EFFECT OF INTERFACIAL ADHESION ON MECHANICAL BEHAVIOR OF BAMBOO FIBER REINFORCED THERMOPLASTIC COMPOSITES

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Abstract
Systematic experimental results describing the dynamic wetting properties of bamboo fibers with different liquids were analyzed by applying the molecular-kinetic theory of wetting. Results suggest that the bamboo fiber surface represents a well defined system for wetting analysis. In this way, meaningful information on interfacial interactions can be obtained with the aim to conduct a study of the adhesion in terms of surface free energies of bamboo fibers with different thermoplastic matrices. In order to improve the compatibility for bamboo fiber, chitosan coating was applied. The effect of this treatment was evaluated by using contact angle measurements following the Wilhelmy technique. The surface free energy components were calculated following the acid-base theory. These values were then used to calculate the theoretical work of adhesion. For this, the contact angles of test liquids on polyvinylidene fluoride (PVDF), polypropylene (PP), and grafted maleic anhydride polypropylene (MAPP) were measured. Surface topography was examined by AFM, and surface chemical analysis was conducted by using XPS. Additionally, unidirectional bamboo fiber composites were tested in order to obtain a direct measure of the effect of fiber modification on the fiber-matrix adhesion by performing 3-point bending tests.

Results indicate that increase in physical adhesion can explain the improved interface and longitudinal strength in bamboo-PVDF composites, as compared to PP composites. For MAPP, no increase in physical adhesion is predicted, but for chitosan coated bamboo an increase in longitudinal strength was observed, which may be attributed to a chemical adhesion mechanism.

1 Introduction
The use of thermoplastics as matrices for natural fiber composites represents an approach with low environmental effects due to their recyclability. Natural fiber-reinforced thermoplastic composites can be re-used for a variety of processes such as extrusion or injection molding after their end-of-life [1]. However, the hydrophilic nature of natural fibers reduces their potential as reinforcing agents due to low interfacial interactions with typically hydrophobic thermoplastic matrices, such as polyethylene and polypropylene.

Among natural fibers, bamboo presents a combination of properties that makes them particularly adequate for being used as reinforcement fiber in (polymer) composite materials: specific mechanical properties which are comparable to glass fiber, natural abundance, low cost, and environmental friendliness [2].

In the case of bamboo technical fibers, the surface is covered with lignin instead of cellulose or hemi-cellulose like most other natural fibers [3]. Even though lignin has a less hydrophilic nature, chemical modifications should still be considered to optimize the interface, depending on the selected thermoplastic matrix Other problems arise when using thermoplastic matrices, such as the lack of occurrence of covalent bonding and the high viscosity of molten thermoplastics, making maximization of the physical adhesion indispensable to obtain better composites.

Bonding between the reinforcing fiber and the matrix has a significant effect on the properties of the composite since stress transfer and load distribution efficiency at the interface is determined by the degree of adhesion between the components. Using the experimental data obtained from wetting measurements, fibers and matrices can be examined and matched in terms of their surface energy components; predicting and verifying their compatibility allows more suitable combinations and therefore better composites to be made.

In this study, a novel procedure based on an autoclave treatment is presented, allowing stable and reproducible advancing contact angles to be measured on bamboo fibers. The wetting behavior of bamboo fibers and thermoplastic matrices (polyvinylidene fluoride (PVDF), polypropylene (PP) and grafted maleic anhydride polypropylene (MAPP)) is characterized with the Wilhelmy technique, the molecular-kinetic theory of wetting is used to interpret the contact angle experimental data, and the fiber surface is characterized by AFM and XPS. Surface energy components of bamboo fibers and thermoplastic matrices are estimated by using the acid-base approach. Furthermore, the surface of the bamboo is coated with chitosan in order to change the surface energy components. In order to obtain a direct measure of the effect of physical adhesion, unidirectional bamboo fiber composites are tested by performing 3-point bending tests (transverse and longitudinally).

2 Materials and testing methods
2.1 Materials
Technical bamboo fibers of the species Guadua angustifolia were extracted from bamboo culms with a purely mechanical extraction process in the Department of Metallurgy and Materials Engineering (MTM) at KU Leuven. With the aim to smoothen the lignin at the fiber surface, bamboo fibers were also further put in an autoclave under 3 bars of pressure at 150 °C for one hour (for more details on this procedure see our previous publication [3]).

Polypropylene, 0.3% maleic anhydride grafted polypropylene and polyvinylidene fluoride (Solef 1008) were obtained from Propex, Dupont, and Solvay respectively in the form of films. These films were washed with a detergent (RBS-35 from Chemical Products) at a concentration of 4% v/v in water during one hour, and next rinsed in ultrapure water at 90°C for one hour.

2.2. Contact angle measurements and wetting analysis
Advancing and receding contact angles of various test liquids on the polymer films were measured under controlled conditions: temperature of 20 °C and humidity of 60%, with a Krüss K100 tensiometer using the Wilhelmy technique. The equilibrium contact angle is

estimated by using the equation proposed by Andrieu et al. [4], corresponding to the average of the cosines of the advancing (θ_{adv}) and receding (θ_{rec}) angles, as shown in equation 1.

$$\cos\theta_0 = 0.5\cos\theta_{adv} + 0.5\cos\theta_{rec} \qquad (1)$$

For the natural fibers, the same method was used. However, only advancing angles could be measured due to surface irregularities [3]. By using dynamic contact angle measurements with various test fluids on bamboo fibers, and by applying the MKT theory [5], it is possible to verify the quality of the measurements by monitoring if the expected immersion velocity dependence, reproducibility and stability of the advancing contact angle data are obtained. This would then indicate that the measured contact angles are the true advancing contact angles. More details are shown in our previous studies [3].

2.3 Surface energy components and work of adhesion
Surface energies and components of the surface energies of the fibers and matrices can be estimated using the contact angle data of various test liquids on the fibers and matrices. Van Oss, Chaudhury and Good developed a model that considers the acid-base interaction between molecules, dividing the surface energy into a Lifshitz-van der Waals (γ^{LW}), an acid (γ^+) and a base (γ^-) component [6], as is shown in equation 2.

$$\gamma_s = \gamma_s^{LW} + 2\sqrt{\gamma_s^+ \gamma_s^-} \qquad (2)$$

The calculation of the acid-base surface free energy components was performed by using SurfTen 4.3 software [7].

The work of adhesion, Wa, is described as the work required to disjoint a unit area of the solid-liquid interface [8], and it is defined in terms of surface free energies by the Dupré equation:

$$W_a = \gamma_l + \gamma_s - \gamma_{sl} \qquad (3)$$

Where γ_S is the surface energy of the solid, γ_L is the surface energy of the liquid or matrix and γ_{SL} is the interfacial energy.

2.4 Surface characterization: X-ray photoelectron spectroscopy (XPS)
XPS analyses were performed on a Kratos Axis Ultra spectrometer (Kratos Analytical – Manchester – UK) equipped with a monochromatized aluminium X-ray source (powered at 10 mA and 15 kV). More information regarding the XPS analysis procedure can be found in [3].

2.5 Composite interfacial bond test and flexural testing
Unidirectional composites were prepared by compression molding of stacks of prepregs consisting of technical fibers, compressed between thermoplastic films. The applied pressure was 20 bar and temperatures of 175°C and 200°C were used depending on the polymer used. Flexural three point bending tests were performed on a universal testing machine (Instron 4426) based on ASTM D790, both in transverse direction to obtain a value for the interface strength and in longitudinal direction to evaluate composite strength.

2 Results and discussion

2.1 Wetting behavior

In the case of natural fibers, a direct measurement of the equilibrium or even static advancing contact angle is problematic, and so their wetting behavior is difficult to study. The Wilhelmy technique represents a reliable method to study the wetting behavior of bamboo fibers at different immersion speeds [3]: We showed that by using autoclave treatment we could minimize surface waviness, roughness and liquid penetration, without changing surface chemistry. Thus the bamboo fiber surface represented a well defined system and so its wetting behavior could be studied and a meaningful interpretation of wetting data was ensured (Fig. 1).
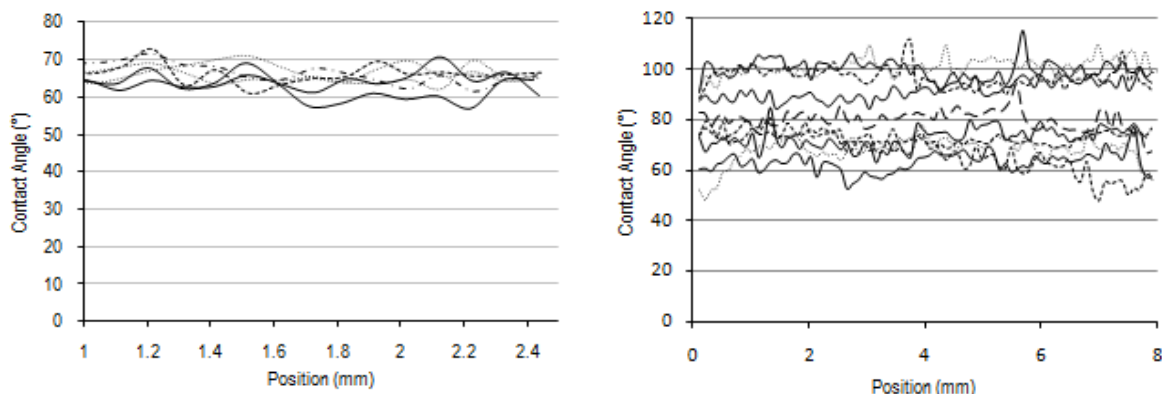

Figure 1. Advancing contact angle for autoclaved (left) and non-autoclaved (right) bamboo fibres in water. The results indicate a reduction of scatter caused mainly by fibre surface irregularities reduction at different length scales due to the autoclave treatment [3].

For this to be the case, contact angles of bamboo fibers must show an expected dependency to immersion velocity. The molecular-kinetic theory [5] provides a reasonable fit to the data, confirming the expected immersion velocity dependency, reproducibility and stability of the advancing contact angle in a bamboo-water system; indicating that the measured contact angle is the true advancing contact angle (Fig. 2).
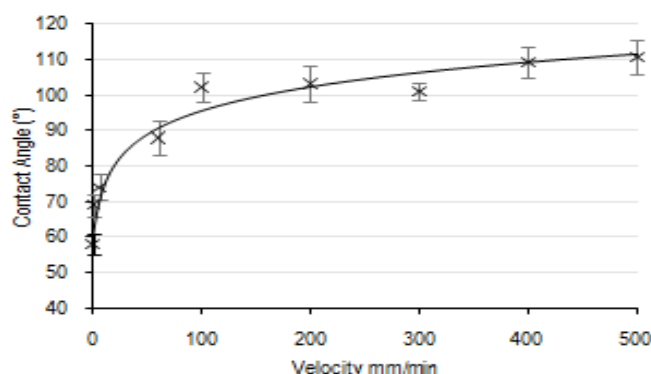

Figure 2. Dynamic contact angle as a function of wetting velocity for water on bamboo technical fibre, according to the molecular kinetic theory. The theoretical curve through the data was obtained by nonlinear regression of experimental data; the extrapolated static angle is obtained.

2.2 Surface chemical composition

Figure 3 shows the XPS results regarding surface chemical constituents of both autoclave-treated and non-treated technical bamboo fibers obtained from the decomposition of the high resolution carbon 1s spectrum for each fiber. Lignin content on the fiber surface was analyzed

by determining the oxygen-to-carbon atomic ratio, and the relative concentration of the C1 component. The results clearly indicate that technical bamboo surface constituents are close to our references for lignin, indicating that bamboo technical fibers may be homogeneously covered with lignin and possibly some other molecules, but not with cellulose. On autoclave treatment, the surface chemistry does not change.
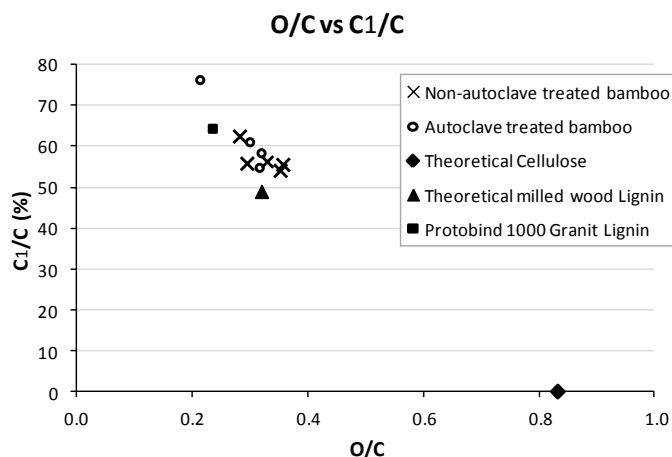

Figure 3. C1/C ratios versus O/C ratios for chemical groups at the surface of bamboo fibres [3]. Theoretical values for cellulose and lignin according to Shchukarev [9].

2.3 Surface energy components and work of adhesion

Once the advancing (static) and equilibrium contact angles of the liquids on the solids have been obtained (see table 1), the surface tension components of the solids can be determined. According to the acid-base theory, the total surface tension of the bamboo fibers was estimated to be 38 mN/m, with an acid and base contribution of 0.3 mN/m and 10 mN/m respectively and a total polar component of 3.5 mN/m (see also figure 4). Accordingly, the fiber's surface is relatively hydrophobic and a Lewis base; this means that a strong acidic Lewis matrix would give the best physical adhesion performance. For optimal physical adhesion, the surface energy of the solid substrate should be as high as possible, the two phases should have the same Lifshitz-van der Waals components and the acidic component of the substrate should be equal to the basic component of the liquid and vice versa [10].

Material	Water	EG	MI
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

Table 1. The advancing contact angles of water, ethylene glycol (EG), and methylene iodide (MI) on untreated and chitosan treated bamboo fibers and the equilibrium contact angle of these liquids on thermoplastic films according to the approach of Andrieu et al. [4].

The measured contact angles are given in table 1, and the there from calculated surface tension components are shown in figure 4. As expected, PVDF possesses higher acidity among the three examined matrices due to the different electro-negativities of carbon, fluorine, and hydrogen. Accordingly, the total surface energy of PVDF is higher than that of PP and MAPP, with a higher polar fraction [11].

For the case of PP, we found a small anomaly in the magnitude of the polar surface energy

component, which is expected to be zero, since pure PP is a nonpolar polymer. This effect may be related to aging processes or surface contamination.

The work of physical adhesion was calculated for the different materials by using equation 3 with bamboo as the substrate. The following values for Wa were obtained: 75 mJ/m^2 for PVDF, 67 mJ/m^2 for MAPP and 69 mJ/m^2 for PP.
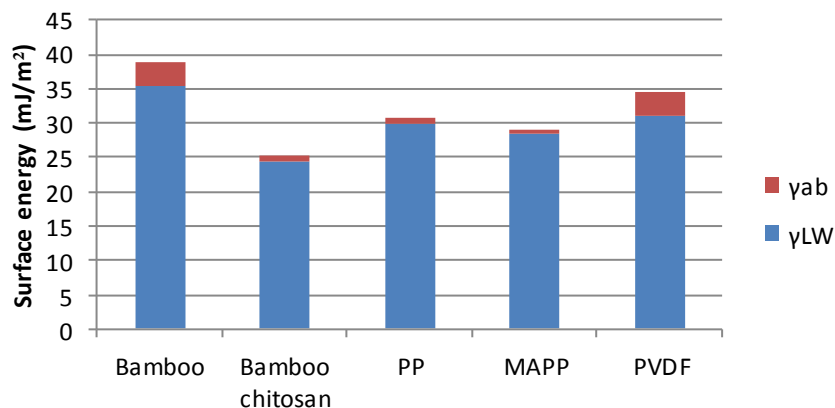

Figure 4. Surface energy components of the treated and untreated bamboo fibers and thermoplastics.

According to these values, the bamboo-PVDF system is expected to show good adhesion and more or less the same adhesion is expected for PP and MAPP. It has to be noted that these values only relate to intra-molecular forces and do not relate to chemical bonding.

Figure 5 shows the transversal and longitudinal flexural properties of MAPP, PP and PVDF bamboo composites made with the same procedure either at 175 °C or 200 °C and with a fiber volume fraction of 40%.
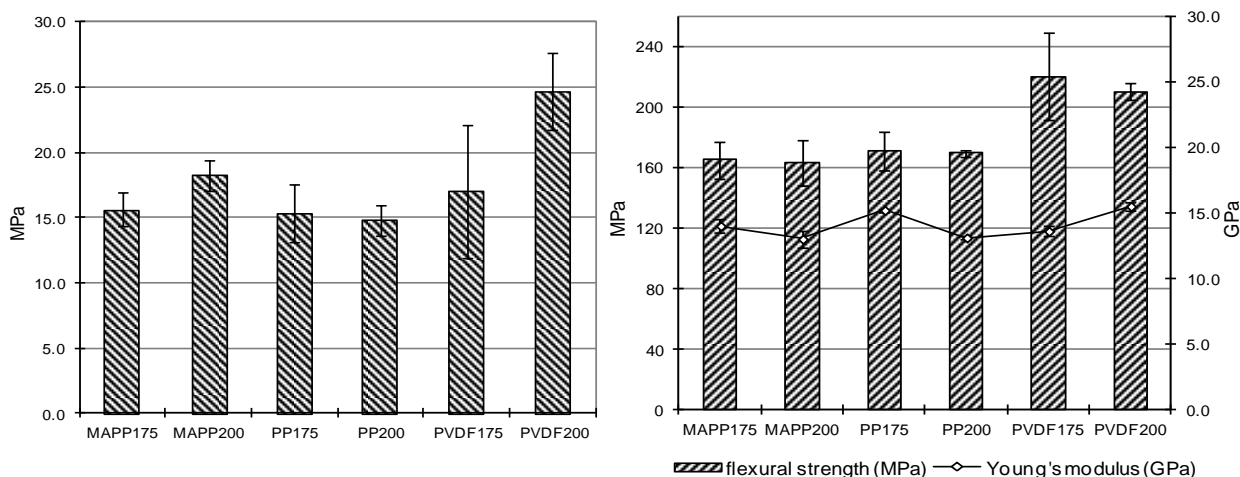

Figure 5. (Left) Transversal flexural strength of MAPP, PP and PVDF bamboo fiber composites at different processing temperatures. (Right) Longitudinal flexural properties of MAPP, PP and PVDF bamboo fiber composites.

The calculated values for the work of adhesion correlate reasonably well with the obtained results for the transversal properties, shown in figure 5. As predicted by the calculated work of adhesion, mechanical test results for PVDF are better than for the other matrices (once the PVDF is properly molten at 200°C), proving that the work of adhesion has really improved.

2.4 Bamboo fiber surface treatments

Bamboo fibers and prepregs were coated using a chitosan solution [12]. The purpose of this treatment is to increase the amount of available hydroxyl-groups on the surface. In this way, the properties of MAPP-bamboo composites might be increased, since lignin has fewer hydroxyl-groups at the surface, and MAPP has the capability to form covalent bonds with hydroxyl groups through esterification.

The obtained surface energy results shown in figure 4 for MAPP are very similar to the results obtained for PP. The small differences in values may be created by the presence of the maleic anhydride in MAPP and aging processes [13].

The change is relatively small because we worked with a 0.3 wt% MAPP. Calculating the work of adhesion of MAPP with chitosan as the substrate (56 mJ/m2), we see that this is reduced for the chitosan coated fiber if compared with untreated fibers. So theoretically we would expect lower mechanical properties with chitosan coated bamboo, considering just physical interactions. However, chitosan may increase the presence of hydroxyl groups at the surface and may promote chemical bonding with maleic anhydride, increasing the mechanical properties of the composite. Looking at figure 6, we only see this improvement in the longitudinal direction. We have an increase of 22% for the longitudinal strength while the transverse strength remains the same. So, the transversal test does not confirm the improvement of adhesion strength, possibly because of lower transverse strength of the chitosan coating. Further tests need to be carried out to evaluate this hypothesis.
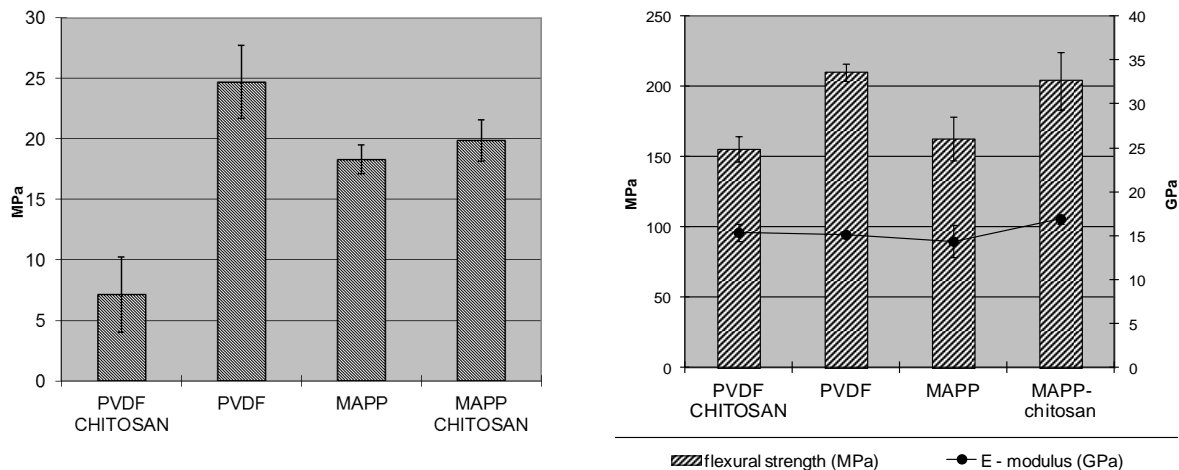

Figure 6. (Left) Transverse flexural strength of chitosan coated and uncoated bamboo fibre MAPP and PVDF composites. (Right) Longitudinal properties of chitosan coated and uncoated bamboo fibre MAPP and PVDF composites.

The calculated work of adhesion for PVDF with chitosan coated bamboo (59 mN/m) is much smaller than for PVDF with untreated bamboo (75 mN/m). So theoretically one would expect a composite made with bamboo and PVDF to be much stronger than a composite made with chitosan coated bamboo and PVDF, since there are no chemical bonding mechanisms. The results of the three point bending tests correspond with the theory and are shown in figure 6.

The composite with the uncoated fiber is about 28% stronger in the longitudinal direction and about 300% better in the transversal direction, showing that the adhesion is better in the uncoated fiber. Both composites show about the same longitudinal stiffness, which is around 80% of the theoretical value of 19.2 GPa according to the rule of mixtures, indicating similar levels of wetting.

3 Conclusions

The high concentration of lignin on the surface of technical bamboo fibers, as concluded from XPS results, seems to be responsible for their wetting properties, whereas fluctuations during wetting experiments between bamboo fibers may be due more to surface topography than to any other type of non-equilibrium phenomena. Autoclave treatment was used to smoothen the lignin surface layer.

The wetting behavior of bamboo fibers appears to conform well to the predictions of the molecular-kinetic theory. Therefore, it was possible to obtain experimental wetting data on bamboo fibers with reasonable accuracy, allowing meaningful information on interfacial interactions to be deduced. In this way, surface components of bamboo fibers and thermoplastic matrices were matched, resulting in improvement of the physical adhesion in bamboo fiber composites revealed by 3-point bending test results. Accordingly, the properties of PVDF lend themselves well for the preparation of untreated bamboo fiber composites with high interface strength.

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