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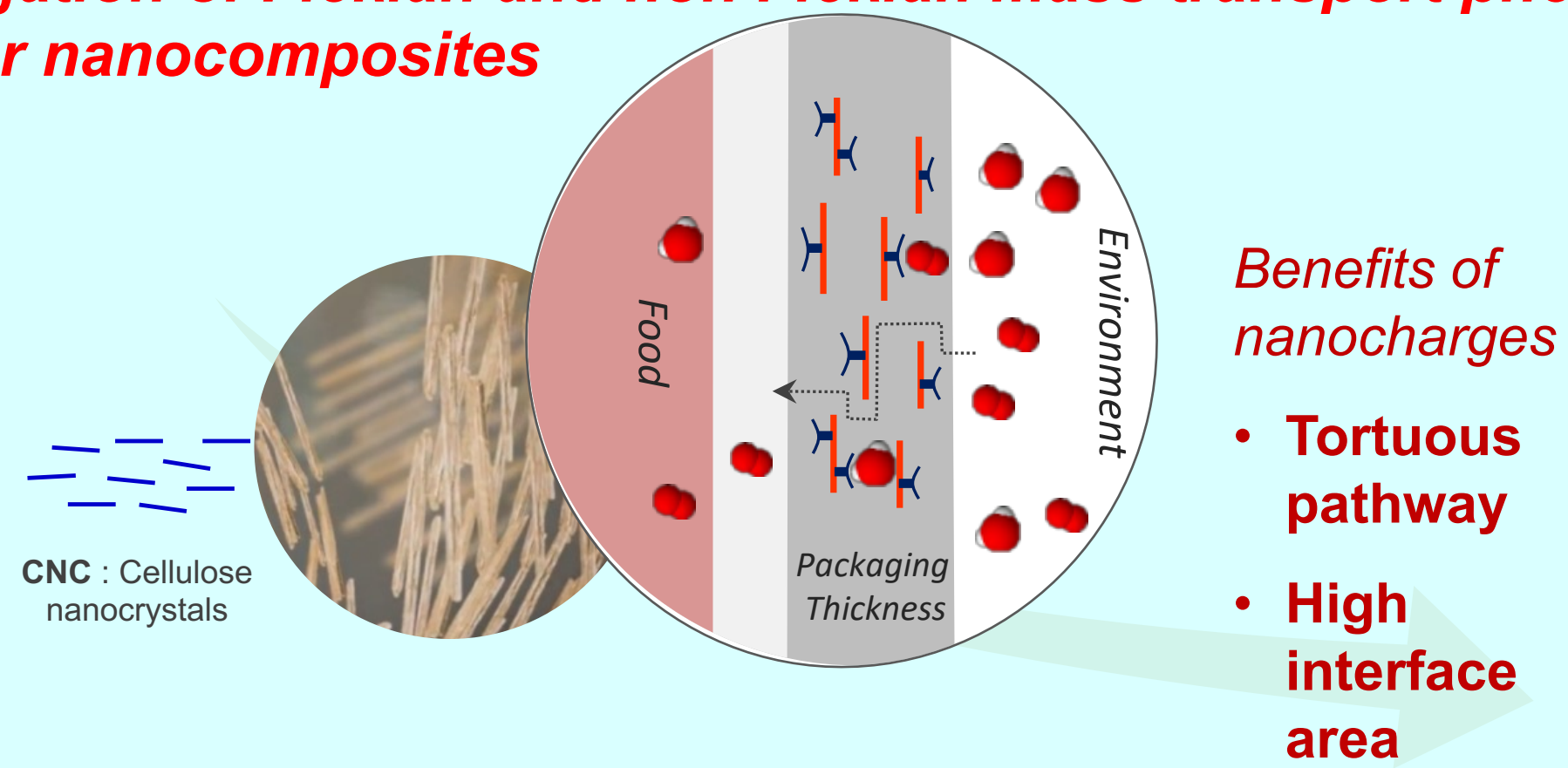
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Introduction

Nanocomposites are an opportunity to increase the performance of polymer membranes by fine-tuning their morphology. In particular, the understanding of the contribution of the polymer matrix/nanofiller interface to the overall transport properties is key to design membranes with tailored selective and adsorptive properties. In that aim, cellulose nanocrystals (CNC)/polylactide (PLA) nanocomposites were fabricated with interfaces, which were ensuring the compatibility between the components. A detailed analysis of the mass transport behaviour of different permeants in CNC/PLA nanocomposites was carried out. In that aim a model based on the inverse method was developed able to discriminate Fickian and polymer relaxation driven mass transport phenomena. The water vapour caused significant swelling of the CNC, which created a preferential pathway for mass transport. CNC surface grafting could attenuate this phenomenon and decrease the water transport rate. Anisole, an aromatic organic vapour, became reversibly trapped at the specifically designed CNC/PLA interface, but without any swelling or creation of an accelerated pathway. This caused the decrease of the overall mass transport rate. The latter finding could open a way to the creation of materials with specifically designed barrier properties by designing nanocomposites interfaces with specific interactions towards permeants.

Objective

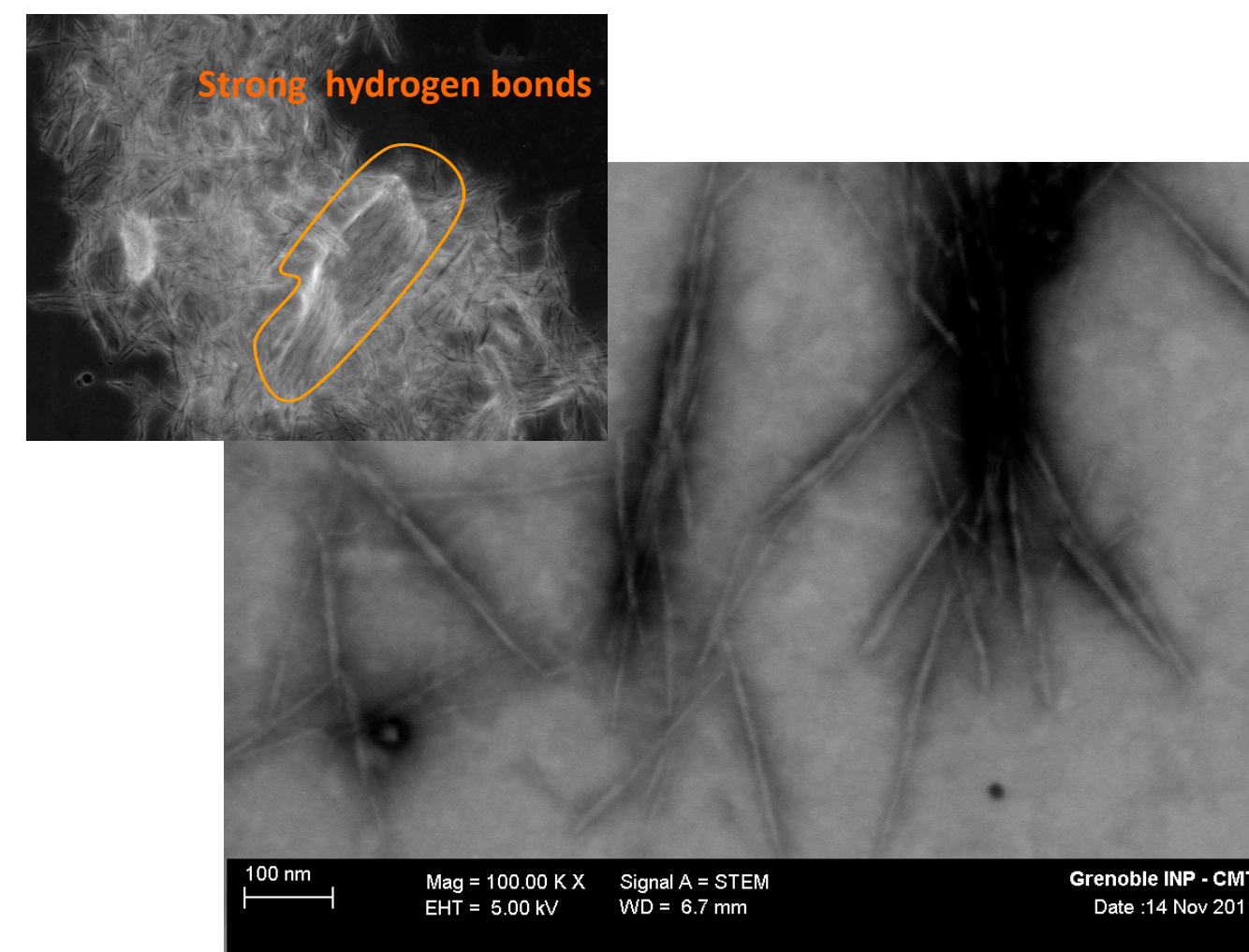
Investigation of Fickian and non Fickian mass transport phenomena in polymer nanocomposites



Materials and Methods

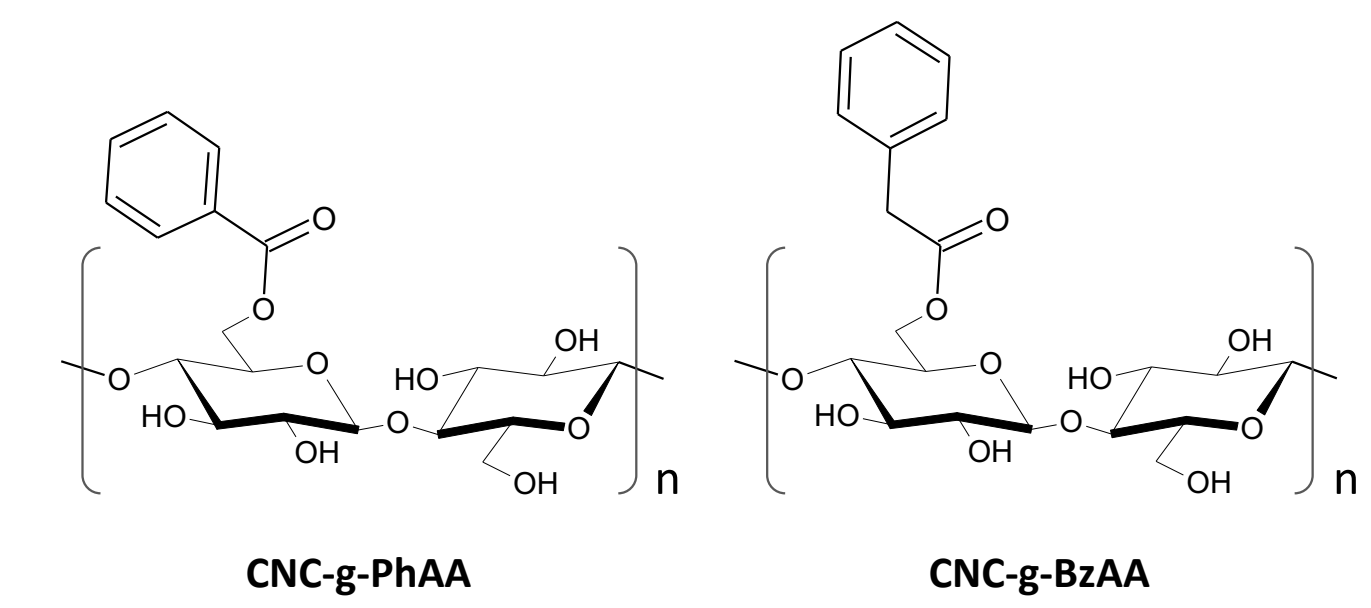
PLA NatureWorks 4060D

Cellulose Nanocrystals (CNC)



Extraction from microcrystalline cellulose (Ref. 1)

Surface grafting of CNC



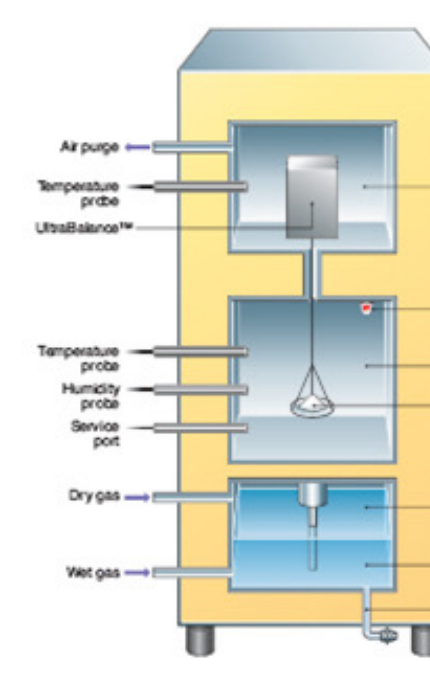
SolReact Method, Ref. 1

Sample	l (nm) [*]	d (nm) [*]	DS
CNC	155 ± 43	17 ± 5	-
CNC-g-PhAA	131 ± 36	10 ± 2	0.3
CNC-g-BzAA	145 ± 52	13 ± 3	0.5

Water vapour and aroma sorption kinetics

Water vapour sorption

Dynamic Vapour Sorption (DVS)

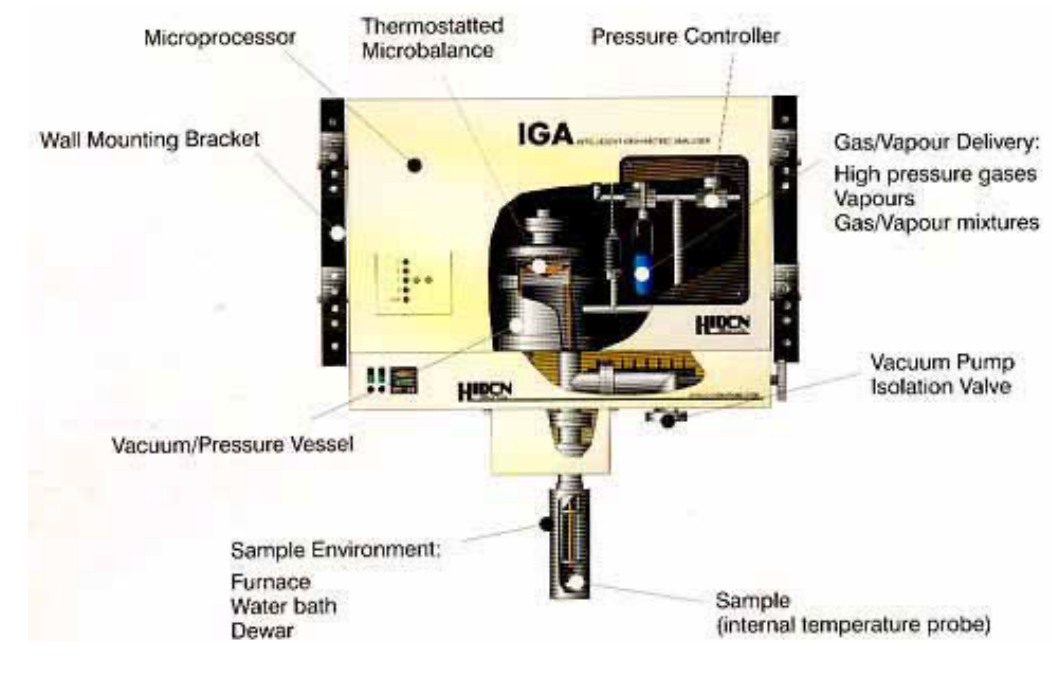


25° C
Water vapour activity 0.9
CNC powder
Adsorption-desorption

25° C
Anisole activity 0.9 (5 days)
Thickness < 60µm
Adsorption
A special sample holder was developed.

Aroma sorption

Electronic microbalance



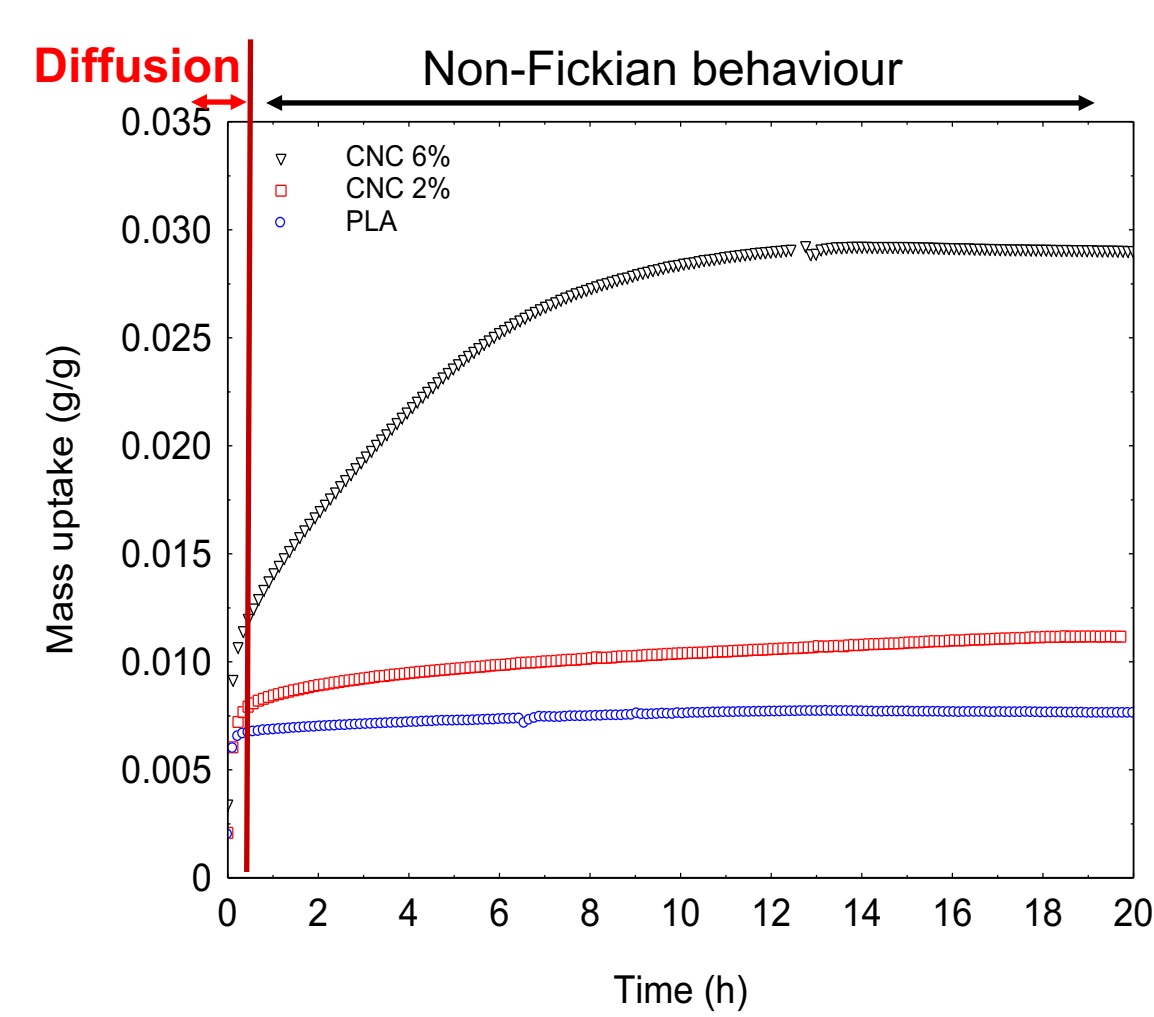
40° C & 0% RH
Anisole activity 0.2
CNC powder
Adsorption

40° C & 0% RH
Anisole activity 0.2 (5 days)
Thickness < 60µm
Adsorption

(Ref. 2)

Inverse model

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Distributed micro-models

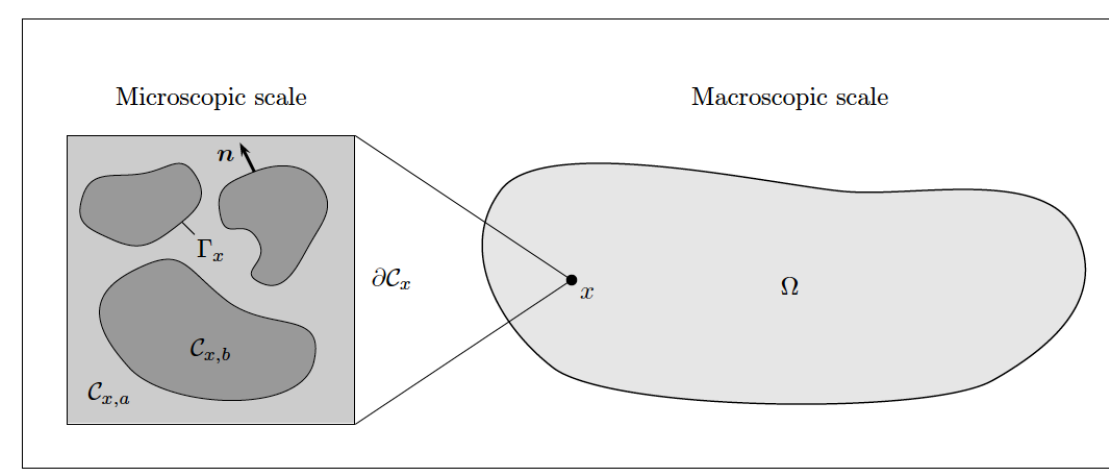


Figure 2: Two-scale configuration: at each point $x \in \Omega$, there exists a micro-cell C_x . (Ref. 3)

$$\varepsilon_a \frac{\partial \Psi_a}{\partial t} + \nabla_x \cdot Q_a = S, \quad x \in \Omega$$

$$\frac{\partial \psi_b}{\partial t} + \nabla_y \cdot q_b = 0, \quad y \in C_{x,b}$$

$$u_b = U_a, \quad y \in \Gamma_x$$

$$S = \frac{1}{|C_x|} \int_{\Gamma_x} q_b \cdot n \, ds$$

Memory effect

$$\frac{\partial X(x, t)}{\partial t} + \nabla \cdot (D_{eff} \nabla X_{eq}(x, t)) = 0$$

$$X(t) - X_{ini} = \int_0^t \varphi(t-\tau) \frac{\partial X_{eq}}{\partial \tau} d\tau$$

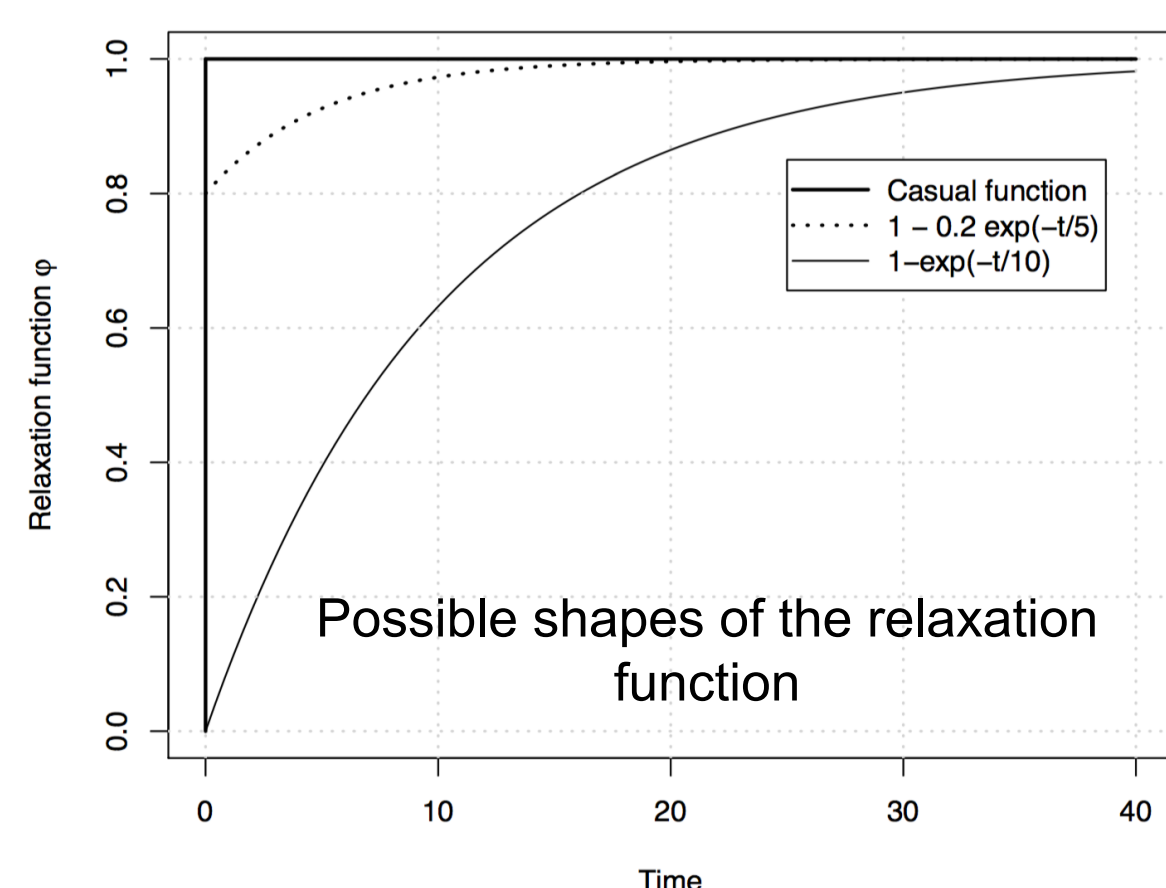
$$\frac{\partial}{\partial t} \left(a X_{eq}(x, t) + \int_0^t k(t-\tau) X_{eq}(x, \tau) d\tau \right) + \nabla \cdot (D_{eff} \nabla X_{eq}(x, t)) = 0$$

where

$$a = \varphi(0) \quad \text{and} \quad k = \frac{\partial \varphi}{\partial t}$$

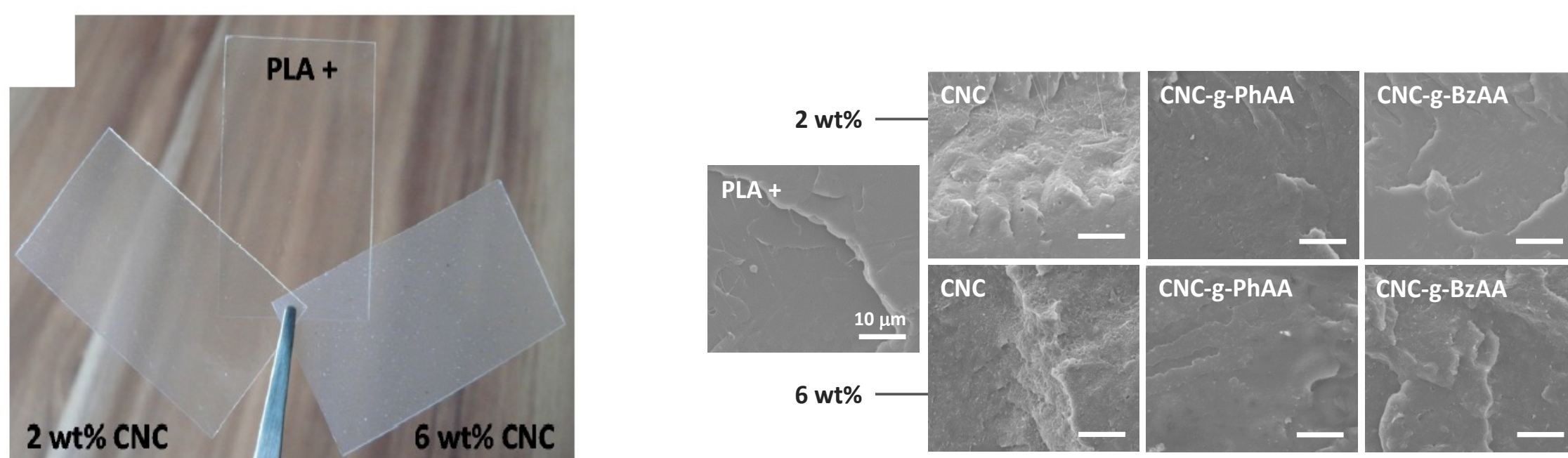
An easy way to transfer at the macroscopic level memory effects due to :

- Non-local equilibrium at the microscopic scale
- Molecular relaxation



Morphology PLA/CNC nanocomposites

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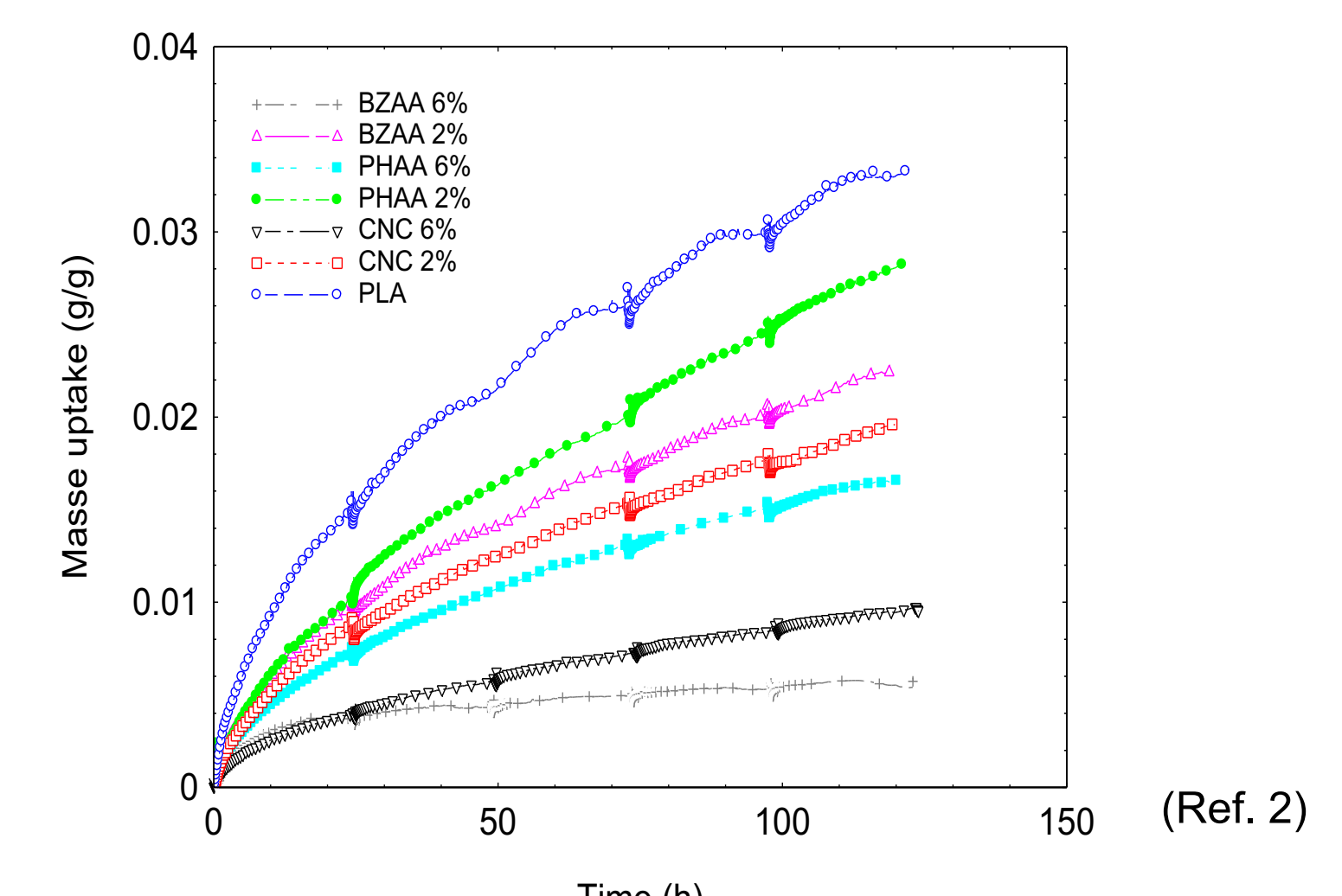
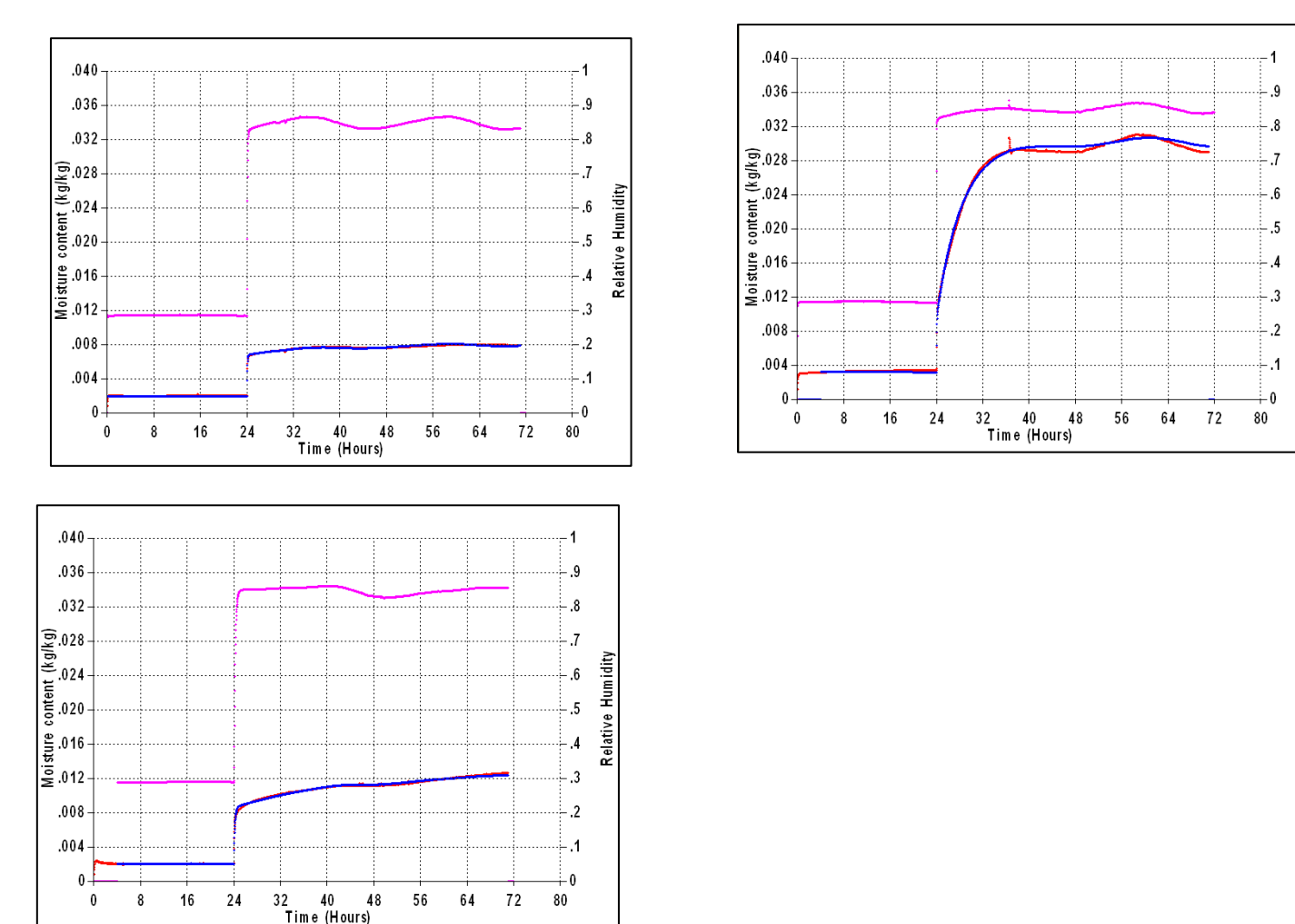


References and Acknowledgement

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- Espino Perez, E., Bras, J., Almeida, G., Plessis, C., Belgacem, M. N., Perre, P., & Domenek, S. (2017). Submitted to *Carbohydrate Polymers*.
- Perre, P., Pierre, F., Casalinho, J., & Ayouz, M. (2015). *Drying Technology*, 33(9), 1068-1075.

Identification of transport parameters sorption

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	CNC (wt%)	D x 10 ⁻¹⁵ (m ² s ⁻¹)	m _{eq,F} (wt%)	τ (h)
PLA	0	5.6	0.0050	18.7
PLA/CNC	2	3.6	0.0061	19.8
PLA/CNC	6	2.6	0.0055	4.1
PLA/CNC-g-PhAA	2	4.2	0.0048	
PLA/CNC-g-PhAA	6	2.2	0.0059	
PLA/CNC-g-BzAA	2	5.3	0.0049	
PLA/CNC-g-BzAA	6	3.0	0.0053	

	CNC (wt%)	D x 10 ⁻¹⁵ (m ² s ⁻¹)	m _{eq,F} (wt%)	m _{r,120h} (wt%)
PLA	0	3.2 ± 1.6	2.6 ± 0.2	0.7
PLA/CNC	2	1.6 ± 0.8	1.4 ± 0.2	0.6
PLA/CNC	6	3.7 ± 1.8	0.4 ± 0.2	0.6
PLA/CNC-g-PhAA	2	11 ± 6	0.6 ± 0.2	2.2
PLA/CNC-g-PhAA	6	3.9 ± 2.0	0.6 ± 0.2	1.0
PLA/CNC-g-BzAA	2	2.5 ± 1.3	1.2 ± 0.2	0.9
PLA/CNC-g-BzAA	6	8.7 ± 4.3	0.3 ± 0.2	0.2

Conclusion

The inverse model successfully allowed for the separation of Fickian and polymer relaxation related mass transfer in PLA/CNC nanocomposites. Fickian mass transport behaviour showed that the CNC exhibited only a small tortuosity effect to be expected from CNC and surface-grafted CNC. The analysis of the polymer relaxation controlled mass transport regime showed that water swelled the CNC charges, which significantly increased the water solubility in the system and produced a preferential pathway for water transport through the nanocomposites with small relaxation times. The surface grafting of CNC successfully attenuated the effect, but without completely eliminating it. The CNC grafted with benzyl acetic acid had apparently a specific effect on anisole, which seemed to yield no swelling of CNC and decrease the polymer relaxation.

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