Wood pulp fiber reinforced melamine-formaldehyde composites

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In comparison to other fibrous materials, plant fibers show a number of advantages, namely low density, biodegradability, and a neutral CO_2 balance during their cycle of life [1]. On the other hand, consisting predominantly of cellulose, plant fibers are subject to swelling when exposed to humidity, which causes dimensional instability and degradation of mechanical properties. In unmodified solid wood, the hydrophilic cellulose and hemicellulose is partly sealed by the less hydrophilic lignin, which reduces negative effects of water uptake into the cell wall to a certain extent [2]. In consequence, delignified wood is highly susceptible to uptake of water and loses its mechanical integrity in wet conditions [3]. Experiments with solid wood have shown that impregnation of wood fiber cell walls with water soluble melamine-formaldehyde resin (MF) hinders the uptake of water and reduces dimensional instability and deterioration of strength [4, 5]. It was shown that MF penetrates into the amorphous region of cellulose fibrils [6, 7], where it may form covalent bonds with cellulose [8]. Due to the good affinity of MF to cellulosic fibers, the addition of compatibilizers or chemical surface modification of fibers, which is necessary when rather hydrophobic thermoplastic matrices such as PP or PE are used [1, 9–11], is not required. Due to these favorable properties MF appears to have a good potential for application as the polymer matrix in plant fiber reinforced composites, which was already tested using flax fibers [12]. In this study, MF resin is used to produce composite sheets reinforced with wood pulp fibers, in order to investigate basic mechanical properties of the composite.

Sheets of beech sulphite pulp with a size of 30×30 cm^2 and a thickness of 2 mm (Lenzing R&D, Austria) were submerged in Hilamin M562 (61% solids in water) MF resin (Dynea, Krems, Austria), placed in a vacuum vessel, and evacuated to a pressure of 80 mbar. Subsequently, air-pressure was re-established, which forced the liquid MF into the pores of the pulp sheet. Having repeated the vacuum-air pressure cycle three times during 10 min, the pulp sheets were left to air-dry for 24 h. A second batch of pulp sheets was first soaked in water, then submerged in liquid MF for 72 h under air pressure, and finally also left to air dry. The MF-impregnated sheets were cured at a temperature of 120 °C in a hot press for 10 min under a pressure of 20 MPa. The obtained white to yellowish composite sheets were 1.2 mm thick, with a density of 1.4 g/cm^3, an average MF content of 25%, showing no significant difference between vacuum treated and non-vacuum treated samples. Presumably due to the hydrophilicity of the chosen MF resin, a short vacuum treatment suffices to achieve thorough impregnation, and lengthy immersion is not necessary. Specimens 150 mm long and 20 mm wide were cut from the composite sheets in the direction parallel (0 °) and normal (90 °) to the production direction of the pulp sheets and tested in tension on a Zwick 100 kN universal testing machine either in dry state or in wet condition after 2 h boiling in water. The load was applied in displacement controlled mode at a rate of 0.5 mm/min until fracture. After tensile testing, small pieces containing the fracture surface were cut from the specimens, sputter-coated with gold, and observed in an SEM (Zeiss-LEO).

The results of the mechanical tests are shown in Table I. No significant difference was found in the mechanical properties of vacuum treated and non-vacuum treated samples, therefore they are not listed separately. Fig. 1 shows typical stress strain graphs from the tensile tests. The obtained properties compare favorably with nonwoven flax fiber reinforced MF composites,
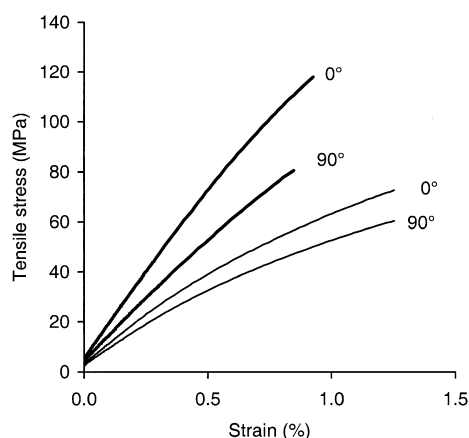
Figure 1 Stress-strain curves of tensile tests with pulp-fiber melamine-formaldehyde composites (thick line: dry composite, thin line: wet composite boiled in water for 2 h).

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TABLE I Young's modulus (E), tensile strength (σ_{max}), and elongation at break (ε_{max}) of beech pulp fiber MF composite sheets ($n = 80$)

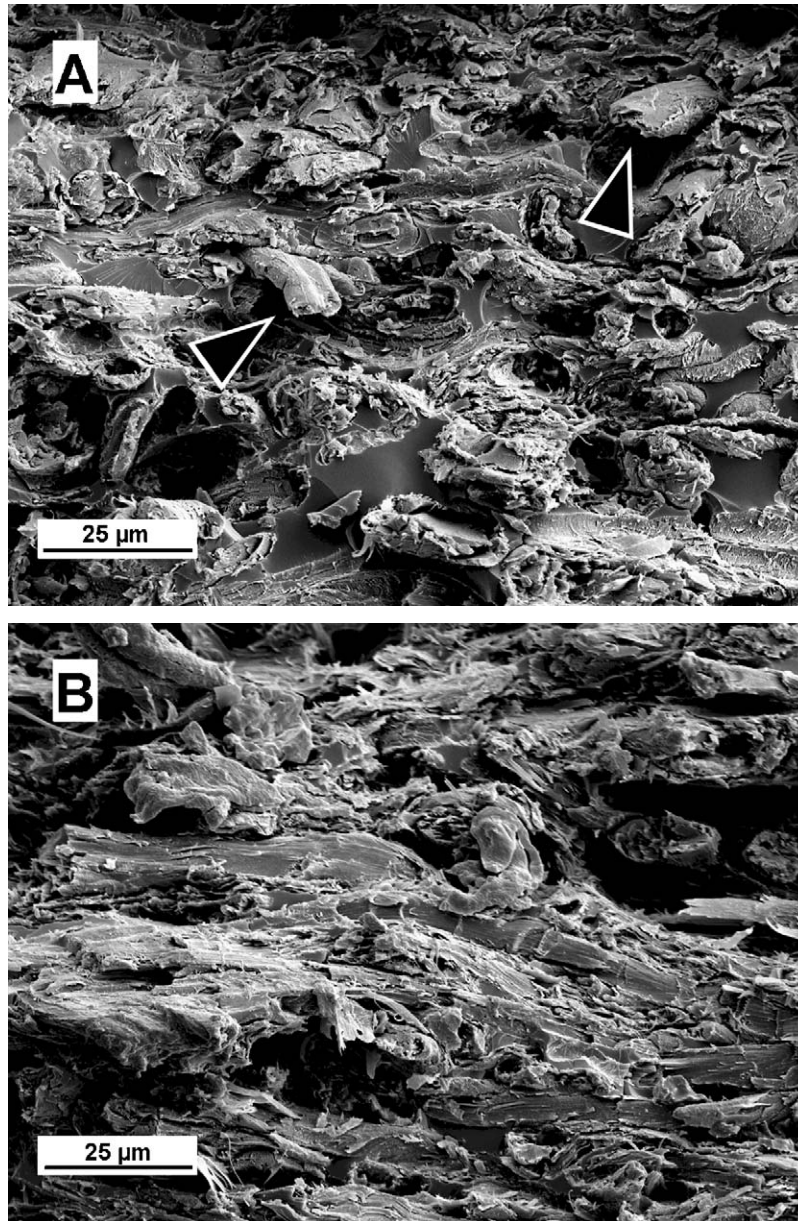|	E (GPa)		σ_{max} (MPa)		ε_{max} (%)	
	0°	90°	0°	90°	0°	90°
Dry	12.9 ± 1.0	10.2 ± 0.9	97.1 ± 19	85.9 ± 14	0.81 ± 0.16	0.91 ± 0.18
Wet	7.6 ± 0.7	6.1 ± 0.6	66.8 ± 7	58.1 ± 6	1.29 ± 0.19	1.32 ± 0.19

Figure 2 Fracture surface of pulp-fiber melamine-formaldehyde composite. A: orientation parallel to the direction of production of the pulp sheet (0°), arrowheads indicate occurrence of fiber pull-out, B: orientation normal to the direction of production of the pulp sheet (90°).

where, at a fiber content of 22%, a Young's modulus in warp/weft direction of 13.5/10.7 GPa, a tensile strength of 43/37 MPa, and an elongation at break of 0.36/0.41% was measured [12]. The strength and stiffness of cellulose diacetate (CDA) and cellulose acetate butyrate (CAB) composites reinforced with random-oriented wood pulp fiber is clearly surpassed by using an MF matrix. Using CDA, a Young's modulus of 2–8 GPa, a tensile strength of 35–80 MPa, and an elongation at break of 0.1–0.55% was obtained [13], whereas the use of CAB yielded values of 0.4–1.3 GPa for Young's modulus, a tensile strength of 15–33 MPa, and an elongation at break of 3–8%, respectively [14]. The direction of the production of beech pulp sheets apparently influences the stiffness and strength of the pulp fiber MF composite, which is on average 20% lower in the direction normal to the direction of production (Table I). SEM micrographs (Fig. 2) support this observation, as they indicate that fibers are not randomly oriented in the pulp sheet, but show a preferential orientation in the direction of production. Fiber pullout (Fig. 2a) is infrequent, and the overall appearance of the fracture surface is brittle, suggesting excellent bonding between the MF matrix and the beech pulp fibers as
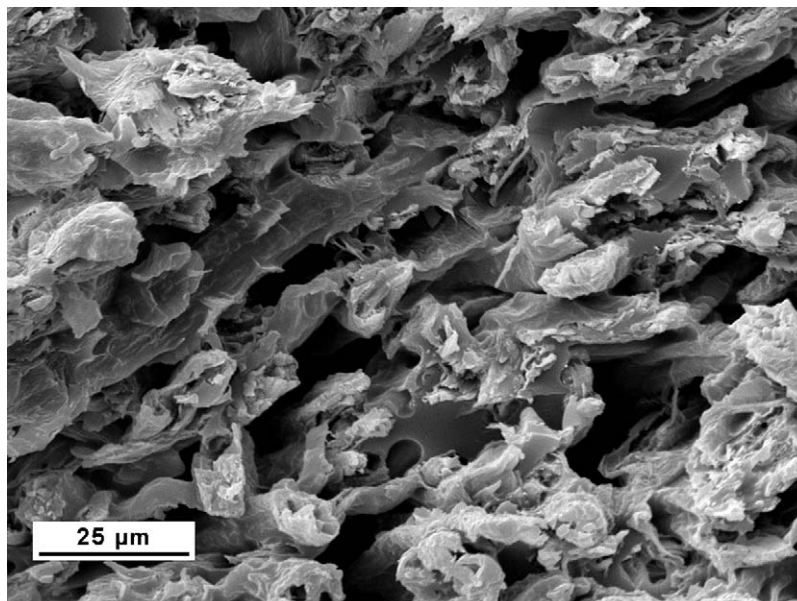
Figure 3 Fracture surface of wet pulp-fiber melamine-formaldehyde composite (orientation 0 °).

well as penetration of MF into the cell wall of the fiber [15]. A certain brittleness was also observed with flax fiber MF composites [12] and with MF modified solid wood [15].

Boiling the samples in water for 2 h had a significant negative effect on mechanical properties, but 60% of the Young's modulus, and 70% of the tensile strength in dry state were preserved. The brittle character of the composite diminished slightly after boiling in water, as the elongation at break increased by 45–60% (Table I, Fig. 1). The appearance of the fracture surface of boiled samples was also different (Fig. 3). Clearly the fibers and matrix underwent separation to a higher degree during fracture than in dry samples, and failure due to fiber pullout is the dominant mode of failure in the boiled samples. A similar reduction of mechanical properties due to moisture is also observed in untreated solid wood [16].

In conclusion it has been demonstrated that the mechanical properties of wood pulp fiber MF composite sheets are competitive with other wood pulp fiber reinforced polymer composite materials in terms of strength and stiffness, at the price of a comparably low elongation at break [13, 14]. The advantage of MF lies in the good compatibility with cellulosic fibers, and composites with pulp sheets, which are available in large quantity and size, are easily produced by vacuum impregnation and compression molding.

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