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LEUVEN

INTERFACIAL ADHESION OF BAMBOO FIBRE COMPOSITES

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World Bamboo Congress – Antwerp - April 2012

Composite Materials group

Content

Overview

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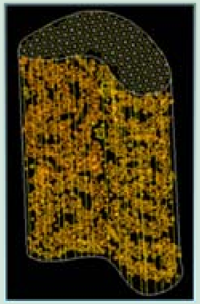
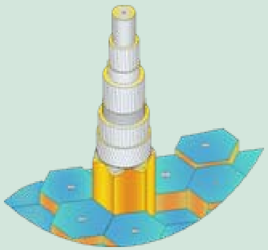
Microstructure → **Surface** → **Wetting** → **SEC theories** → **Adhesion Improvement**

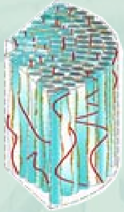
Microstructure



Technical fibre ~100 – 300 μm



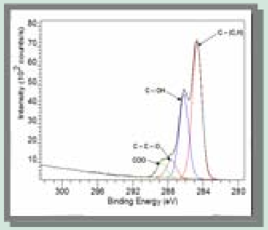
Elementary fibre ~10 – 20 μm



Nano fibril ~1 – 10 nm

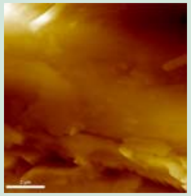
Surface

Chemical composition

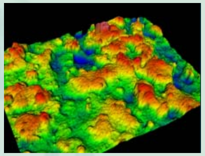


X-ray photoelectron spectroscopy (XPS)

Topography



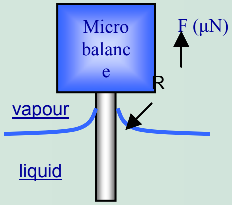
AFM



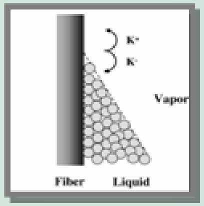
Profilometer

Wetting

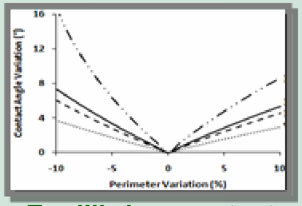
Fibre and matrix



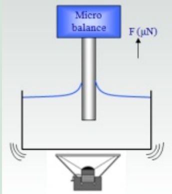
Molecular kinetic theory



Effect of liquid absorption and perimeter variation

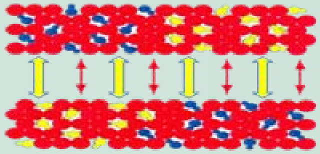


Equilibrium contact angle (sound vibration)



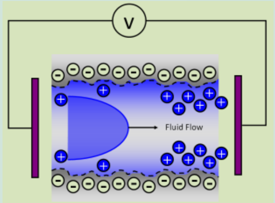
SEC theories

Acid/base



$$\gamma_{L,i}(1+\cos\theta_i) = 2\left(\sqrt{\gamma_{L,i}^{LW}\gamma_S^{LW}} + \sqrt{\gamma_{L,i}^{+}\gamma_S^{-}} + \sqrt{\gamma_{L,i}^{-}\gamma_S^{+}}\right)$$

Streaming Potential



Adhesion Improvement

3 approaches:

1. Make a good match with untreated fibre:

   Polyvinylidene fluoride (PVDF)

2. Treat the surface to get a good match:

   Chitosan layer, Silanes

3. Make an entire bio-degradable composite:

   Gluten, PLA

Interface Characterization

Micromechanical test: Pull-out test

Flexural test: 3 point bending test

Composite materials group

Introduction : Bamboo Fibres

Bamboo specie:
Guadua angustifolia

Culms:
Average height: 20-30m
Average diameter: 10-13cm
Culm internodes are about 20 cm long

Rapid growth: 21 cm daily growth in height

Higher productivity: it reaches its maximum height (15 - 30 m) in the first six months of growth

Mechanical and Physical Properties:
Strength: ~800 MPa
Stiffness: ~40 GPa
Density: 1.44 g/cm^3

GOAL: Understanding the interfacial bonding of bamboo fibre composites

Objectives:
- **study the fibre's surface and structure**
- **study the wetting behavior of bamboo fibres and matrices**
- **study the mechanical properties of the interface**

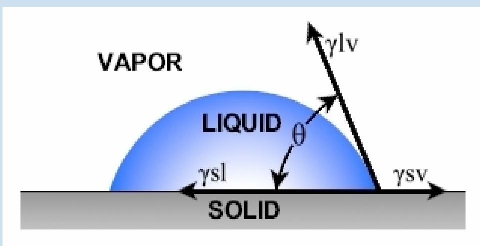
www.guaduabamboo.com

Introduction: Theory

Interfacial interactions:

- **Physical adhesion**: controlled by wettability, surface energy/surface tension of fibre and matrix
- **Chemical bonding**: chemical reaction at the interface
- **Mechanical interlocking**: fibre's surface roughness

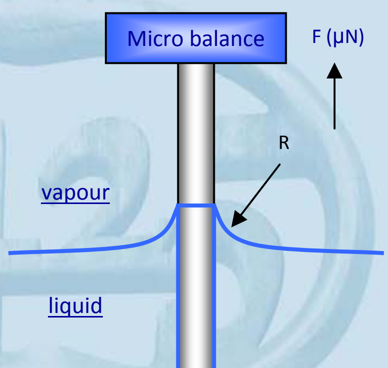
Young's equation



$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv}\cos\theta$$

Expresses the balance of forces per unit length of three phase contact line.

Wilhelmy method (tensiometer)



Wilhelmy equation

$$\cos\theta = \frac{F}{p\gamma_{lv}}$$

F is the measured force,
P is the fibre perimeter,
γ_l the liquid surface tension

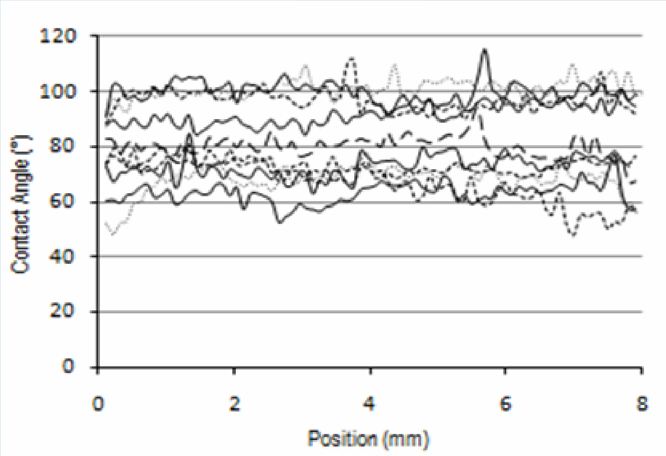
Determination of fibre perimeter using Hexane

$$F_{measured} = p\gamma$$

Introduction: Contact Angle and Natural Fibres

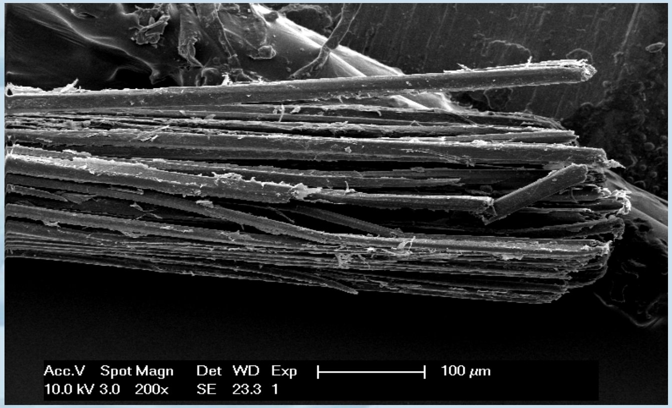
In natural fibres, the wetting measurements are obscured by non-equilibrium phenomena:

- Roughness and chemical heterogeneity of fibre's surface.
- Surface topography.
- Liquid sorption/diffusion
- Swelling of the fibre by the liquid.
- Diffusion of extractives from fibre's surface to liquid.



Advancing dynamic contact angle versus fibre position for water on bamboo fibres

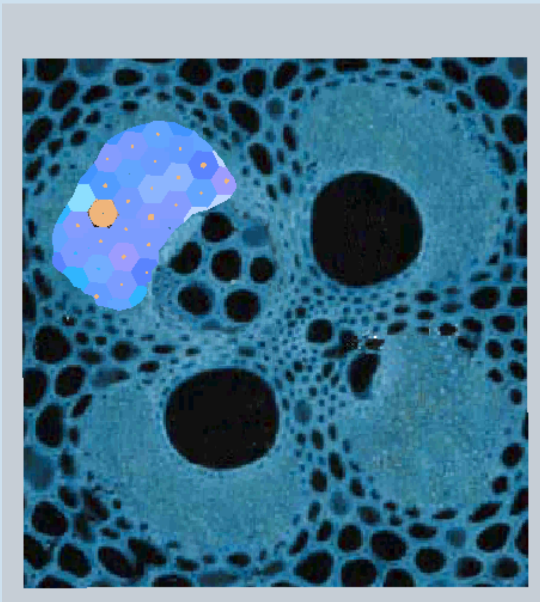
Bamboo Fibres



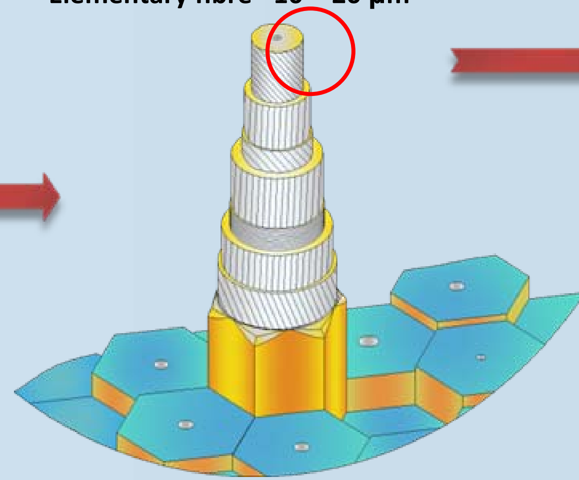
- Damage produced by the extraction process.

Structure of Bamboo Fibre

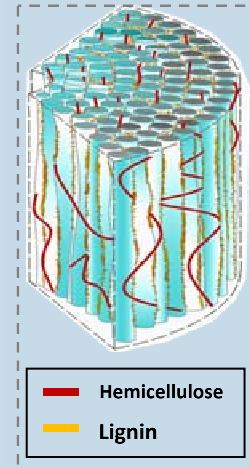
Technical fibre ~100 – 300 µm



Elementary fibre ~10 – 20 µm

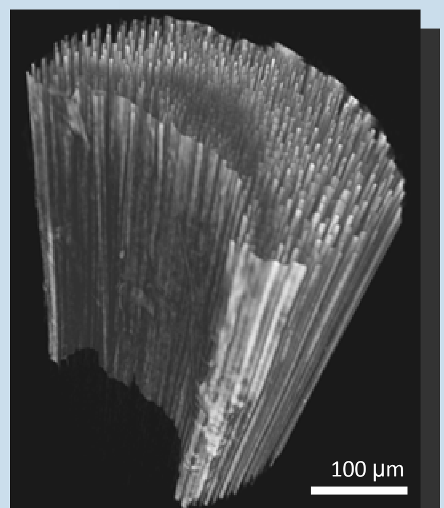


Nano fibril ~1 – 10 nm

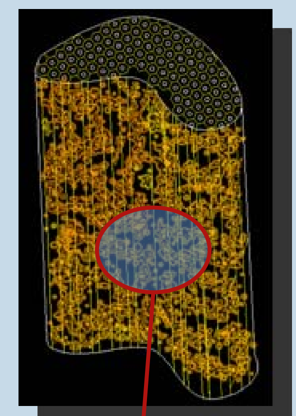


Chemical Composition:
(Technical fibre)

Cellulose: ~60%
Lignin: ~40%
Hemicelluloses:

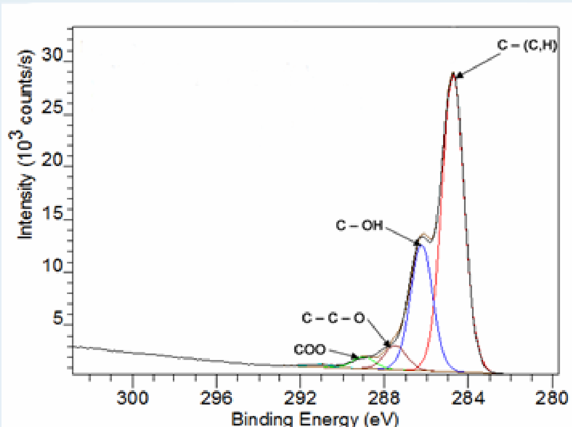


Micro-CT image of a technical bamboo fibre

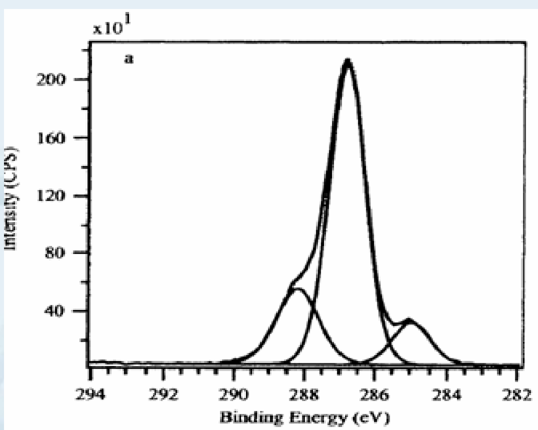


Cellulose and lignin ?

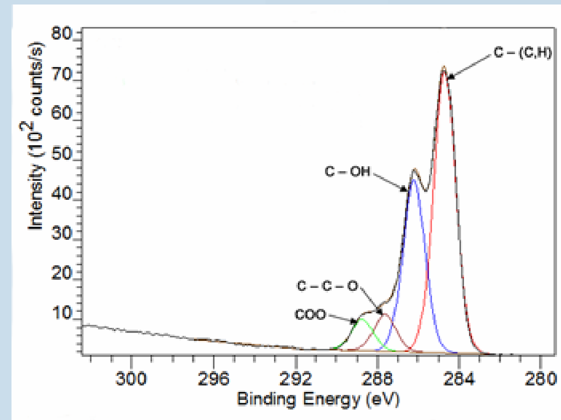
Surface Chemical Composition: XPS



XPS spectra Lignin from Granit



Cellulose - XPS study of living tree, Andrei Shchukarev



XPS spectra bamboo fibre surface

C (%)	O (%)	N (%)	Si (%)	O/C	Binding energy (eV)			
					284.8	286.3	287.6	289.0
					C1 (%)	C2 (%)	C3 (%)	C4 (%)
74.3 ± 1.5	22.9 ± 0.3	1.8 ± 0.7	0.6 ± 0.4	0.31 ± 0.02	58.0 ± 3.1	28.8 ± 2.3	7.6 ± 1.3	5.6 ± 0.4

Theoretical O/C value for lignin: 0.32

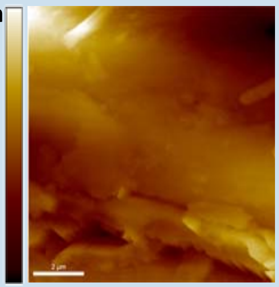
Surface Chemical Composition: Autoclave Treatment

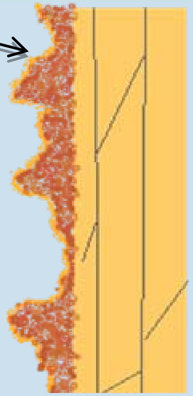
Tg: 90 - 180 °C

Lignin

3085 nm

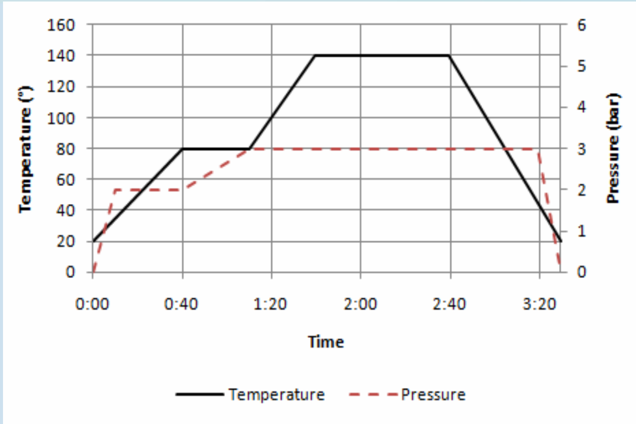
0 nm



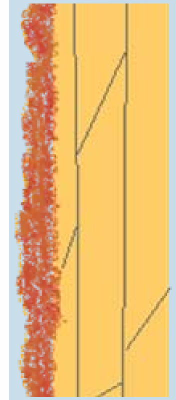


Before

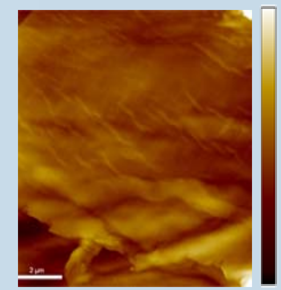
RMS roughness of 481 nm



Autoclave



After



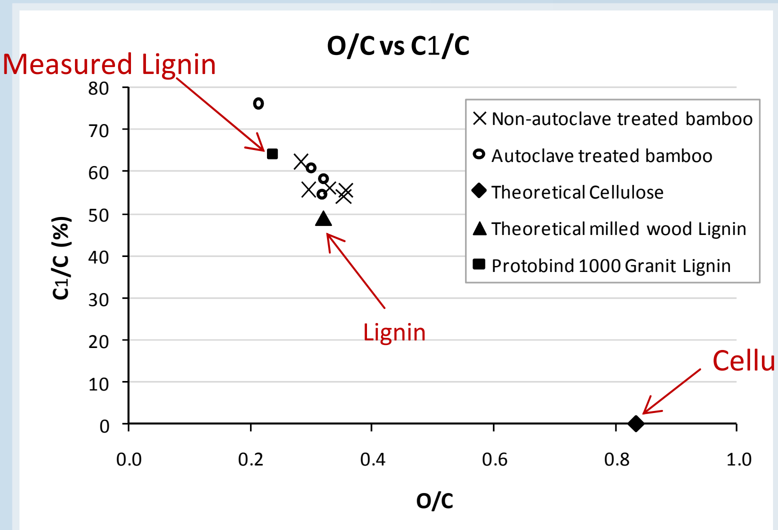
620 nm

0 nm

RMS roughness of 64 nm

C1/C ratios versus O/C ratios for chemical groups at the surface of bamboo fibres, autoclave treated bamboo fibres, lignin from Granit, and theoretical values for cellulose and lignin according to Shchukarev

Measured Lignin



Cellulose

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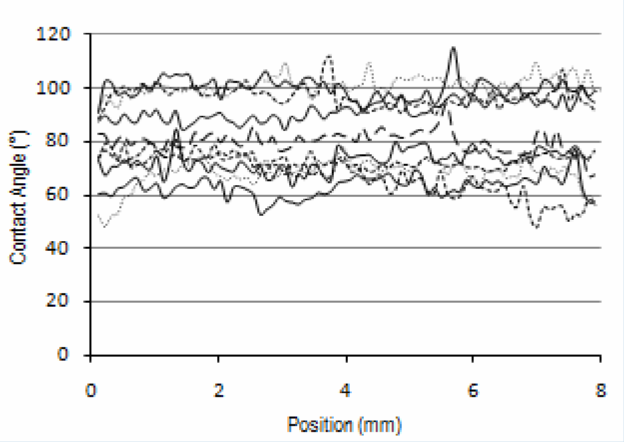
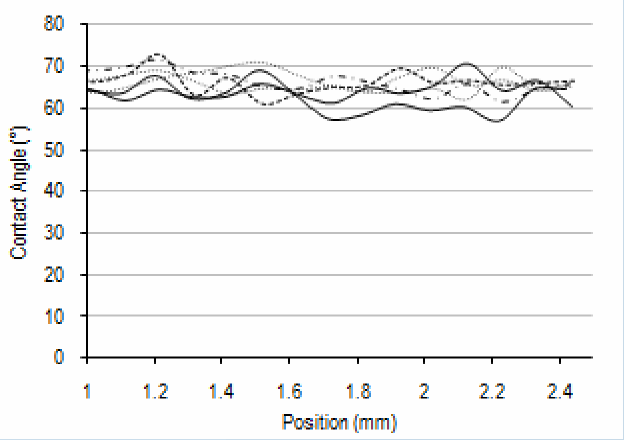
Surface Chemical Composition: Autoclave Treatment

Without Autoclave



Non -autoclave Treated Fibres (1.5mm/min)			
Fibre No	Contact Angle (°) First Measurement	Contact Angle (°) Second Measurement	Variation %
1	72.6 ± 7.2	95.1 ± 7.6	23.7
2	97.0 ± 8.2	84.2 ± 3.8	15.3
3	98.0 ± 4.3	81.5 ± 7.4	20.2
4	101.0 ± 2.1	105.0 ± 3.7	3.8
5	72.8 ± 9.1	92.3 ± 6.6	21.1
6	83.3 ± 2.4	72.0 ± 3.8	15.7
7	98.6 ± 6.7	80.0 ± 4.3	23.0
8	99.9 ± 7.1	89.0 ± 9.1	12.2
9	84.6 ± 8.6	86.0 ± 2.7	1.6
10	68.7 ± 4.3	100.0 ± 3.8	31.3
Average	87.7 ± 14.7	88.5 ± 10.4	

Autoclave



Autoclave Treated Fibres (1.5mm/min)			
Fibre No	Contact Angle (°) First Measurement	Contact Angle (°) Second Measurement	Variation %
11	67.4 ± 1.1	66.1 ± 2.3	1.9
12	69.3 ± 1.7	67.3 ± 2.2	2.9
13	66.3 ± 2.2	65.6 ± 1.4	1.1
14	71.8 ± 3.4	67.1 ± 2.7	6.5
15	68.9 ± 1.3	66.0 ± 1.9	4.2
16	68.8 ± 2.3	66.4 ± 3.8	3.5
17	67.6 ± 3.4	68.0 ± 1.7	0.6
18	69.8 ± 3.8	69.3 ± 2.4	0.7
19	70.2 ± 4.1	68.9 ± 4.4	1.9
20	67.9 ± 2.1	69.1 ± 1.2	1.8
Average	68.8 ± 3.2	67.1 ± 2.3	

Perimeter and absorption evaluation

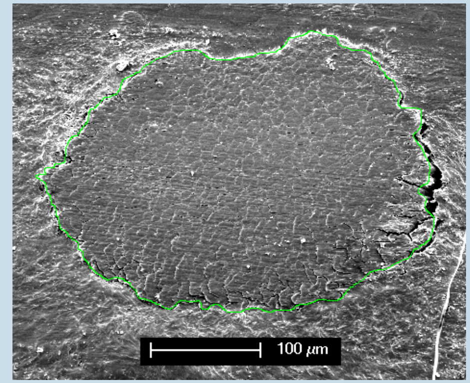
Wilhelmy equation

$$\cos\theta = \frac{F}{p\gamma_{lv}}$$

Determination of fibre perimeter using Hexane

$$F_{measured} = p\gamma$$

Typical cross section of a technical bamboo fibre

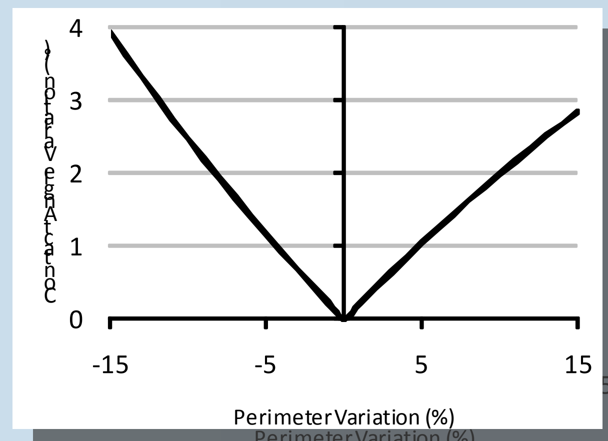


Fibre	Fibre No	Methods Wetting Analysis (µm)	Image Analysis (µm)	Relative Error (%)
Non-autoclave Treated Bamboo	1	1022 ± 24	1030 ± 38	0.8
	2	1032 ± 30	1108 ± 42	7.4
	3	1087 ± 38	1122 ± 71	3.2
	4	998 ± 18	1005 ± 54	0.7
	5	1124 ± 25	1201 ± 78	6.9
Autoclave Treated Bamboo	1	1042 ± 29	1095 ± 35	5.1
	2	887 ± 23	949 ± 36	7.0
	3	1205 ± 26	1199 ± 25	0.5
	4	1083 ± 22	1159 ± 28	7.0
	5	1033 ± 34	1077 ± 63	4.3

7.4 %

7.0 %

Perimeter evaluation of technical bamboo fibres, based on SEM images and on wetting measurements in hexane.



$$\theta = \arccos\left(\frac{F_{measured}}{p\gamma}\right) = \arccos\left(\frac{D}{\Delta p}\right)$$

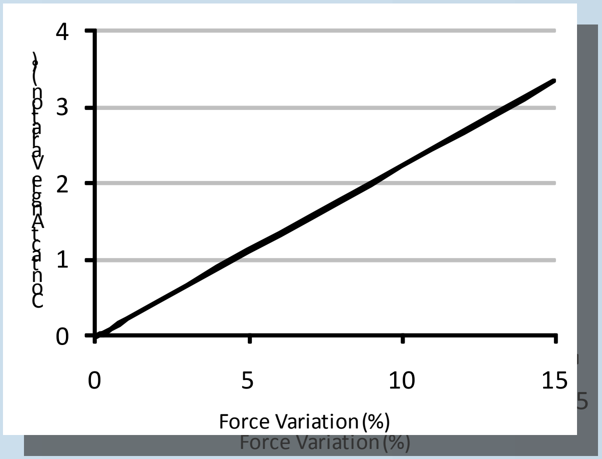
Perimeter and absorption evaluation

	Non -autoclave Treated Fibres				Autoclave Treated Fibres		
Fibre No	Absorbed Water (mN)	Wetting Force (mN)	%	Fibre No	Absorbed Water (mN)	Wetting Force (mN)	%
1	4.22	27.8 ± 2.8	15.2	1	1.51	24.4 ± 1.8	6.2
2	1.40	11.2 ± 1.2	12.5	2	2.15	30.2 ± 3.1	7.1
3	0.60	7.1 ± 1.4	8.4	3	1.88	31.9 ± 2.1	5.9
4	4.55	30.9 ± 1.7	14.7	4	1.20	25.0 ± 1.7	4.8
5	4.46	27.0 ± 3.6	16.5	5	2.26	31.3 ± 1.6	7.2
6	1.37	8.9 ± 1.1	15.4	6	1.86	27.4 ± 2.8	6.8
7	4.63	30.3 ± 4.3	15.3	7	1.76	30.3 ± 1.3	5.8
8	1.93	13.7 ± 0.7	14.1	8	1.33	26.1 ± 2.1	5.1
		Average	14.0			Average	6.1

14 %   6 %

Measured values of water absorption (in force units) for non-autoclave treated and autoclave treated bamboo fibres.

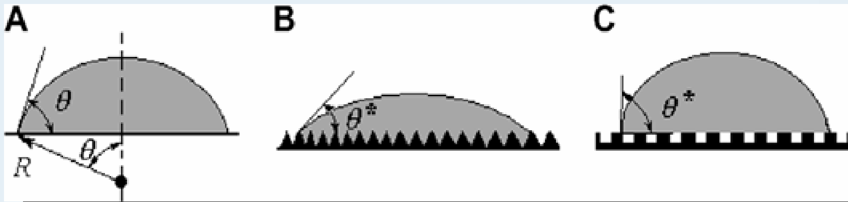
$$\theta = \arccos\left(\frac{F_{measured}}{p\gamma}\right) = \arccos(D \times \Delta F)$$



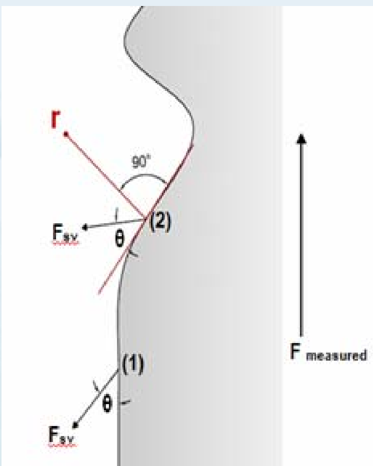
Composite Materials group

Effect of roughness and waviness

Schemes of different wetting regimes

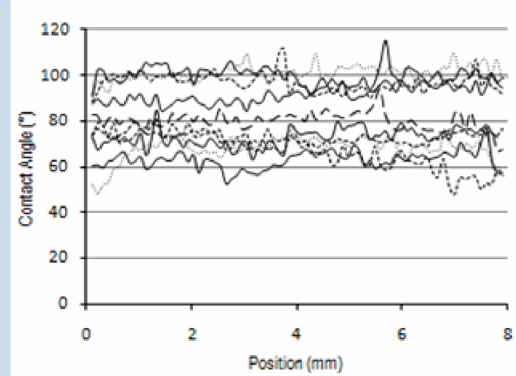


The radius of curvature of the fibre surface is constantly changing

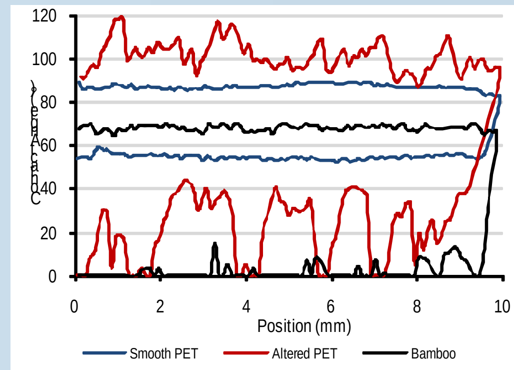


Position (1): smooth fibre

Position (2): fibre with surface irregularities.



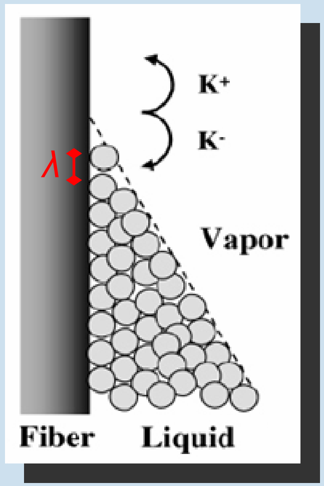
Advancing dynamic contact angle versus fibre position for water on bamboo fibres



Advancing and receding contact angles of a smooth and altered PET fibres, and a typical autoclave treated bamboo fibre

C.A. Fuentes et al., Wetting behaviour and surface properties of technical bamboo fibres, Colloids and Surfaces A. 2011

Wetting kinetics – Molecular Kinetic Theory (MKT)



M. Vega, D. Seveno, T. Blake (Langmuir 2007)

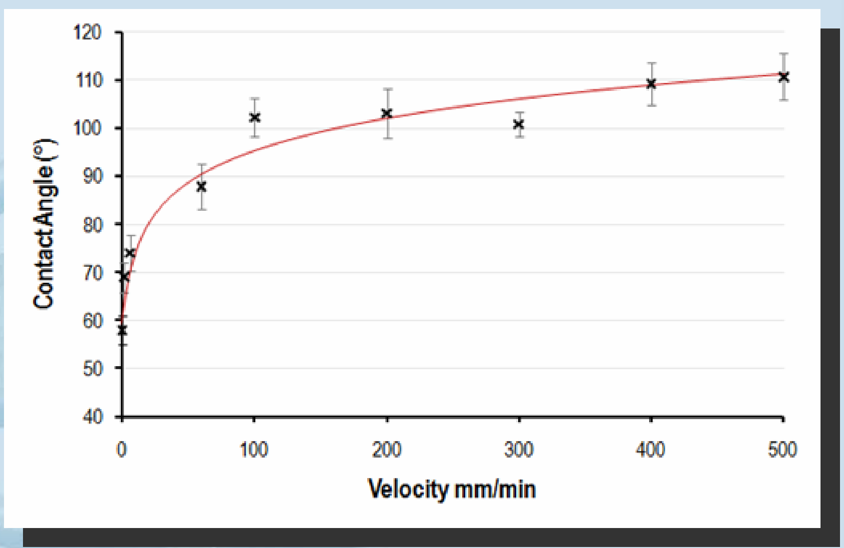
Ko: Equilibrium displacement frequency

λ : average length of each molecular displacement

k : Boltzmann constant

T : absolute temperature

$$v = 2K_0 \lambda \sinh\left[\frac{\gamma\lambda^2}{2kT}(\cos\theta_0 - \cos\theta)\right]$$



PET

85.1° ± 1.2
λ=1.16 nm
R^2=0.94

82.5°
λ=1.10 nm
R^2=0.96

TD Blake

Bamboo

K_0 (×10^6)	λ (nm)	θ_0 (°)	R^2
0.059 ± 0.005	0.826 ± 0.010	60.3 ± 2.3	0.90

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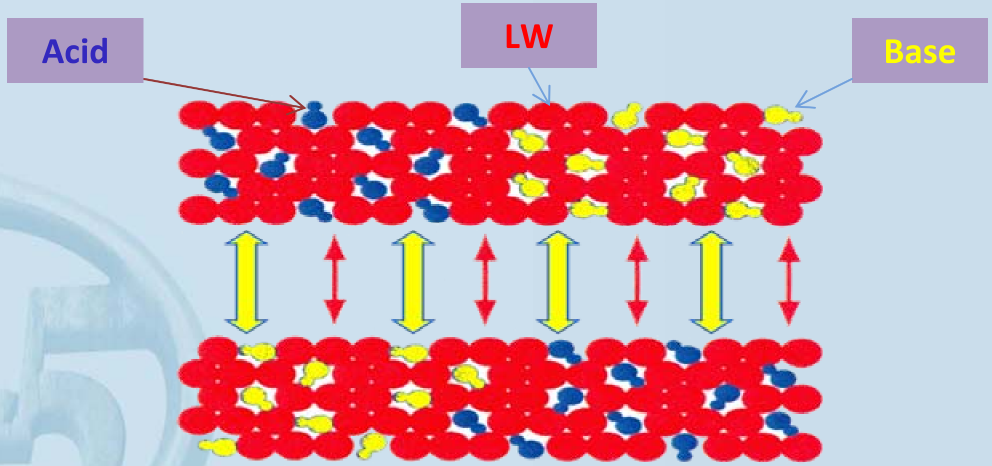
Surface Energy Components Theory

Surface energy of a solid can be described in **acid**, **base** and **Lifshitz-van der Waals** components

$$\gamma_{L,i}(1+\cos\theta_i) = 2\left(\sqrt{\gamma_{L,i}^{LW}\gamma_S^{LW}} + \sqrt{\gamma_{L,i}^{+}\gamma_S^{-}} + \sqrt{\gamma_{L,i}^{-}\gamma_S^{+}}\right)$$

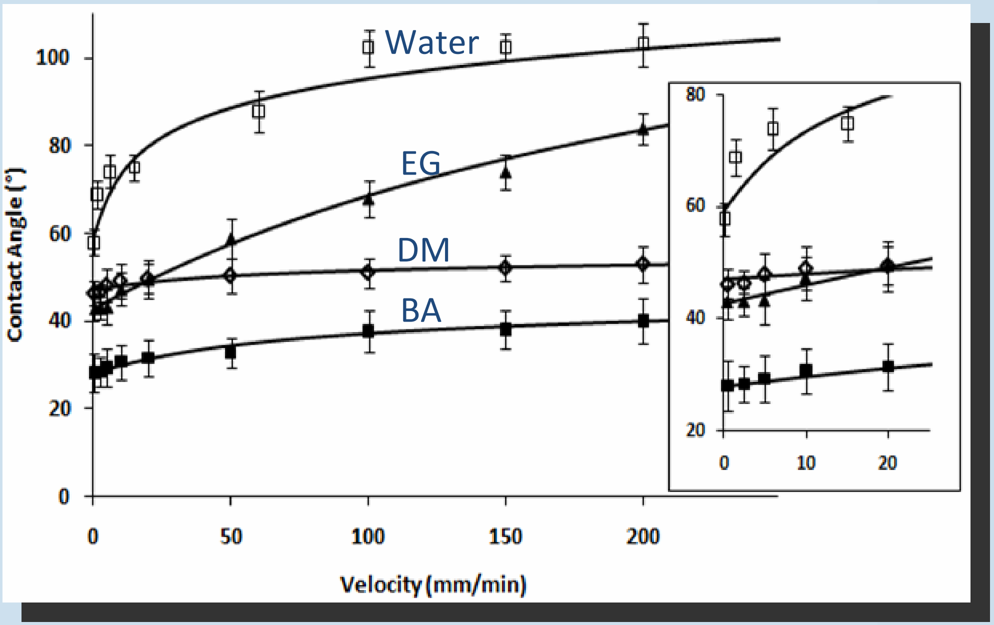
In matrix notation Ax = b

$$A = \begin{bmatrix} \sqrt{\gamma_1^{LW}} & \sqrt{\gamma_1^{+}} & \sqrt{\gamma_1^{-}} \\ \sqrt{\gamma_2^{LW}} & \sqrt{\gamma_2^{+}} & \sqrt{\gamma_2^{-}} \\ \sqrt{\gamma_3^{LW}} & \sqrt{\gamma_3^{+}} & \sqrt{\gamma_3^{-}} \end{bmatrix} \quad x = \begin{bmatrix} \sqrt{\gamma_S^{LW}} \\ \sqrt{\gamma_S^{-}} \\ \sqrt{\gamma_S^{+}} \end{bmatrix} \quad b = \frac{1}{2}\begin{bmatrix} \gamma_1(1+\cos\theta_1) \\ \gamma_2(1+\cos\theta_2) \\ \gamma_3(1+\cos\theta_3) \end{bmatrix}$$



Strong Interaction

Surface Energy Components Theory



Molecular Kinetic Theory (MKT)

Ko: Equilibrium displacement frequency
λ : average length of each molecular displacement
k : Boltzmann constant
T : absolute temperature

$$v = 2K_0 \lambda \sinh\left[\frac{\gamma\lambda^2}{2kT}(\cos\theta_0 - \cos\theta)\right]$$

Physical characteristics of test liquids

Test liquid	ρ (g/cm3)	η (mPa/s)	γ (mN/m)
Water	1.00	1.0	72.8
Diiodomethane	3.40	2.8	50.8
Ethylene glycol	1.11	16.1	47.7
Benzyl alcohol	1.04	8.0	39.0

Surface free energy components of used liquids

	γ^{tot} (mJ/m^2)	γ^{LW} (mJ/m^2)	γ^{+} (mJ/m^2)	γ^{-} (mJ/m^2)
Water	72.8	26.25	48.50	11.16
Diiodomethane	50.8	50.80	0.00	0.00
Ethylene glycol	48.0	33.90	0.97	51.60
Benzyl alcohol	39.0	-	-	-

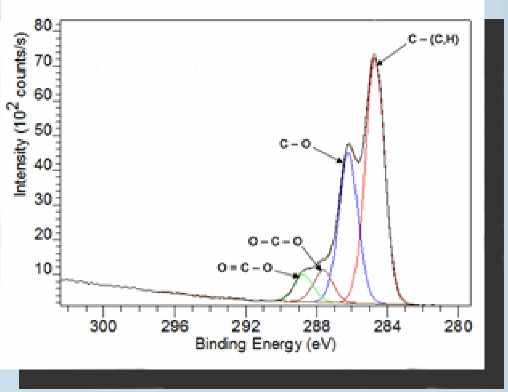
Surface Energy Components Theory

	K_0 (×10[6])	λ (nm)	θ_0 (°)	R^2
Water	0.059 ± 0.005	0.826 ± 0.010	60.3 ± 2.3	0.90
Diiodomethane	0.069 ± 0.003	2.422 ± 0.021	47.9 ± 1.1	0.96
Ethylene glycol	1.618 ± 0.205	0.603 ± 0.004	42.8 ± 0.8	0.99
Benzyl alcohol	0.118 ± 0.080	2.158 ± 0.018	28.0 ± 1.5	0.98

Material	γ^{tot} (mJ/m²)	γ^{LW} (mJ/m²)	γ^{ab} (mJ/m²)	γ^{+} (mJ/m²)	γ^{-} (mJ/m²)
Bamboo	38.82 ± 0.76	35.44 ± 0.06	3.37 ± 0.57	0.28 ± 0.06	10.13 ± 1.25
Water	72.80	26.25	46.53	48.50	11.16

X-ray photoelectron spectroscopy (XPS)

C (%)	O (%)	N (%)	Si (%)	O/C	Binding energy (eV) 284.8 C1 (%) (C-C)	286.3 C2 (%) (C-O)	287.6 C3 (%) (C=O)	289.0 C4 (%) (O-C=O)
74.29 ±1.54	22.86 ±0.25	1.75 ±0.71	0.63 ±0.43	0.31 ±0.02	58.02 ±3.07	28.80 ±2.34	7.63 ±1.31	5.59 ±0.41



C1: C–C linkages of lignin, hemicelluloses and extractives.

C2: OH groups of cellulose, hemicelluloses, lignin and extractives, OCH groups of lignin, and C–O–C linkages of extractives.

→ BASIC

C3: C=O groups in lignin and extractives, O–C–O linkages in cellulose and hemicelluloses.

C4: CH_3CO groups of hemicelluloses, HOOC groups of hemicelluloses, COO and COOH groups of extractives.

→ ACID

Surface Treatment: Chitosan Layer

2 approaches to improve interface compatibility

1. Make a good match with untreated fibre:

   Polyvinylidene fluoride (PVDF)

Advantages:
-Recyclable (injection moulding)
-Fibres don't need treatment
-Provides protection against UV rays

2. Treat the surface to get a good match:

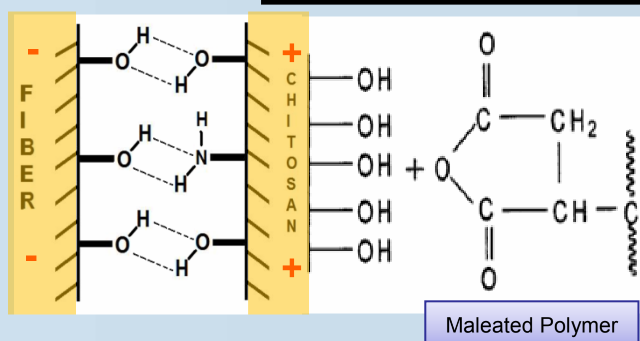
   Chitosan layer

Advantages:
-Protection against biodegradation
-Treatment is environmentally friendly
-Use of common matrices
-Recyclable

Crab exoeskeleton

Acid base interactions between the fibre and the chitosan layer:

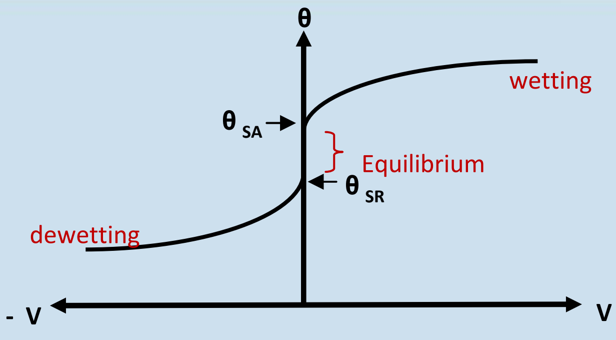
hydrogen bonding



Chemical bonding between chitosan and MAPP:

covalent bonds & hydrogen bonding

Adhesion Optimization



$$\cos\theta_{equ} = 0.5\cos\theta_{adv} + 0.5\cos\theta_{rec}$$

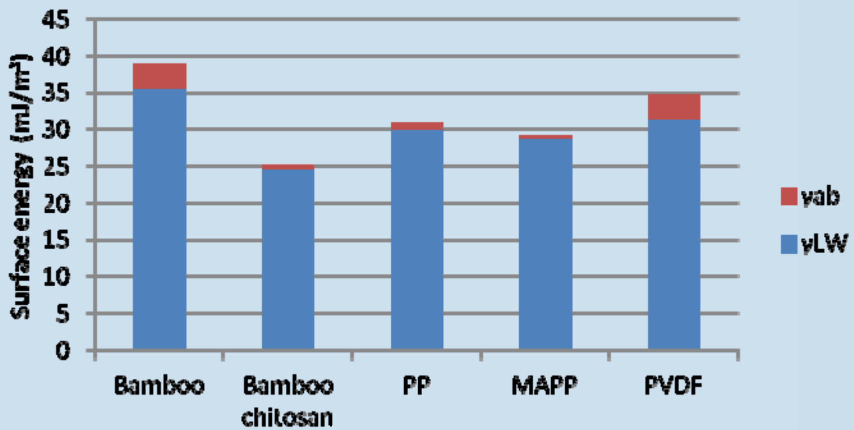
Advancing, receding and equilibrium contact angles of probe liquids on thermoplastic surfaces

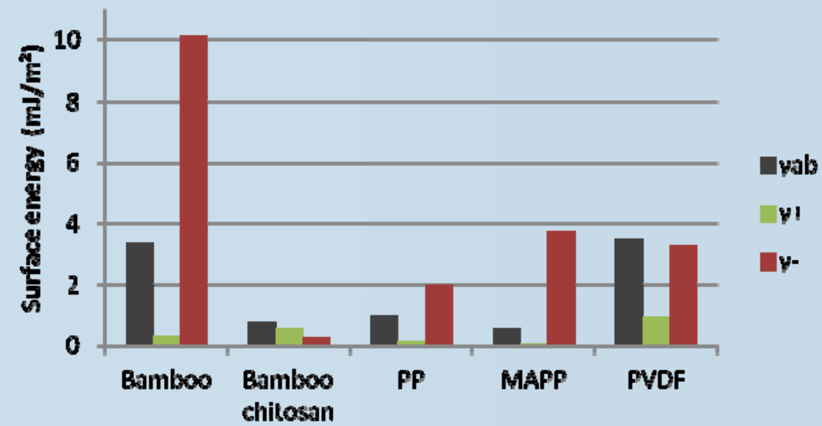
Material	Water	EG	DIO
Bamboo	60.3 ± 2.3	42.8 ± 0.8	47.9 ± 1.1
Chitosan	98.0 ± 4.1	64.1 ± 5.8	67.3 ± 4.2
PP	86.0 ± 1.1	49.4 ± 1.7	57.7 ± 1.0
MAPP	82.8 ± 0.7	65.3 ± 0.9	61.1 ± 0.6
PVDF	66.2 ± 0.3	36.0 ± 0.4	32.8 ± 0.3

Surface Energy Components (Acid-base approach)

Material	γ^{tot} (mJ/m²)	γ^{LW} (mJ/m²)	γ^{ab} (mJ/m²)	γ^{+} (mJ/m²)	γ^{-}(mJ/m²)
Bamboo	38.82 ± 0.76	35.44 ± 0.06	3.37 ± 0.57	0.28 ± 0.06	10.13 ± 1.25
Bam-chitosan	25.13 ± 1.42	24.39 ± 1.38	0.74 ± 0.44	0.53 ± 0.26	0.26 ± 0.18
PP	30.87 ± 0.52	29.90 ± 0.47	0.97 ± 0.20	0.12 ± 0.05	1.97 ± 0.31
MAPP	29.07 ± 0.37	28.52 ± 0.31	0.56 ± 0.20	0.02 ± 0.01	3.72 ± 0.32
PVDF	34.64 ± 0.53	31.16 ± 0.47	3.48 ± 0.23	0.93 ± 0.10	3.26 ± 0.23

Adhesion Optimization



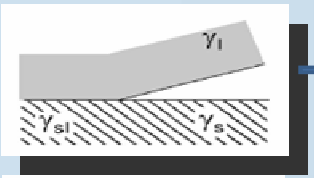


Adhesion optimization

Interfacial Energy

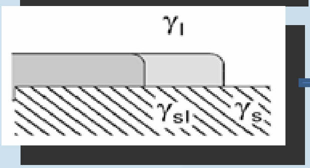
$$\gamma_{sl} = \gamma_s^{LW} + \gamma_l^{LW} + 2\left[(\gamma_s^+\gamma_s^-)^{1/2} + (\gamma_l^+\gamma_l^-)^{1/2} - (\gamma_s^{LW}\gamma_l^{LW})^{1/2} - (\gamma_s^+\gamma_l^-)^{1/2} - (\gamma_s^-\gamma_l^+)^{1/2}\right]$$

Work of adhesion



$$W_a = \gamma_l + \gamma_s - \gamma_{sl} = \gamma_l(1+\cos\theta)$$

Spreading coefficient



$$S = \gamma_s - (\gamma_{sl} + \gamma_l)$$

Adhesion Optimization

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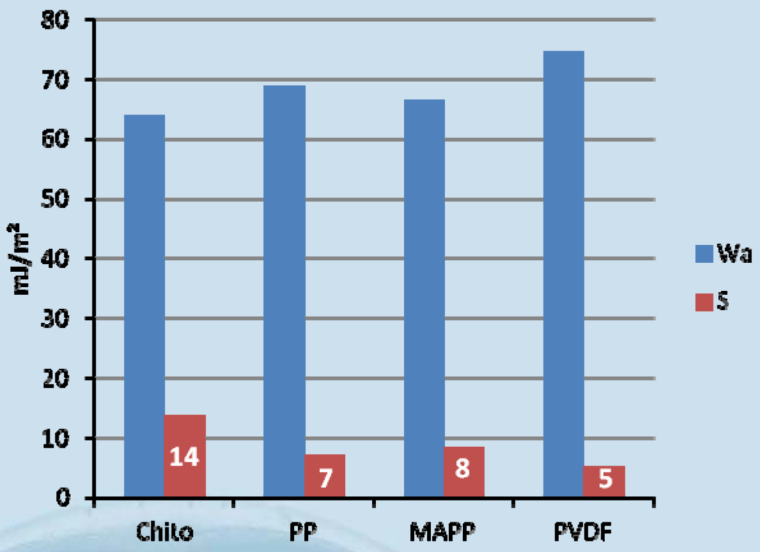
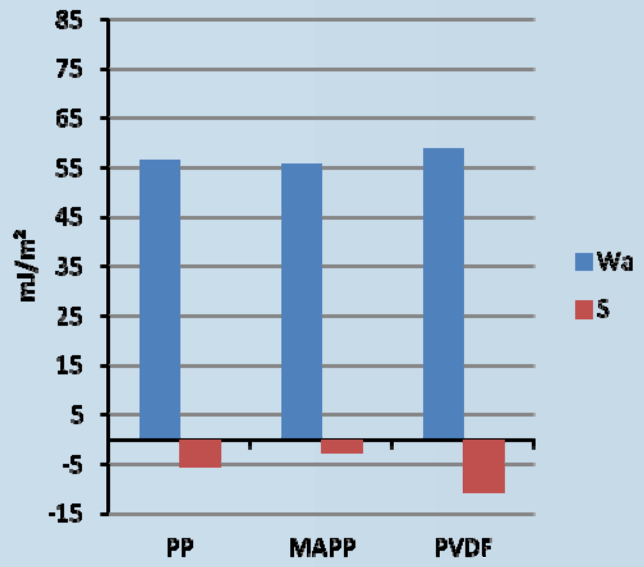
Bamboo as Substrate



Chitosan Coated Bamboo as Substrate

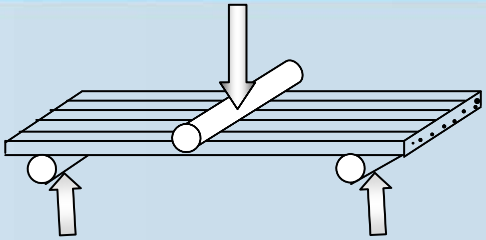


Physical Adhesion: Predictions for PVDF-untreated bamboo are the best !!!

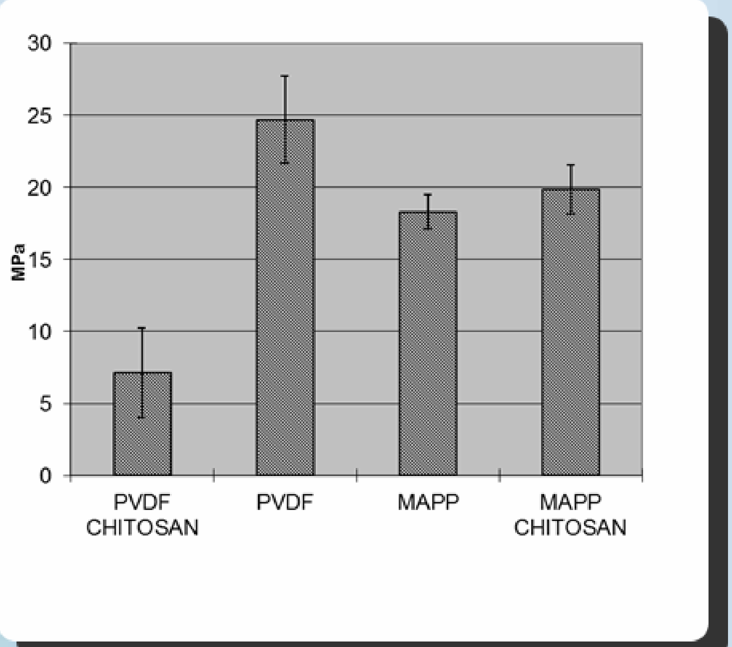
Composite materials group

Interfacial Strength

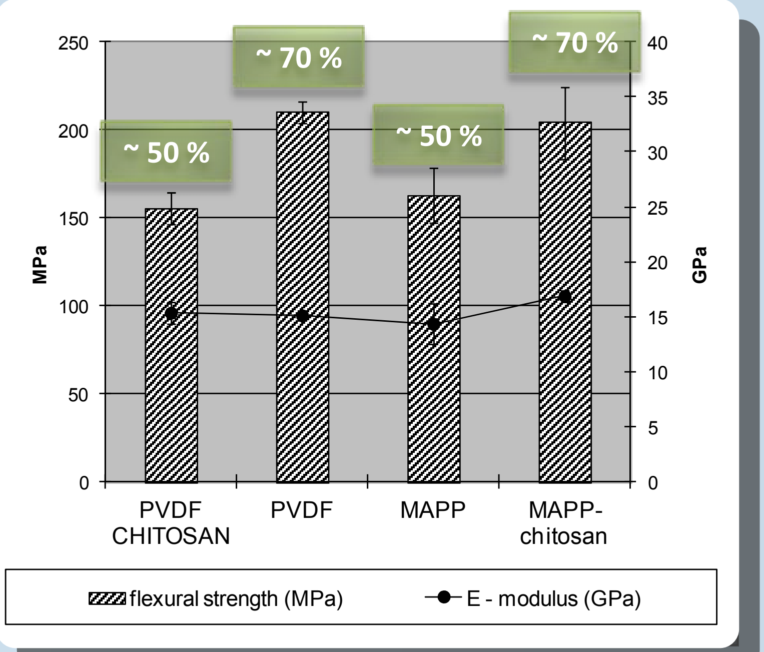
Three point bending tests



Transversal properties



Longitudinal properties



Conclusions

Surface energy components and wetting parameters obtained from contact angle measurements are useful and valuable tools for evaluating the compatibility of natural fibres and matrices for making composites.

As predicted, PVDF-bamboo composites present the best combination of wetting parameters, showing a high Wa, as well as a positive S value helping to achieve a better wetting of the melted polymer on the bamboo fibre. Chitosan treatment improves the mechanical properties of bamboo composites.

Bamboo fibres' surface represents a well defined system and so its wetting behaviour can be studied and a meaningful interpretation of wetting data is ensured.

Thank you for your attention