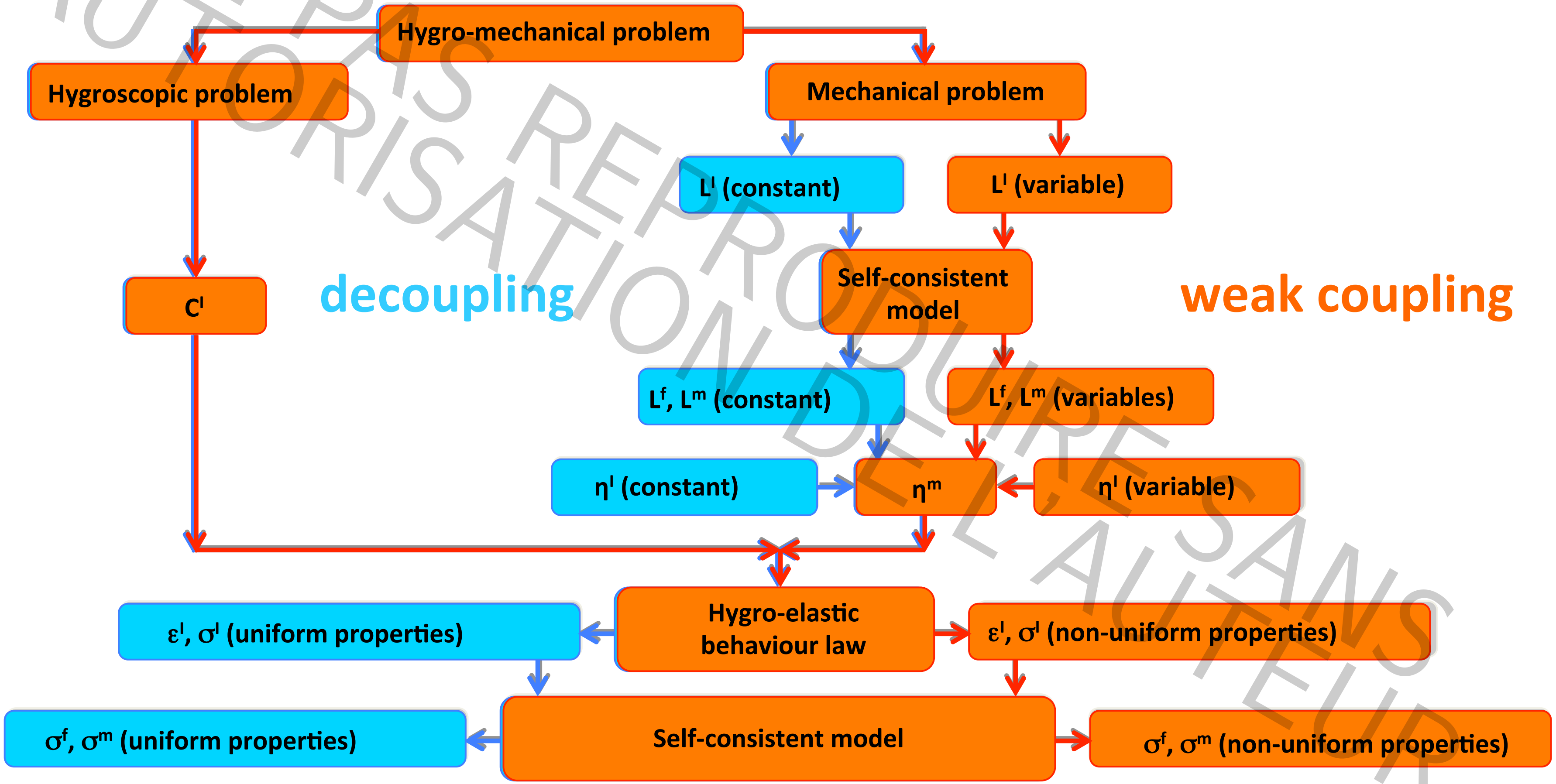
Ratio depending on the constitutive materials

**Multi-scale stresses estimations in composite structures submitted to environmental conditions**

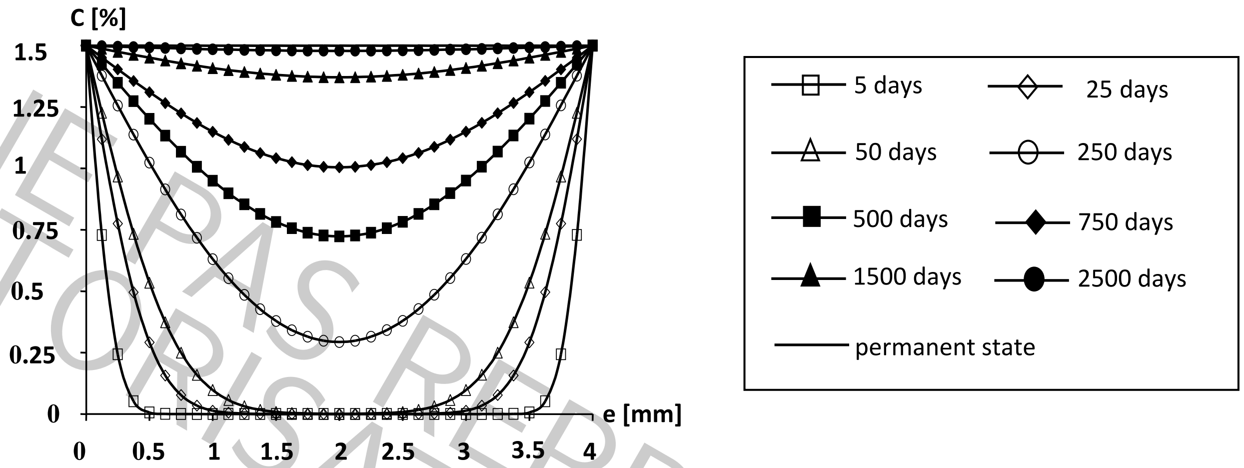
| Macroscopic stresses | Local stresses |
|---|---|
| ➢ Constitutive laws of hygro-elastic orthotropic materials | ➢ Local stress-strain relation in constituents |
| ➢ Strain-displacement relations | ➢ Scale transition relation for the strains in fibers (Eshelby for example) |
| ➢ Compatibility and equilibrium equations and boundary conditions | ➢ Local mechanical states in the matrix (Hill for example) |

## Plasticization effects on the multi-scale internal stresses

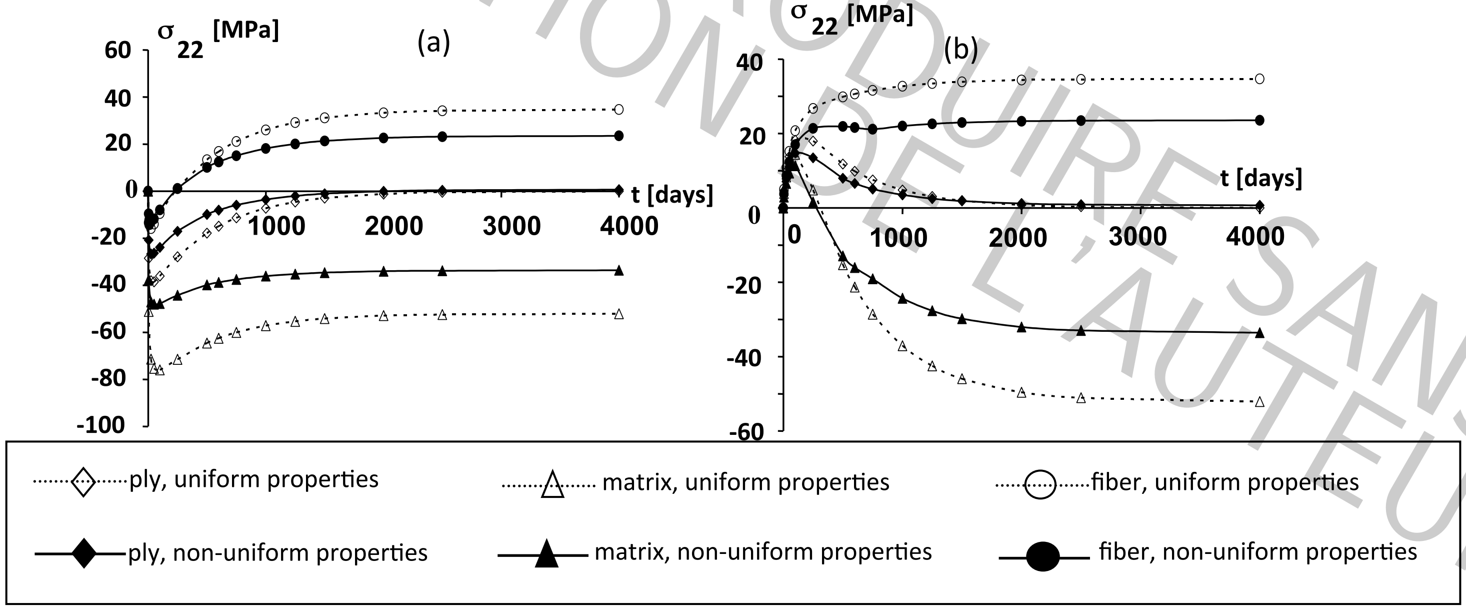
plasticization effects related to the evolution, as a function of the moisture content, of the hygro-elastic properties on the internal stress states



# Plasticization effects on the multi-scale internal stresses




Time and space dependent moisture content profiles in the composite structure.




Effect of the plasticization on the multi-scale stress states in (a) the external ply / (b) the central ply of a uni-directional composite during the transient part of the moisture diffusion process.

**Coupling moisture diffusion and internal mechanical states in composite materials**

**F. Jacquemin, A. Célino, S. Fréour**

UNIVERSITÉ DE NANTES

Institut de Recherche en Génie Civil et Mécanique



The free volume theory

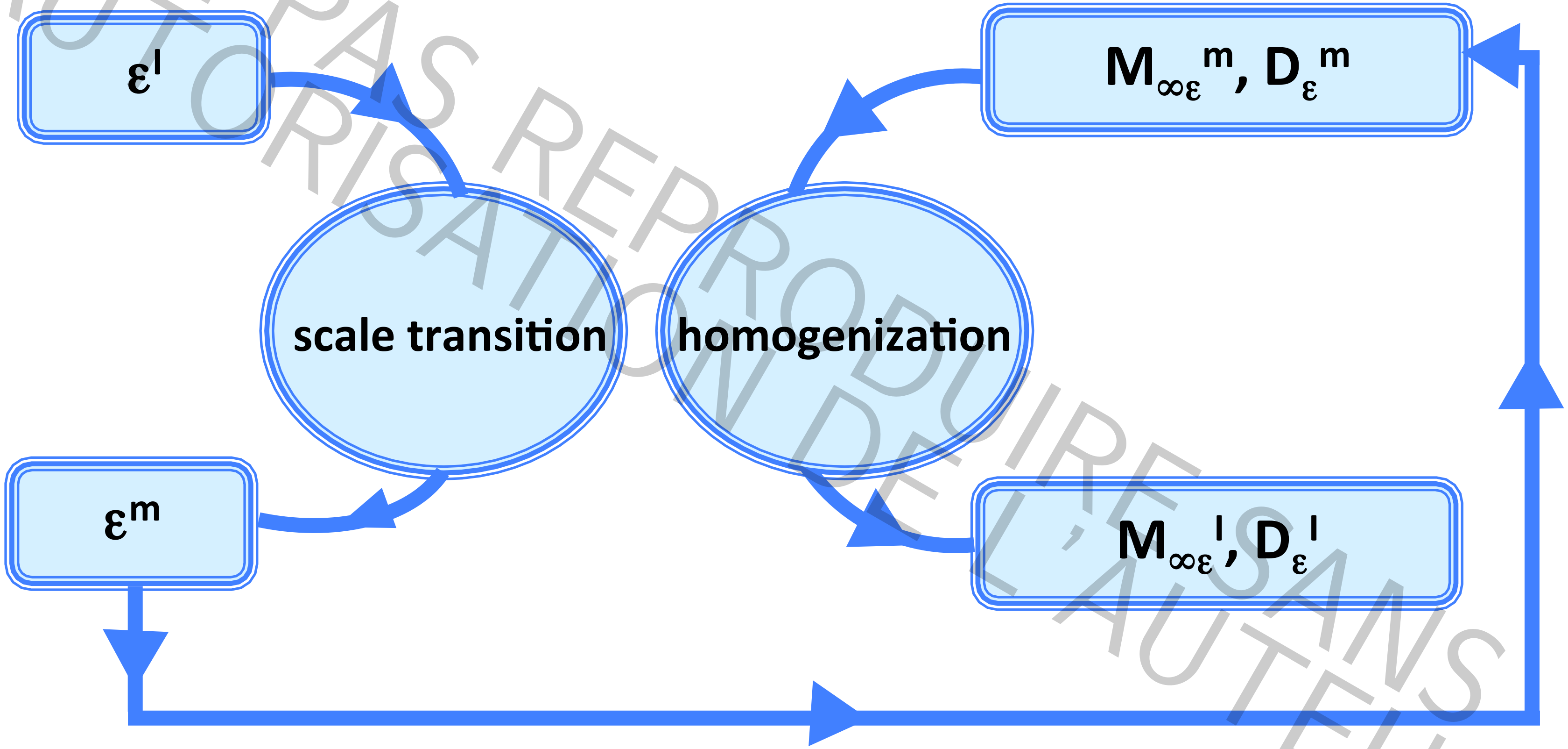
The thermodynamical approach

**Multi-scale stresses estimations in composite structures submitted to environmental conditions**

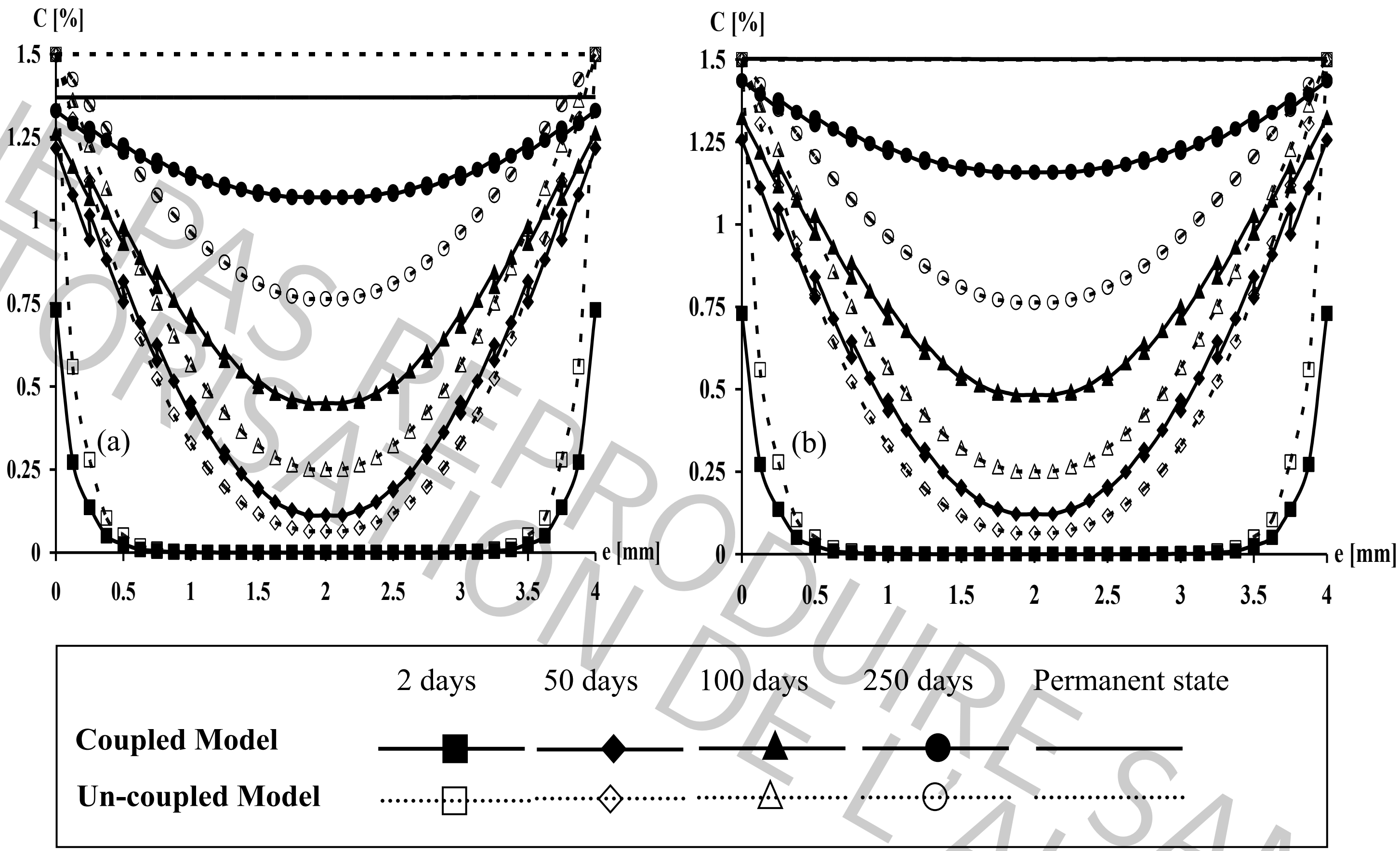
- Hygro-elastic effective properties
- Plasticization effects
- **Stress dependent moisture diffusion**

…and the biocomposites

**The free volume theory**



## The free volume theory




**Macroscopic moisture content profiles in the (a) ± 55° composite / (b) unidirectional composite structure.**

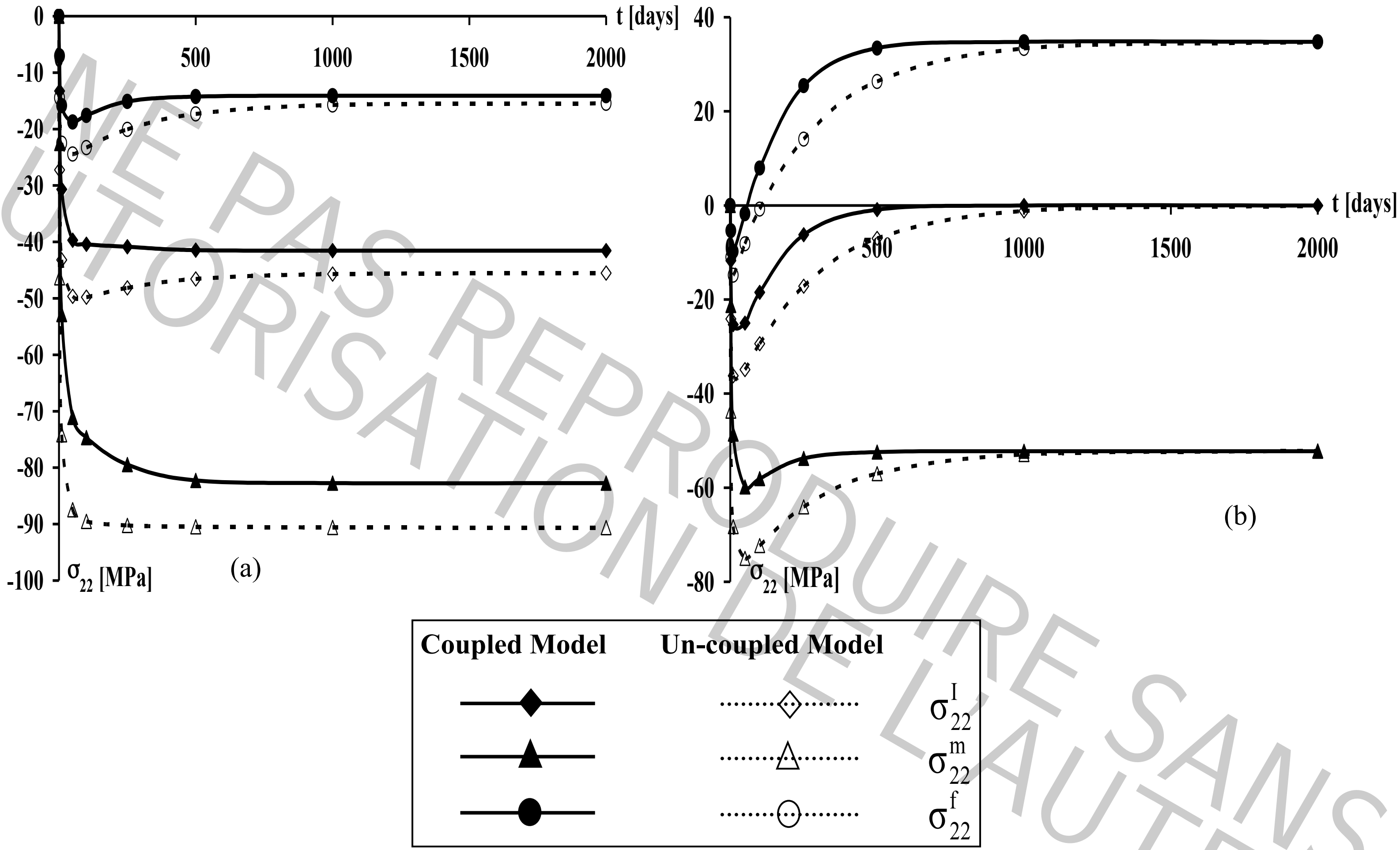
Uncoupled Model:

Identical moisture content profile evolution versus time in both the structures.

Coupled Model:

The strong evolution of the moisture content at the boundaries is attributed to the variation of the maximum moisture absorption capacity.

## The free volume theory




**Multi-scale transverse stress states in the internal ply of the (a) ± 55° composite / (b) unidirectional composite structure.**

The coupled model predicts transverse stresses states the absolute value of which is weaker than that predicted by the corresponding uncoupled approach.

**Coupling moisture diffusion and internal mechanical states in composite materials**

**F. Jacquemin, A. Célino, S. Fréour**



UNIVERSITÉ DE NANTES

Institut de Recherche en Génie Civil et Mécanique

The free volume theory

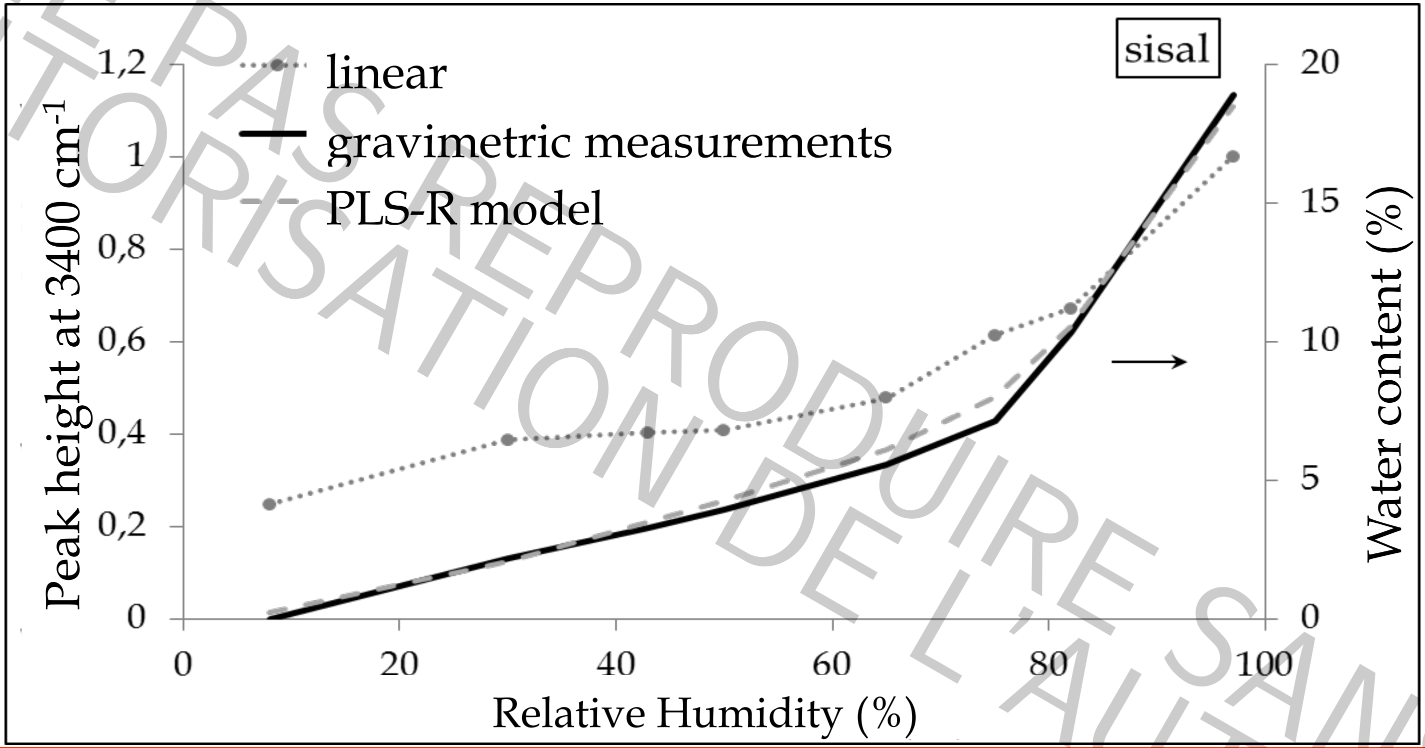
The thermodynamical approach

Multi-scale stresses estimations in composite structures submitted to environmental conditions

- Hygro-elastic effective properties
- Plasticization effects
- Stress dependent moisture diffusion

**…and the biocomposites**

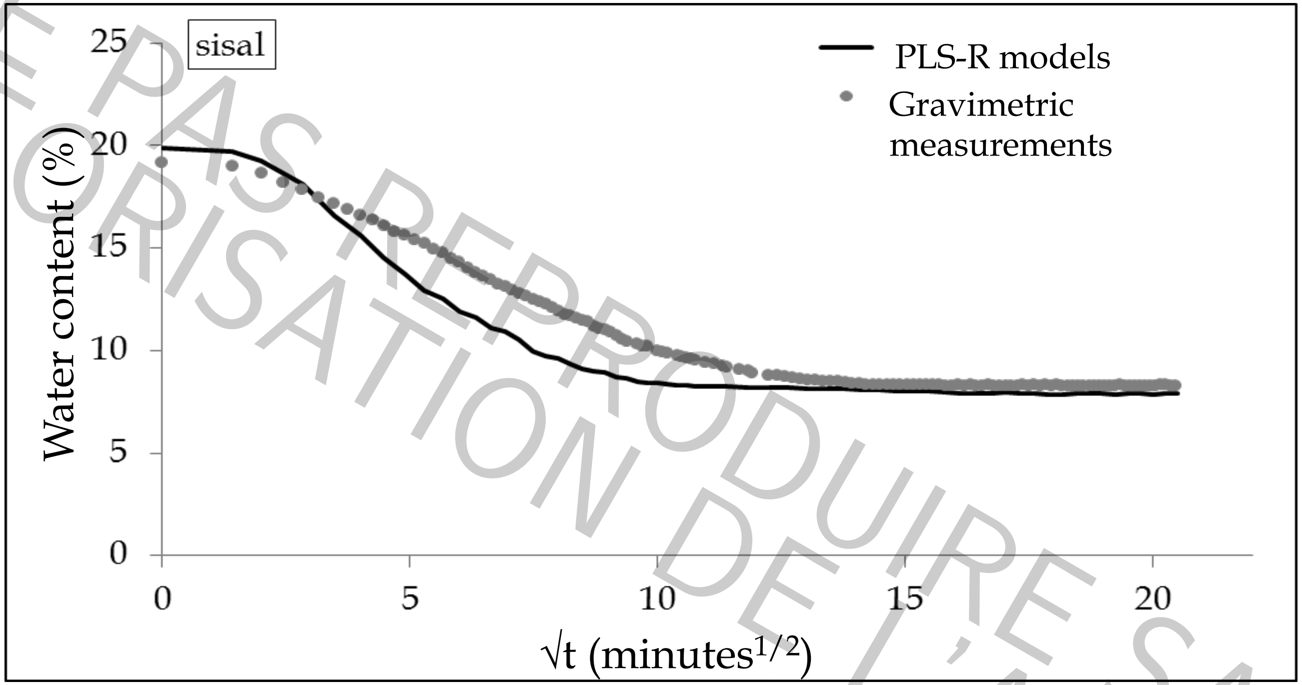
## Qualitative and quantitative assesment of water sorption in natural fibers using FTIR-ATR spectroscopy






- Sorption isotherm characteristic of natural fibres: **Sigmoidal shape**
- Univariate model doesn't fit the experimental curve $R^2 < 90$ %
- Validation of multivariate model: **$R^2 = 99.79$ %**

# Qualitative and quantitative assesment of water sorption in natural fibers using FTIR-ATR spectroscopy

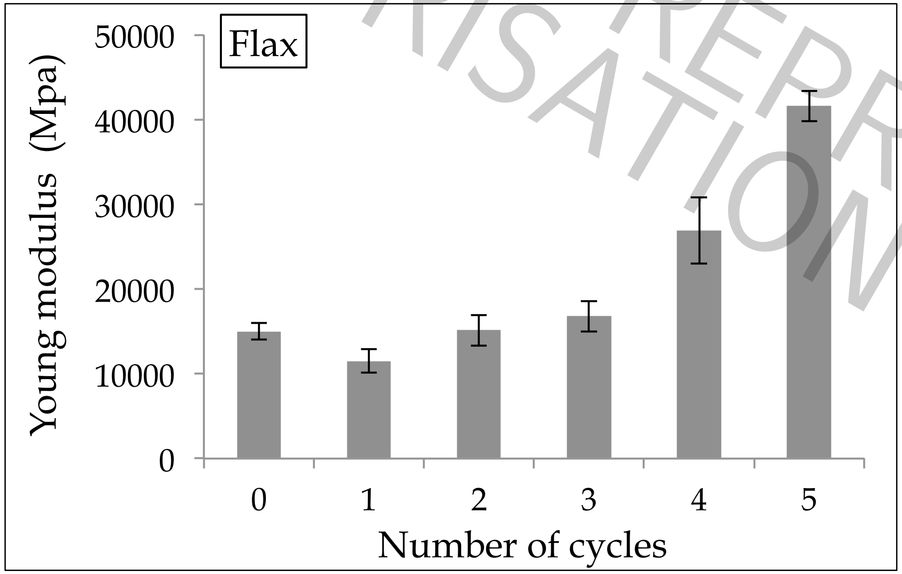



- Straightforward determination of the drying kinetics (comparison with the gravimetric measurements)
- Good correlation between the two methods: The slope deviation could be explained by the ATR method

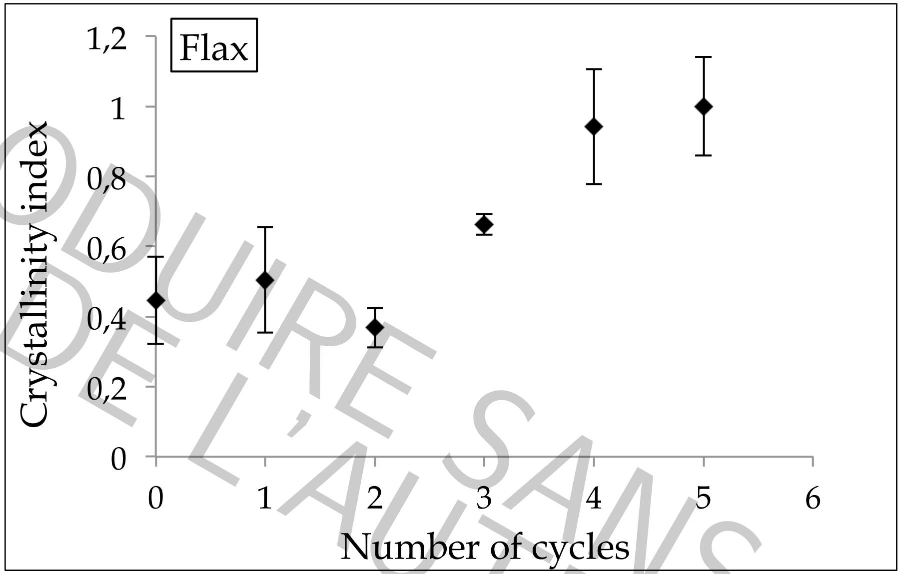
**Advantages** Informations at the first time of the kinetics / informations at the molecular scale

# Qualitative and quantitative assesment of water sorption in natural fibers using FTIR-ATR spectroscopy

- Sorption/desorption cycles (80 % → 30 %)
- Tensile test and crystallinity index calculation every cycle




Young modulus versus number of sorption/desorption cycles




Crystallinity index evolution versus number of sorption/desorption cycles

- Young modulus increases with the number of cycles
- Relationship between Young modulus and crystallinity

# Coupling moisture diffusion and internal mechanical states in composite materials



The aim of the present work is to propose models enabling to take into account:

• **water-mechanical property coupling** due to **plasticization** phenomenon

• coupling between moisture diffusive behavior law and internal mechanical states according to the **free volume theory** or the **thermodynamic approach**.

Such models can be used to represent several typical diffusive behaviors met experimentally.

Ongoing experimental studies should provide results to be compared with the numerical predictions.