Conference paper

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Composites containing bamboo with different binders

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Abstract: We have obtained composites on the basis of dry bamboo powders and in turn several binders, including polyethylene (PE) and alkoxysilanes. The composites were studied by Fourier transformation infrared spectroscopy (FTIR), optical and scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). Some mechanical properties were determined along with thermal stability by thermogravimetry; water absorption was also determined. FTIR results show formation of primary chemical bonds between bamboo surface active groups and the binders. Mechanical property improvement goes symbatically with the thermal stability.

Keywords: bamboo filler; composites; composite thermal stability; POLYCHAR-25; polyethylene composites; thermal properties.

Introduction

The composites containing dry wood materials – including wood + polymer composites (WPCs) – attract increasing attention of scientists and engineers [1, 2]. Low specific weight, high mechanical strength, stability in a variety of atmospheric environments, high durability and low cost are some of the advantageous properties of these composites (an incomplete list). Advantageous from the point of view of environment preservation is the use of renewable raw materials (including leaves and needles), also combined with the natural waste materials such as sawdust. Sebe and Brook [3] as well as Mai and Militz [4] used a silicone to waterproof maritime pine wood surfaces. The silicones appear to be attached to the wood by covalent bonds. Brebner and Schneider [5] have impregnated aspen using γ-methacryloxypropyltrimethoxysilane as the coupling agent; hygroscopicity and resistance to shrinking were determined before and after water extraction. WPCs include those based on high density polyethylene (HDPE) and containing sawdust as the filler. Silane coupling was used as to modify the sawdust by 3-methacryloxypropyltrimethoxysilane, and thereby forming chemical bonds [6].

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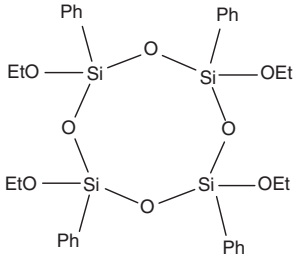
Good results were obtained in creation of WPCs involving silicon-organic compounds [7, 8] and sol-gel systems [9, 10]; organofunctional silanes were applied in combination with organo alkoxysilanes (sol-gel process) as well as chlorosilanes and trimethylsilyl derivatives for impregnation of wood. Various treatments resulted in an increase in dimensional stability, durability and fire resistance of wood, as well as enhanced hydrophobicity. There is extensive literature about bamboo, including books [11, 12].

The objective of our work is the development of new composites with improved properties containing dispersed bamboo particles (with length less than 50 μm). The binders were: polyethylene, PhES-50, PhES-80, liquid glass (LG), colophony and wood glue (see below).

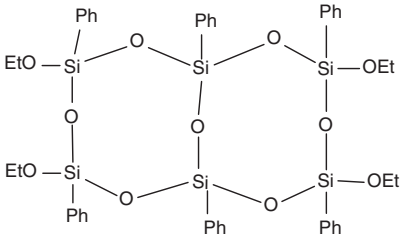
Experimental

Materials

Our samples were obtained using an installation for shredding of dry bamboo. We have prepared the composites based on dry sawdust plus in turn PE (melting temperature 137 °C), alkoxysilanes (PhES-50 or PhES-80), wood glue of animal origin [13] which does not undergo creep, and liquid glass (LG) with the formula Na_2SiO_3. The chemical formulae of the alkoxysilanes are:



PhES-50



PhES-80

(1, 2)

Processing

The binders were applied in turn by dry mixing. Then compression molding was performed using pressures 8–17 MPa and temperatures 90–150 °C in a mold during 10 min. We have prepared two types samples: cylindrical (for investigations of water absorption) and rectangular for other testing. Various pressures and temperatures were applied to see the effect of changes of these parameters on properties.

1. *Fourier transformation infrared spectra* were determined with a Varian 660-IR FT-IR Spectrometer. The KBr pellets of samples were prepared by mixing (1.5–2.0) mg of samples, finely grounded, with 200 mg KBr (FTIR grade) in a vibratory ball mixer for 20 s.

Optical microscopy

A NMM-800RF/TRF microscope was used. One centimeter long samples were abraded with emery paper for 1 h and then polished on a coarse calico.

1. *Scanning electron microscopy* observations were made using a JSM-6510LV SEM with the resolution of 3.0 nm at 30 kV.
2. *Thermogravimetry* was performed with a MOM-Paulik-Paulik-Erdey apparatus, with the temperature increase rate of 10 K/min in the air atmosphere.

3. *Bending testing* is performed on parallelepipeds with the length of 10 cm and the vertical square cross-section of 1 cm^2. The specimen is placed on two prisms, with the distance between the prisms equal to 8 cm. The indenter is a metal cylinder with the diameter of 10 mm applied from above to the midpoint of the specimen. Bending strength is defined as the stress needed to create a breaking point (a crack) in the outer surface of the test specimen.
4. *Impact viscosity* determination, also called *shock viscosity* determination, is a technique applied to soft solids [14] and is essentially a drop impact test. The drop height h is the vertical difference between the upper surface of the tested material (h_1) and the bottom surface of the drop hammer at the end of the impact event (h_2). One determines the work performed by falling hammer mg ($h_1 - h_2$) and then normalizes it with respect to the horizontal cross-section of the specimen.
5. *Vicat softening depth*, also known as *Vicat hardness*, is the depth of the indentation with respect to the top surface caused by a flat ended indenter with the cross-section of 1 mm^2. The load applied is 10 or 50 N and the cross-section of the indenter end is circular.
6. *Water absorption* is determined simply as the percentage weight change of the sample after submersion in water for 24 h.

Probable chemical reactions

It is known that the bamboo contains cellulose, hemicelluloses, lignin and pentosan structural rings with hydroxyl groups. As noted above, phenylethoxysilanes (PhES-50 and PhES-80) contain ethoxyl and hydroxyl groups. Processes that occur during the curing are complex and varied. An overview of the curing liquid glass and of processes in the various homogeneous and heterogeneous systems, the most widely encountered in practice, is presented in a number of reviews [5, 10, 15]. The curing leads to three-dimensional structures. Formation of such structures is accelerated by the use of Na_2SiF_6; we have actually used this compound together with liquid glass, but the properties of the resulting composites were hardly affected.

We expect that the following reactions may occur between the pulverized bamboo and some of the binders:

$$-OH + C_2H_5O\text{–}Si\equiv \rightarrow -O\text{–}Si\equiv + C_2H_5OH \tag{3}$$

$$\equiv SiOH + HO- \rightarrow \equiv SiO- + H_2O \tag{4}$$

$$\equiv SiOH \rightarrow \equiv Si\text{–}O\text{–}Si\equiv + HO- \tag{5}$$

Thus, reactions (3) and (4) provide + ≡SiO– needed for the formation of ≡Si–O–Si≡ bonds.

FTIR spectra

For brevity we do not include here the FTIR spectra. We only note two significant facts. In bamboo containing composites one finds the absorption bands characteristic for asymmetric valence oscillation of ≡Si–O–Si≡ bonds, with the maximum near 1055–1070 cm^{-1}. These bands correspond to the siloxane bonds in the cyclotetrasiloxane fragment.

In the spectrum one can see the absorption bands 1243–1248, 1376, 1453–1463, 1515, 1613–1620, 1735, 2800–2950, 3421–3434 cm^{-1} typical for methyl groups, C–H bond absorption (–C/C–/CH_3), CH_2 cellulose–lignin, C=C aromatic, C=C alkene, (C=O etheric bond), C–H methyl, methylene and phenyl groups, O–H alcoholic group, respectively. This O–H stretching indicates also the phenolic compound that has excellent antioxidant properties [16]. This applies to composites including bamboo with different binders.

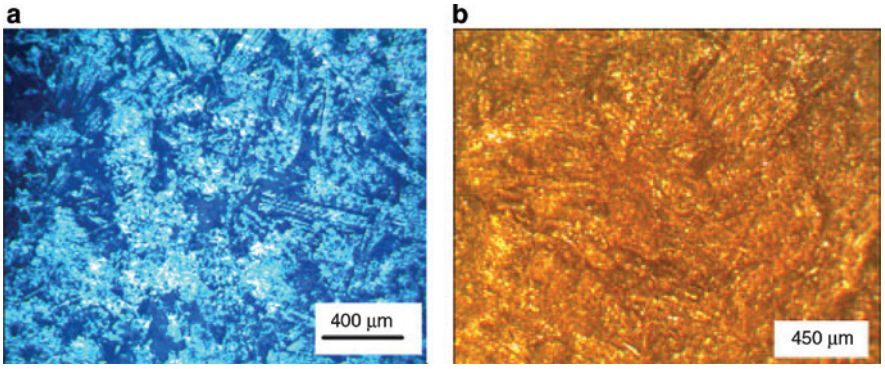


Fig. 1: Optical microscopic results: (a) bamboo; (b) bamboo (95 %) + LG (5 %) composite; magnification ×50.

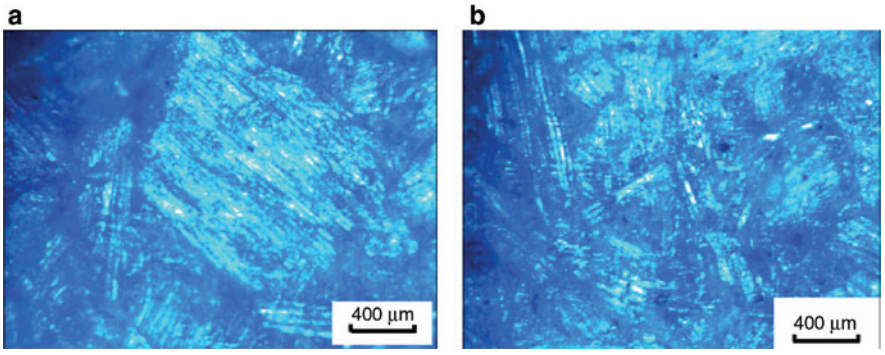


Fig. 2: Optical microscopic results: (a) for bamboo (95 %) + PhES 80 (5 %); (b) for bamboo (90 %) + wood glue (10 %).

Optical microscopy observations

In Figs. 1 and 2 we display some of the micrographs. One notices the fibrous character of supramolecular structures. Comparing Fig. 1a and b, we see how 5 % of liquid glass changes the color dramatically. Fairly uniform distribution of components is seen. In Fig. 2 we see some scratches remaining after grinding.

SEM and EDS results

SEM micrograms were obtained at various (×100–×1000) magnifications. We show two examples in Fig. 3 of impact fracture surfaces. We see the epidermis (the outer layer) of the bamboo; it has a well-organized corrugated structure. The structure includes the sharpened ridge inserts, which have a linear profile. Ridges and grooves in the epidermal cell are a consequence of fiber inclusion. Outer surface of the hills includes knobs of various sizes. Two major constituents of bamboo are the rhizomes and the culms. The rhizome is the underground part of the stem and is mostly sympodial (the main stem is terminated, the growth continued by one or more lateral stems) or, to a much lesser degree, monopodial. The culm is the hollow stem in a plant. Interfacial gaps between fibers and the polymer matrix are clearly seen in Fig. 3, in both a and b parts. We see different surfaces created by the minority components, liquid glass and PhES-80.

The variation of the microscopic pattern changes in depending on the type and concentration of the ingredients. It can be assumed that the white regions of the Fig. 3a correspond to the liquid glass on the background of the bamboo tissue, and the spherical bright spots in the Fig. 3b are a collection of drops of the molten binder (PhES). The picture clearly shows the randomness of the distribution of ingredients in the composite.

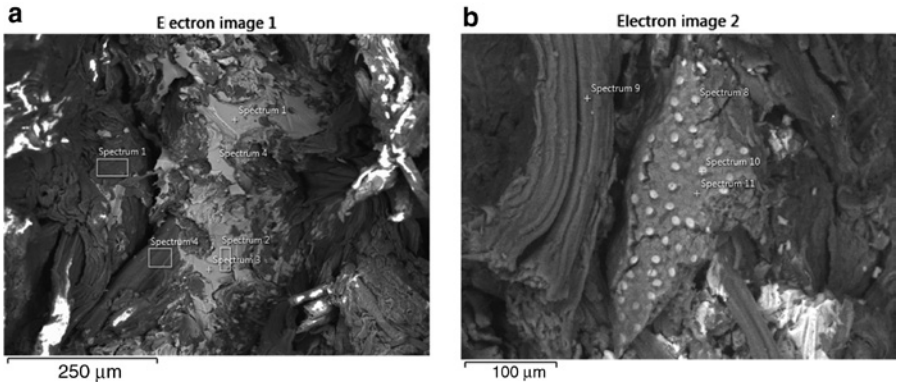


Fig. 3: SEM micrographs for composites: (a) bamboo (95 wt.%) + LG (5 %), (b) bamboo (95 %) + PhES-80 (5 %).

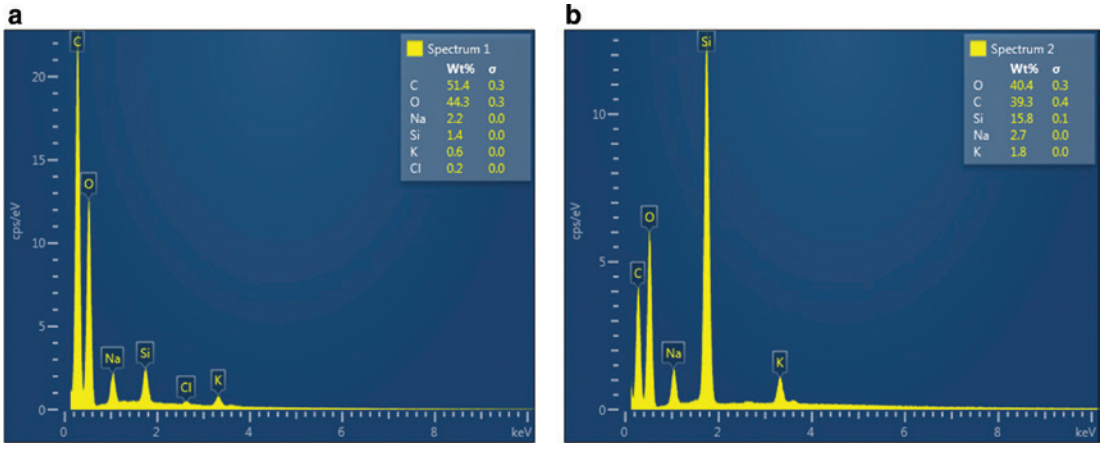


Fig. 4: Energy dispersion micro X-ray spectral analysis of composite: bamboo (95 %) + LG (5 %) (a) spectrum 1, (b) spectrum 2.

In Fig. 4 we show some EDS spectra which provide information about elemental composition. These spectra correspond to different region of the composite sample, allowing us to estimate the degree of homogeneity of distribution of microelements in the composite.

Analogical investigation was provided for other composites based on bamboo with different binders.

Our bamboo-based composites contain the following elements: C, O, Si, Ca, Na, K, S, Fe, Mg, Cl and Al. The content of elements in samples changes only little when different binders are used.

Mechanical properties

We report bending strength and impact viscosity results in Table 1 for two dozens of compositions. As noted, the results depend on the pressure and the temperature applied during compression molding, hence the first two columns in the table.

Consider first the bamboo + liquid glass composites. The dependence of the impact viscosity on LG concentration shows a maximum at 10 wt.%, while no such maximum is seen for the bending strength. Possibly in the latter case there is a maximum but at a still higher liquid concentration.

For composites containing PhES-50 and PhES-80 we see maxima of the impact viscosity at the binder concentrations of 10 wt.%. The respective maxima of bending strength are at 5 and 10 wt.%. These results can

Table 1: Bending strength and impact viscosity.

#	Composite (wt.%)	Pressure, kg/cm²	Temperature (T), °C	Strength in bending, MPa	Impact viscosity, kJ/m²
1	Bamboo (97) + liquid glass (3)	150	130	2.0	56.7
2	Bamboo (95) + liquid glass (5)	150	130	2.0	58.5
3	Bamboo (90) + liquid glass (10)	150	130	2.3	61.1
4	Bamboo (85) + liquid glass (15)	150	130	2.6	57.9
5	Bamboo (97) + PhES-50 (3)	250	130	1.2	47.2
6	Bamboo (95) + PhES-50 (5)	250	130	2.3	48.8
7	Bamboo (90) + PhES-50 (10)	150	130	1.3	52.2
8	Bamboo (85) + PhES-50 (15)	150	130	1.8	50.5
9	Bamboo (97) + PhES-80 (3)	150	130	1.2	50.4
10	Bamboo (95) + PhES-80 (5)	150	130	1.7	48.0
11	Bamboo (90) + PhES-80 (10)	150	130	2.2	53.9
12	Bamboo (85) + PhES-80 (15)	150	130	1.8	53.6
13	Bamboo (95) + PE (5)	150	130	2.0	53.9
14	Bamboo (90) + PE (10)	150	130	2.5	56.9
15	Bamboo (85) + PE (15)	150	130	2.4	60.5
16	Bamboo (80) + PE (20)	150	130	1.9	54.3
17	Bamboo (95) + colophony (5)	150	130	2.0	61.8
18	Bamboo (90) + colophony (10)	150	130	2.9	54.8
19	Bamboo (85) + colophony (15)	150	130	2.5	56.6
20	Bamboo (80) + colophony (20)	150	130	1.8	51.1
21	Bamboo (95) + wood glue (5)	150	130	2.0	60.3
22	Bamboo (90) + wood glue (10)	150	130	2.9	64.5
23	Bamboo (85) + wood glue (15)	150	130	3.4	62.8
24	Bamboo (80) + wood glue (20)	150	130	1.8	49.1

be explained in terms of the spatial distribution of the components. At relatively high content of the binder, each binder "attempts" to create its own phase; hence the appearance of the maxima.

Somewhat but not dramatically better mechanical properties are provided by the composites containing polyethylene, colophony or wood glue. Apparently, we have here homogenous distributions of the binders – caused by good wettability of bamboo at the compression molding stage.

We have also tried a combination of two binders, namely 10 wt.% each of PhES-50 and liquid glass. The resulting value of the impact viscosity is 64.8 kJ/m², higher than any value listed above in Table 1. Thus, improvement of mechanical properties by using a combination of binders is possible.

Thermal stability from TGA and Vicat softening temperatures

In Fig. 5 we show TGA diagrams for some of our composites.

Approximately 10 % mass losses are seen in the temperature range 200–210 °C. Unreacted hydroxyl and ethoxyl groups might possibly be reacting in this temperature range. Rapid falls of the TGA curves is seen between 230 and 280 °C. We see in Fig. 5a that liquid glass enhances the thermal stability more than PhES 50 or PhES 80. Significant thermal degradation for LG containing composite begins only near 280 °C. From Fig. 5b we can conclude that PE is also better in this respect than PhES 80. Full thermal degradation is seen between 500 and 600 °C, with the ash remaining. Overall, the binders used do not affect much the thermal stability of the composites.

The dependence of the Vicat softening depths of our composites on temperature is shown in Figs. 6 and 7. We recall from Section 2 that those depths represent the indentation with respect to the top surface caused by a flat ended indenter. Such results are of interest for polymer-containing composites since no polymers are fully crystalline, hence the melting temperatures – if they exist – provide only a part of the story [2].

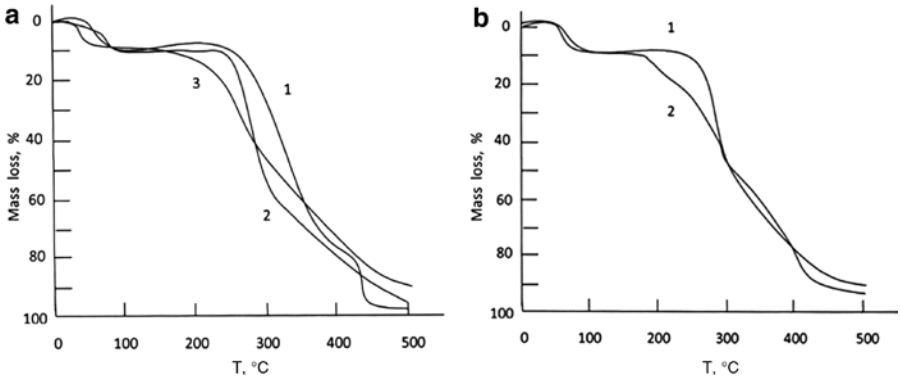


Fig. 5: TGA diagrams for composites based on bamboo with binders: (a) curve 1 for liquid glass (5 %), curve 2 for PhES-50 (5 %), curve 3 for PhES-80 (5 %); (b) curve 1 for PE (10 %) and curve 2 for PhES-80 (15 %).

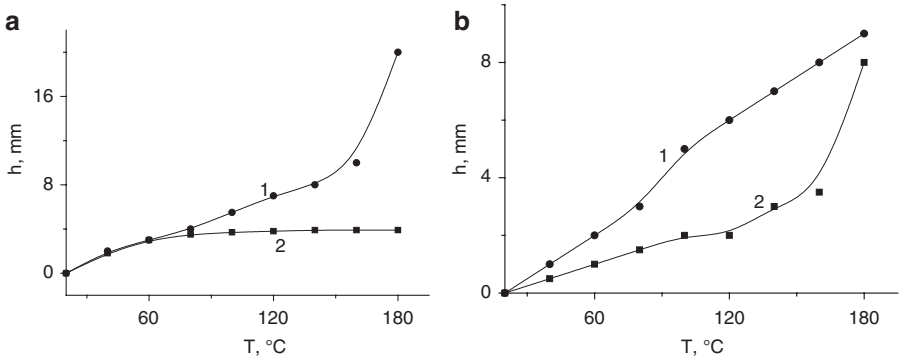


Fig. 6: Dependence of the Vicat softening on temperature: (a) curve 1 for bamboo (90 %) + liquid glass (10 %) and curve 2 for bamboo (90 %) + PhES-80 (10 %); (b) curve 1 for bamboo (90 %) + PE (10 %), curve 2 for bamboo (90 %) + PE (15 %).

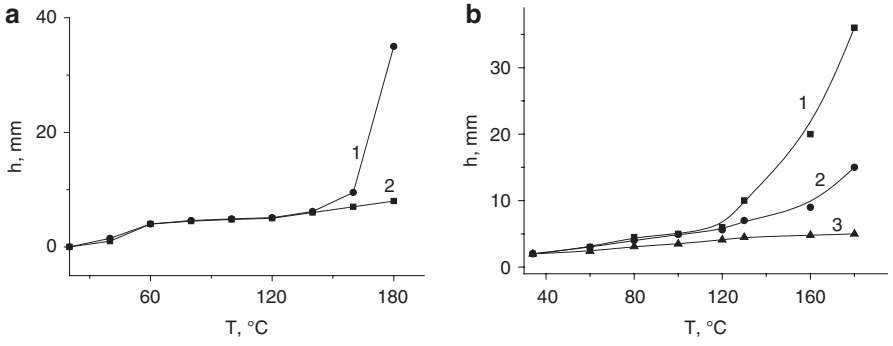


Fig. 7: Dependence of the Vicat softening on temperature: (a) curve 1 for bamboo (90 %) + wood glue (10 %); curve 2 for bamboo (85 %) + wood glue (15 %); (b) curve 1 for bamboo (95 %) + liquid glass (5 %), curve 2 for bamboo (95 %) + PhES-50 (5 %) and curve 3 for bamboo (95 %) + PhES-80 (5 %).

Figures 6 and 7 show us the overall 'winner': the composite containing 10 wt.% of liquid glass, curve 1 in Fig. 6a, with the depth never exceeding 4 mm up to 190 °C. Expectedly now, the second best is the material with 5 % of liquid glass, curve 1 in Fig. 7b, with the depth never exceeding 7 mm up to 180 °C. When we now return to Table 1, we find that liquid glass provides outstanding mechanical properties, along with wood glue at 10 wt.%. Indeed, the respective curve of the Vicat depth, curve 1 in Fig. 7a, shows the depth not exceeding 7.5 mm. We find that the dimensional stability at elevated temperatures goes symbatically with mechanical properties.

Table 2: Water absorption of composites based on bamboo and different binders.

#	Composite (wt.%)	Mass, g	Volume, cm^3	Density, g/cm^3	Weight after 24 h exposition in water, g	Water absorption after 24 h expos. in water, %
1	Bamboo (97) + liquid glass (3)	4.77	3.34	1.43	5.01	5.03
2	Bamboo (95) + liquid glass (5)	3.89	2.82	1.38	4.28	10.02
3	Bamboo (90) + liquid glass (10)	3.80	2.82	1.35	3.98	4.73
4	Bamboo (85) + liquid glass (15)	3.86	2.82	1.37	4.04	4.66
5	Bamboo (97) + PhES-50 (3)	3.95	2.82	1.40	4.06	2.78
6	Bamboo (95) + PhES-50 (5)	3.83	2.82	1.36	3.93	2.61
7	Bamboo (90) + PhES-50 (10)	3.78	2.82	1.34	3.86	2.11
8	Bamboo (85) + PhES-50 (15)	3.46	2.46	1.41	3.54	2.31
9	Bamboo (97) + PhES-80 (3)	3.94	2.82	1.40	4.03	2.28
10	Bamboo (95) + PhES-80 (5)	3.89	2.82	1.38	3.97	2.05
11	Bamboo (90) + PhES-80 (10)	3.66	2.64	1.39	3.74	2.18
12	Bamboo (85) + PhES-80 (15)	3.70	2.64	1.40	3.80	2.70
13	Bamboo (95) + PE (5)	3.88	2.82	1.38	4.41	13.66
14	Bamboo (90) + PE (10)	3.73	2.82	1.32	3.81	1.87
15	Bamboo (85) + PE (15)	3.83	2.99	1.28	3.91	2.08
16	Bamboo (80) + PE (20)	3.65	2.82	1.29	3.74	2.47
17	Bamboo (95) + colophony (5)	3.92	2.82	1.39	3.99	1.79
18	Bamboo (90) + colophony (10)	3.78	2.82	1.34	3.85	1.85
19	Bamboo (85) + colophony (15)	3.50	2.64	1.33	3.57	2.00
20	Bamboo (80) + colophony (20)	3.55	2.64	1.34	3.65	2.82
21	Bamboo (95) + wood glue (5)	3.92	2.82	1.39	4.40	12.24
22	Bamboo (90) + wood glue (10)	3.95	2.82	1.40	4.09	3.54
23	Bamboo (85) + wood glue (15)	3.93	2.82	1.39	4.19	6.61
24	Bamboo (80) + wood glue (20)	3.85	2.64	1.46	4.54	17.92

Two other factors deserve to be noted. The composite containing 10 wt.% PE exhibits a good dimensional stability up to 150 °C, this in contrast to the composite with 15 % PE. Possibly PE in the first composite is distributed fully on the surfaces of bamboo particles, whereas at 15 wt.% polyethylene creates the own phase. We see that the melting temperature of PE, here around 140 °C, is clearly reflected in curve 1 in Fig. 6b.

Water absorption

The results obtained are summarized in Table 2.

The first overall observation from the above table is the fact that water absorption results are generally on the low side, acceptable for many applications. We infer that the chemical structure and the spatial microstructure of bamboo favor formation of chemical and physical bonds with the binders (adhesives). As expected, the water absorption depends on the concentration of the binder. Thus, for the composites contained liquid glass, the absorption decreases from 5.03 down to 4.66 % when the concentration of the binder changes from 3 to 15 %. For composites with PhES-50 at 3–15 % the absorption is in the range 2.31–2.78, comparable to the values 2.28–2.70 for composites with PhES-80. A good result is seen for the composite with 10 % PE, namely the absorption equal to 1.87 in our units. A good result is also seen for 5 % colophony, namely 1.79.

Concluding remarks

Our composites based on bamboo and some organic-inorganic binders have generally advantageous properties for a variety of applications. Apparently chemical bonds are formed between bamboo surface active groups and binder molecules.

Bamboos include some of the fastest growing plants in the world. Certain species of bamboo can grow up approximately 90 cm in 24 h. While bamboos have long been used as a food source, they also have extensive application as construction materials. The reinforcement provided by our binders can extend that application range. In the future one can consider using bamboo with our binders as a constituent in polymer concretes [17]. Possibly more importantly, one can envisage applications in aviation and automotive industries.

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References

[1] W. Brostow, T. Datashvili, H. Miller. *J. Mater. Ed.* **32**, 125 (2010).
[2] W. Brostow, H. E. Hagg Lobland. *Materials: Introduction and Applications*, John Wiley & Sons, Hoboken, NJ, USA (2017).
[3] G. Sebe, M. A. Brook. *Wood Sci. Tech.* **35**, 269 (2001).
[4] C. Mai, H. Militz. *Wood Sci. Tech.* **37**, 339 (2004).
[5] K. I. Brebner, M. H. Schneider. *Wood Sci. Tech.* **19**, 75 (1985).
[6] W. Brostow, T. Datashvili, P. Jiang, H. Miller. *Eur. Polymer J.* **76**, 28 (2016).
[7] O. Mukbaniani, J. Aneli, G. Buzaladze, E. Markarashvili, T. Tatrishvili. *Oxid. Comm.* **39**, 2763 (2016).
[8] P. Gascón-Garrido, M. F. Thévenon, H. Militz, C. Mai. *Wood Sci. Tech.* **49**, 177 (2015).
[9] C. Mai, H. Militz. *Wood Sci. Tech.* **37**, 453 (2004).
[10] O. Mukbaniani, J. Aneli, G. Buzaladze, T. Tatrishvili, E. Markarashvili. Proceedings of the 6th Nordic Wood Biorefinery Conference, NWBC 2015, Helsinki, Finland, 20–22 October (2015), 467.
[11] J. J. A. Janssen. *Building with Bamboo*, 2nd ed., p. 65, Intermediate Technology Publication Ltd., London (1995).
[12] D. Ohrnberger. *The Bamboos of the World*, p. 273, Elsevier, Amsterdam (1999).
[13] https://en.wikipedia.org/wiki/Animal_glue.
[14] C. Liu, Y. Tanaka, Y. Fujimoto. *World J. Mech.* **5**, 33 (2015).
[15] A. A. Kliosov. *Wood-Plastic Composites*, John Wiley & Sons, New York (2007).
[16] G. Xu, L. Wang, J. Liu, J. Wu. *J. Appl. Surface Sci.* **280**, 799 (2013).
[17] G. Martinez-Barrera, E. Vigueras-Santiago, O. Gencel, H. E. Hagg Lobland. *J. Mater. Ed.* **33**, 37 (2011).