Effects of Material Parameters on the Diffusion and Sorption Properties of Wood-Flour/Polypropylene Composites

Vera Steckel,[1] Craig M. Clemons,[2] Heiko Thoemen[1]

[1]Department of Wood Science, University of Hamburg, Germany
[2]USDA Forest Service, Forest Products Laboratory, Madison, Wisconsin

ABSTRACT: Composites of wood in a thermoplastic matrix (wood–plastic composites) are considered a low maintenance solution to using wood in outdoor applications. Knowledge of moisture uptake and transport properties would be useful in estimating moisture-related effects such as fungal attack and loss of mechanical strength. Our objectives were to determine how material parameters and their interactions affect the moisture uptake and transport properties of injection-molded composites of wood-flour and polypropylene and to compare two different methods of measuring moisture uptake and transport. A two-level, full-factorial design was used to investigate the effects and interactions of wood-flour content, wood-flour particle size, coupling agent, and surface removal on moisture uptake and transport of the composites. Sorption and diffusion experiments were performed at 20°C and 65 or 85% relative humidity as well as in water, and diffusion coefficients were determined. The wood-flour content had the largest influence of all parameters on moisture uptake and transport properties. Many significant interactions between the variables were also found. The interaction between wood-flour content and surface treatment was often the largest. The diffusion coefficients derived from the diffusion experiments were different from those derived from the sorption experiments, suggesting that different mechanisms occur. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 752–763, 2007

Key words: wood-flour; polypropylene; composites; diffusion; sorption; moisture

INTRODUCTION

The recent growth of the wood–thermoplastic composites' (WPCs) market is mainly caused by the desire for low maintenance wood products that are durable in outdoor applications without painting, staining, or toxic additives and treatments. When taking up moisture, the wood component can become susceptible to fungal attack and the mechanical properties of the composite can be reduced. Inside WPCs, the wood particles are at least partially encapsulated in plastics such as polyethylene (PE) or polypropylene (PP) that are good moisture barriers, helping to protect the wood particles from moisture intrusion. Nevertheless, WPCs still sorb some moisture.

Diffusion and sorption in composites, like WPCs, occur in a highly complex way, and rigorous and proven models to describe these mechanisms have not yet been developed.[1,2] Whereas PP is a very hydrophobic polymer with extremely low moisture sorption and diffusion,[3,4] wood is hygroscopic because the surface and the amorphous parts of the cellulose fibrils, as well as the hemicelluloses, contain a large amount of accessible hydroxyl groups. Water molecules easily bond to these hydroxyl groups via hydrogen bonding and push apart the fibrils causing the cell wall to swell.[5] In the cell wall, moisture is transported by bound water diffusion. Single water molecules jump from one adsorption site (i.e., accessible hydroxyl group) to another of greater attractive force. The bound water diffusivity increases with increasing moisture content as more water molecules are less strongly bonded to the sorptive sites than at low moisture contents.[6]

Apart from the properties of the two main components, there are several compositional parameters such as wood-flour content, the wood-flour particle size, and the use of coupling agent that influence moisture uptake and transport properties of wood-flour/ PP composites. Several researchers found that moisture uptake of composites increased with wood content.[7–10] Bledzki and Faruk[10] emphasized that particle geometry is an important parameter with respect to moisture uptake of wood fiber–PP composites. They

found that the composites made with larger wood particles had noticeably higher moisture content than the composites made with smaller particles. According to Raj et al.,[11] small particles are not as easily dispersed as large particles due to a higher specific surface area that exposes more hydroxyl groups. Particles agglomerate by hydrogen bonding with residual water molecules. Coupling agents increase the wettability of wood particles with PP matrix, enhance dispersion, and improve adhesion of the two components.[12] Raj and Kokta[13] also showed that composites made with fibers treated with maleated PP (MAPP) had reduced water absorption compared to composites made without coupling agent. Thorough dispersion and adhesion promote encapsulation of the wood particles with plastic matrix, which reduces moisture uptake.

As a third group of influencing factors, the processing method has a large effect on moisture uptake. The polymer-rich surface layer and the low void content of injection-molded specimens reduce the amount of water entering the composite.[14] In contrast, the surfaces of extruded samples contain less plastic matrix due to lower processing temperatures and pressures. Therefore, the wood particles in extruded composites absorb more moisture than in injection-molded composites.[15]

Many researchers have measured the moisture uptake with respect to material or processing parameters. However, Mohd. Ishak et al.[16] and Marcovich et al.[17] went a step further and determined diffusion coefficients that could be used to predict the moisture uptake and transport behavior of WPCs. They used sorption data (i.e., unsteady and steady state data) from specimens immersed in water or exposed to humid air and Fick's law in Boltzmann's form to calculate the diffusion coefficients. Interestingly, nobody has used diffusion experiments (i.e., exclusively steady state data) yet to determine the diffusion coefficients of WPCs. From measurements on wood fiber boards, it is known that the diffusion and sorption methods may result in considerably different diffusion coefficients.[18] The aim of the study presented in this article was to determine the main effects and interactions of material parameters on moisture sorption and diffusion, and to compare two methods of determining diffusion coefficients. Knowledge of moisture uptake and transport properties is essential for predicting the moisture content and thus for estimating service life of WPCs.

MATERIALS AND METHODS

Experimental design

A two-level, full-factorial statistical design was used to establish the main effects and interaction terms of four material parameters on the sorption and diffusion properties of a wood-flour/polypropylene (PP) composite. The parameters and their levels were

- Wood-flour content: 25 or 50% (by weight)
- Particle size: coarse or fine
- Coupling agent content: 0 or 3% (by weight)
- Surface treatment: surface as molded or surface milled

Additionally, specimens of unfilled PP were prepared both with and without MAPP, and with and without milled surface. Three replicates were prepared of each specimen type.

Preparation of specimens

The plastic was an isotactic PP homopolymer (Pro-fax PD702, Basell Polyolefins, Lansing, MI, USA), with a melt flow index of 35 g/10 min, and a density of 0.902 g/cm^3. The filler was wood-flour made from Pinus ssp., maximum particle size 80 mesh, i.e., 180 μm sieve openings (grade 8020 western pine, American Wood Fibers, Schofield, WI). The wood-flour was fractionated using a shaker and a 100 mesh sieve (U.S. Standard Sieve Series, 150 μm openings). The two fractions obtained were designated as "coarse" and "fine." We used a maleated PP (MAPP) as coupling agent (Epolene G-3015®, Eastman Chemical, Kingsport, TN) that had an acid number of 15 mg KOH/g, molecular weights of 24,800 (number-average) and 47,000 (weight-average), and a density of 0.913 g/cm^3. No further additives were used.

The wood-flour was dried in an oven at 80°C for 48 h to a moisture content of less than 1%. The wood-flour was manually mixed with the pellets of PP, and of MAPP, if required. The mixture was compounded using a 32 mm corotating twin-screw extruder (Davis Standard, Pawcatuck, CT). The feed rate varied between 114 g/min for the blends with 50% wood-flour content and 245 g/min for blends with 25% wood-flour content. The extruder barrel temperatures varied between 140 and 177°C. The pellets were dried in an oven at 80°C for at least 8 h to ensure a moisture content below 0.2% prior to injection molding. The dry pellets were processed in a reciprocating screw injection molder (Cincinnati Milacron, 33 t, Batavia, OH). We used a variable-depth disk mold with a diameter of 102 mm to produce specimens with a thickness of 0.75 and 1.25 mm. The injection molding conditions were varied considerably to produce acceptable specimens of various thicknesses from formulations with different viscosities and without thermally degrading the wood-flour. Injection speeds ranged from 2.54 to 7.62 cm/s, the barrel temperature was 190°C, and the mold temperature was 93°C.

The specimens with a thickness of 1.25 mm were milled to remove 0.25 mm from both surfaces. This

was done using a fly cutter with a single point tool used for metal-working. The cutter had a diameter of 114.3 mm, and rotated at 350 rpm. The specimen was fed at approximately 25.4 mm/min under the cutter and was held by a specially constructed vacuum chuck. Prior to milling, the specimens were dried in an oven at 105°C for 4 h. The dry specimens were measured to obtain initial thickness values necessary for adjusting the milling equipment.

Physical properties

Prior to beginning the experiments, the specimens were dried again because half of them had been exposed to ambient conditions during milling. The second drying was accomplished in a vacuum oven to reduce the impact of heat on the specimens. Drying was carried out for 5 h at 50°C at 9×10^4 Pa. The dry specimens were measured to obtain values for thickness, diameter, and density. The density of the wood particles inside the specimens was calculated using

$$\frac{1}{\rho_c} = \left(\frac{w_w}{\rho_w}\right) + \left(\frac{w_{PP}}{\rho_{PP}}\right) \qquad (1)$$

where ρ_c, ρ_w, and ρ_{PP} are the composite, wood-flour, and PP densities, respectively. w_w and w_{PP} are the wood and PP weight fractions, respectively. A density of 0.902 g/cm^3 for PP was used.

Microscopy

A polarized light microscope (Orthoplan Leitz, Wetzlar, Germany) with a digital camera head (Nikon, Japan) was used to examine the microstructure of 8–10 μm thick, microtomed cross sections. Images of the surfaces were taken with a scanning electron microscope (EVO 40, Zeiss, LEO/NTS, Germany; working distance of 10 mm, 15 kV, secondary electron).

Moisture diffusion experiments

A slightly modified standard laboratory method (DIN 53122-1,[19] similar to ASTM E 96-00[20]) was used to investigate moisture diffusion through specimens at 20°C and 65 or 85% relative humidity (RH). We assembled diffusion set-ups by attaching a specimen on top of a Petri dish, 100 mm in diameter and 20 mm in height, filled with phosphorus pentoxide desiccant to create nearly 0% RH in the sealed Petri dish. To prevent warping of the specimen as well as moisture diffusion through the interface between specimen and container, the specimens were glued to the glass with a low melting point hot melt adhesive (Jet-melt 3792 ''Low Melt''[®], 3M, Neuss, Germany) and the glue-line was sealed with desiccator grease made of paraffin (Exsikkatorfett weiss[®], Carl Roth, Germany). One additional set-up was built for each climate. Instead of

a specimen, a moisture impermeable stainless steel disk was glued and sealed on top of the jar to confirm the effectiveness of the sealing procedure.

The set-ups were placed in 65 and 85% RH rooms, weighed periodically to the nearest 0.0001 g, and the weight gain was plotted over time until steady state, i.e., a constant slope, was reached. The moisture transmission at steady state was determined by a curve fit of the data using

$$w(t) = at - b \times \exp(-kt)/k + c \qquad (2)$$

where w is the weight gain, t is the time, and a is the asymptotic slope, i.e., the moisture transmission at steady state. b, k, and c are fitting parameters. The water-vapor transmission rate, j^d, is then

$$j^d = \frac{a}{A} \qquad (3)$$

where A is the exposed area of specimen.

To calculate effective diffusion coefficients, D_{diff}, using diffusion data, Fick's first law was applied in the following form[18]:

$$j^d = -D_{diff}\frac{M_{H_2O}}{RT_{abs}}\frac{\Delta p}{d} \qquad (4)$$

where D_{diff} is the diffusion coefficient derived from data of diffusion experiments, M_{H_2O} is the molar mass of water, R is the universal gas constant, T_{abs} is the absolute temperature, Δp is the difference in partial water-vapor pressure on both specimen surfaces, and d is the specimen thickness at steady state.

To determine Δp, the partial water-vapor pressure on both specimen surfaces had to be calculated. The RH and the temperature were known. RH, partial water-vapor pressure p_v, and saturated water-vapor pressure p_{sat} are related by

$$RH = \frac{p_v}{p_{sat}} \qquad (5)$$

The saturated water-vapor pressure was calculated using an empirical equation[21]:

$$\log_{10} p_{sat} = 10.745 - \frac{2141}{T_{abs}} \qquad (6)$$

The set-ups were dismantled after steady state was reached to determine the total moisture uptake and the thickness of the specimens. The moisture content of the composites at steady state, MC_{st}, was calculated with the following equation:

$$MC_{st} = \frac{(M_{st} - M_{dry})}{M_{dry}} \times 100 \ (\%) \qquad (7)$$

where M_{st} is the weight of the specimen at steady state and M_{dry} is the dry specimen weight.
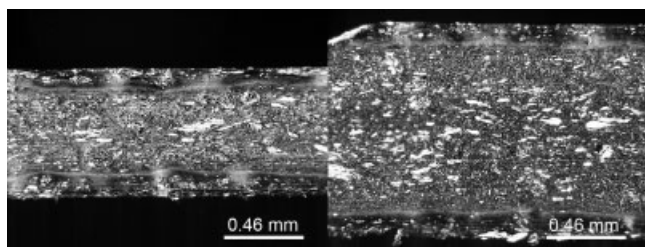
Figure 1 Cross sections of specimens with 25% wood-flour content (magnification: ×6.3).

Moisture sorption experiments

Sorption experiments are described in DIN EN ISO 62[22] (similar to ASTM D 5229[23]). Dry specimens were exposed to 20°C and 85% RH or distilled water. Periodically, specimens were removed and weighed. For specimens immersed in water, surface moisture was removed by blotting with towels prior to weighing.

The moisture content of the specimens was plotted versus the square root of time. Effective diffusion coefficients D_{sorp} were calculated using the initial slope and Boltzmann's form of Fick's general diffusion equation[6,16,24]:

$$D_{sorp} = \pi \frac{d^2}{16 \, EMC^2} \left[\frac{(MC_2 - MC_1)}{(\sqrt{t_2} - \sqrt{t_1})} \right]^2 \qquad (8)$$

where D_{sorp} is the diffusion coefficient derived from sorption data, EMC is the equilibrium moisture content determined from the average of the last five data points after equilibrium is reached, MC_1 and MC_2 are the moisture contents at time t_1 and t_2, and d is the specimen thickness at equilibrium.

After equilibrium was reached, we determined the total moisture uptake and the thickness of the specimens. The EMC of the composites was calculated using

$$EMC = \frac{(M_{eq} - M_{dry})}{M_{dry}} \times 100 \; (\%) \qquad (9)$$

where M_{eq} is the equilibrium specimen weight and M_{dry} is the dry specimen weight.

To compare with our composites, wood-flour of coarse and fine particle size was also exposed to 20°C and 65 or 85% RH, and the EMC was determined. Furthermore, we calculated the moisture content of the wood particles inside the composite by multiplying the EMC of the composite by its wood-flour content, assuming that all moisture was located in the wood particles.

Statistical analyses

The significant main effects and interactions of the material variables were determined for the water-vapor transmission rate, diffusion coefficient (D_{diff}), and moisture content (all at steady state) for the diffusion experiments, and for the EMC and diffusion coefficient (D_{sorp}) for the sorption experiments. We used
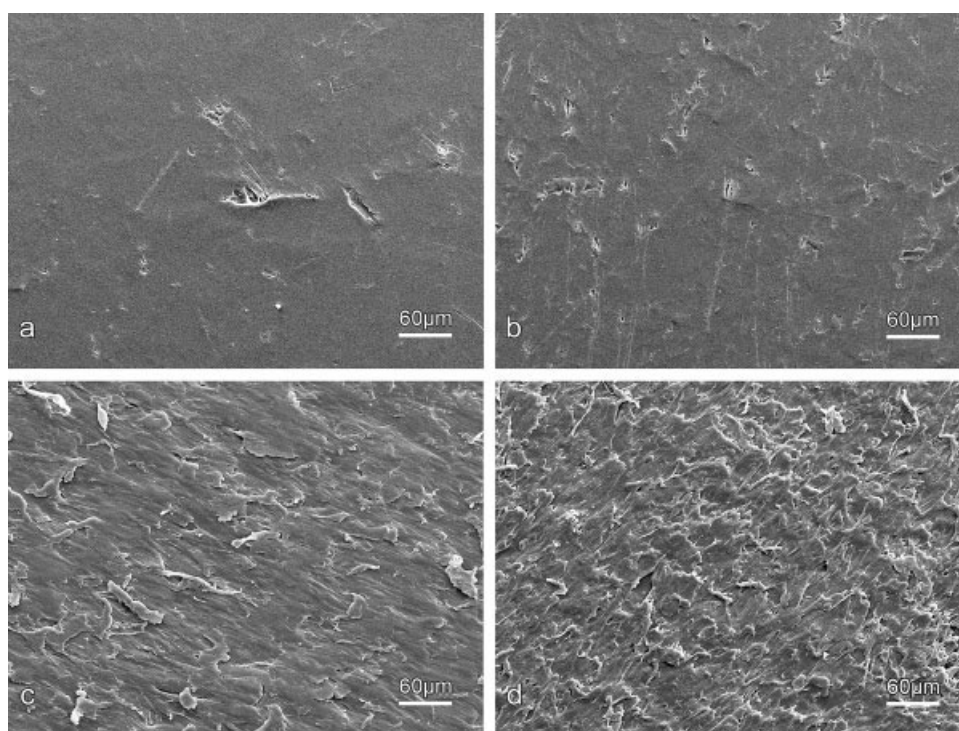
Figure 2 Specimens with intact (a,b) and milled (c,d) surfaces, and 25% wood-flour content (a,c) and 50% wood-flour content (b,d) (magnification: ×75).
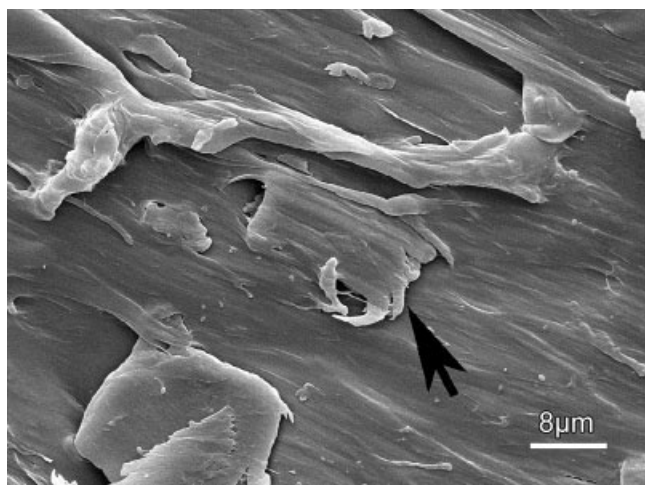
Figure 3 Wood particle on the milled surface of a specimen made with 25% fine wood-flour (magnification: ×600).

the DesignExpert 6.0.10® software (Stat-Ease, Minneapolis, MN) and a confidence level of 95%.

A linear model was developed with the significant effects and interaction terms. The residuals (i.e., the difference between the observations and the model predictions) were used to determine variability and outliers.[25] If one of the 3 replicates was greater than 3.5 standard deviations from the average, it was considered an outlier and was discarded. However, if 2 outliers were found for a particular specimen type, all data points were kept since we did not feel justified discarding 2 of 3 data points.

The statistical analysis for the moisture content response at 65% RH was conducted using the SAS

software (Release 8.1, Copyright 1999–2000, SAS Institute, Cary, NC). This was necessary because of missing data. Hence, the statistical design was unbalanced and could not be evaluated with Design-Expert.

RESULTS AND DISCUSSION

The average density of composites filled with 25 and 50% wood-flour was 0.99 and 1.10 g/cm^3 with an average standard deviation of 0.01 g/cm^3 for both. The calculated average density of the wood particles [eq. (1)] was 1.39 g/cm^3 regardless of wood-flour content. These densities are consistent with previous findings.[15] The densities of the wood particles approached values for cell wall material (about 1.5 g/cm^3)[5] indicating that the wood cells have collapsed or that the lumina may be filled with plastic matrix due to the high pressure applied during injection molding.[15]

It was not possible to meet the desired thickness of 0.75 mm when injection molding specimens with 50% wood-flour content, since the composite melt had a high viscosity due to the high wood-flour content. We did not use additives to overcome this problem because they might influence the moisture uptake and transport behavior. Consequently, specimens with 50% wood-flour were, on average, 0.84 mm thick.

Figure 1 shows cross sections of 1.25 and 0.75 mm thick specimens containing 25% wood-flour with coarse particles and 0% coupling agent. The micrographs show that both specimens are layered and that milling 0.25 mm of both surfaces of the thick specimen removed its outer layer.

TABLE I
Results of Diffusion Experiments at 85% and 65% RH

Specimen type	Moisture content (%) at		Water-vapor transmission rate (10^{-9}) (kg m^{-2} s^{-1}) at		D_{diff} (10^{-10}) (m^2/s) at	
	85% RH	65% RH	85% RH	65% RH	85% RH	65% RH
25% Coarse wood-flour, no MAPP, unmilled	1.21 (0.02)	–[a]	1.16 (0.09)	0.67 (0.03)	0.67 (0.06)	0.38 (0.02)
25% Coarse wood-flour, no MAPP, milled	1.56 (0.03)	1.11 (0.01)	1.38 (0.07)	0.77 (0.03)	0.82 (0.04)	0.44 (0.02)
25% Coarse wood-flour, MAPP, unmilled	1.14 (0.02)	0.94 (0.02)	1.09 (0.03)	0.58 (0.01)	0.64 (0.02)	0.33 (0.01)
25% Coarse wood-flour, MAPP, milled	1.45 (0.02)	1.04 (0.02)	1.18 (0.00)	0.71 (0.02)	0.70 (0.01)	0.41 (0.02)
25% Fine wood-flour, no MAPP, unmilled	1.16 (0.05)	0.88 (0.04)	1.05 (0.03)	0.59 (0.07)	0.62 (0.02)	0.34 (0.04)
25% Fine wood-flour, no MAPP, milled	1.34 (0.02)	0.96 (0.04)	1.13 (0.03)	0.64 (0.03)	0.66 (0.02)	0.37 (0.01)
25% Fine wood-flour, MAPP, unmilled	1.14 (0.01)	0.90 (0.02)	0.94 (0.02)	0.50 (0.01)	0.54 (0.01)	0.29 (0.01)
25% Fine wood-flour, MAPP, milled	1.29 (0.00)	0.93 (0.05)	1.04 (0.02)	0.59 (0.06)	0.61 (0.00)	0.34 (0.03)
50% Coarse wood-flour, no MAPP, unmilled	2.32 (0.03)	1.56 (0.01)	2.71 (0.08)	1.30 (0.13)	1.72 (0.07)	0.80 (0.08)
50% Coarse wood-flour, no MAPP, milled	3.55 (0.14)	2.00 (0.03)	5.89 (0.55)	1.88 (0.10)	3.56 (0.31)	1.11 (0.06)
50% Coarse wood-flour, MAPP, unmilled	2.10 (0.08)	1.41 (0.02)	2.22 (0.18)	1.18 (0.04)	1.54 (0.13)	0.80 (0.03)
50% Coarse wood-flour, MAPP, milled	2.92 (0.17)	1.92 (0.03)	3.01 (0.13)	1.58 (0.05)	1.77 (0.08)	0.92 (0.04)
50% Fine wood-flour, no MAPP, unmilled	2.15 (0.06)	1.51 (0.01)	2.28 (0.04)	1.14 (0.04)	1.44 (0.01)	0.70 (0.04)
50% Fine wood-flour, no MAPP, milled	3.10 (0.11)	1.77 (0.02)	3.58 (0.29)	1.41 (0.17)	2.15 (0.18)	0.82 (0.11)
50% Fine wood-flour, MAPP, unmilled	2.13 (0.05)	1.45 (0.02)	2.18 (0.03)	1.16 (0.03)	1.43 (0.03)	0.74 (0.03)
50% Fine wood-flour, MAPP, milled	2.78 (0.01)	1.73 (0.03)	2.44 (0.07)	1.16 (0.14)	1.43 (0.04)	0.68 (0.08)

Values in parentheses are one standard deviation.
[a] No values available.
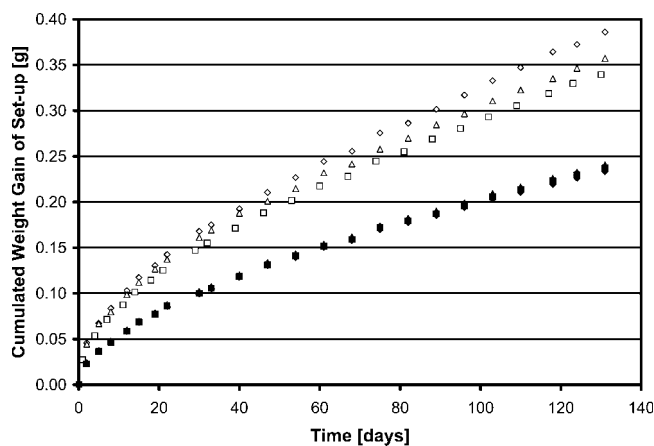
Figure 4 Results from the diffusion experiment at 85% RH. Three replicates of specimens of PP containing 50% wood-flour, no MAPP, with milled surface (open symbols) or unmilled surface (closed symbols).

Figure 2 shows specimens with intact and milled surfaces, and 25 and 50% wood-flour content. While the unmilled surfaces are smooth, resin-rich, and only occasionally disrupted by wood particles, the milled surfaces show no obvious milling marks but are fairly rough, especially in the composite with 50% wood content. The specimens shown were made with fine wood-flour, and no coupling agent. Figure 3 shows an

example of a wood particle exposed on the surface of a milled specimen.

Moisture diffusion experiments

Diffusion experiments were conducted at 20°C and 65 or 85% RH, and the results are summarized in Table I. Figure 4 shows the cumulated weight gain of the diffusion set-ups at 85% RH for PP filled with 50% wood-flour with milled and unmilled surfaces. The initial curved region shows the transient behavior and is followed by a region of constant slope, indicating steady state diffusion.[24] The milled replicates at 85% RH typically spread over time especially for blends without coupling agent. Specimens exposed to 85% RH reached steady state faster than specimens exposed to 65% RH.

At both RHs, moisture content, water-vapor transmission rate, and diffusion coefficient increased with increasing wood-flour content due to the hygroscopic properties of the wood component. The tests at both RHs showed similar trends, but the water-vapor transmission rates and diffusion coefficients were approximately twice as large at 85% RH as at 65% RH. Since the RH had not doubled and the temperature was kept constant, this might suggest that the water-vapor transmission rate and the diffusion coefficient are not linearly dependent on the RH. In fact, Stamm[6]

TABLE II
Complete List of Significant Main Effects and Interaction Terms for Diffusion Experiments at 85% and 65% RH

		Responses					
		Moisture content (%) of specimens at		Water-vapor transmission rate (10^{-9}) (kg s^{-1} m^{-2}) at		D_{diff} (10^{-10}) (m^2/s) at	
	Variable[a]	85% RH	65% RH	85% RH	65% RH	85% RH	65% RH
Main effects[b]	WFC	1.36	0.70	1.92	0.72	1.22	0.46
	PS	−0.16	−0.11	−0.50	−0.19	−0.31	−0.12
	CA	−0.20	−0.06	−0.64	−0.12	−0.37	−0.06
	ST	0.59	0.23	0.75	0.20	0.39	0.09
Interactions[c]	WFC × PS			−0.34	−0.09	−0.22	−0.06
	WFC × CA	−0.12	−0.03	−0.52	−0.05	−0.30	
	WFC × ST	0.34	0.14	0.63	0.10	0.31	0.03
	PS × CA	0.08	0.03	0.27		0.16	
	PS × ST	−0.10	−0.07	−0.32	−0.10	−0.18	−0.05
	CA × ST	−0.10		−0.44	−0.05	−0.30	−0.04
	WFC × PS × CA	0.05		0.26		0.15	
	WFC × PS × ST		−0.04	−0.28	−0.08	−0.16	−0.04
	WFC × CA × ST	−0.08	0.02	−0.42	−0.07	−0.28	−0.05
	PS × CA × ST			0.19		0.13	
	WFC × PS × CA × ST			0.15		0.10	
Overall mean		*1.98*	*1.34*	*2.08*	*1.00*	*1.27*	*0.60*
Standard deviation		*0.07*	*0.03*	*0.17*	*0.08*	*0.10*	*0.05*
Coefficient of variation (%)		*3.51*	*2.03*	*8.17*	*7.66*	*7.95*	*7.85*

[a] WFC is wood-flour content, PS is particle size, CA is coupling agent, ST is surface treatment.
[b] Change in property resulting from the particular variable, averaged over all other variables.
[c] $X \times Y$ interaction = ½ (average effect of X at first level of Y − average effect of X at second level of Y); $X \times Y \times Z$ interaction = ½ the difference between the $X \times Y$ interactions at the two levels of X.[25]
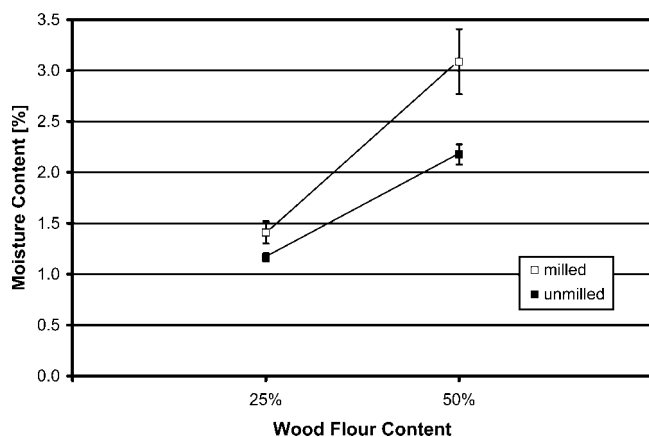
Figure 5 Wood-flour content × surface treatment interaction for moisture content for the diffusion experiment at 85% RH. Points represent the averages of the different levels of coupling agent and particle size. Error bars show plus and minus one standard deviation.

showed that bound water diffusion coefficients of wood cell wall material increased exponentially with an increase in moisture content. However, we would have to conduct experiments at more RHs to establish the relationships between RH and moisture content, water-vapor transmission rate, diffusion coefficient, and time to reach steady state.

Interestingly, the moisture content of the wood particles inside the composites was very similar at both wood-flour levels. For example, at 85% RH, moisture contents of 5.2 and 5.3% were found for composites containing 25 and 50% wood-flour, assuming that all of the moisture is absorbed by the wood-flour. Similar results were found at 65% RH. These moisture contents are averages and do not reflect any differences in moisture distribution over the specimen cross section.

Table II shows the statistical analyses for the diffusion experiments at 85 and 65% RH. The average coefficients of variation ranged from about 2–8%. However, the variability was generally highest for composites that absorbed the most moisture (i.e., those with high wood-flour content, milled surface, no coupling agent, and coarse particles). Since water-vapor transmission rates are directly proportional to the diffusion coefficients [eq. (4)], the trends are similar. Hence, we discuss only the moisture content and the diffusion coefficients. Though all significant main effects and interaction terms need to be included to completely describe the behavior, only the largest influences are discussed here.

Wood-flour content had the largest influence of any main effect or interaction (Table II). However, since the wood-flour content is involved in significant interaction terms, its effect is not consistent at different levels of the other variables. Hence, these interactions must be considered to adequately describe the behavior. For example, Figure 5 shows the interaction

between the wood-flour content and surface treatment at 85% RH. The wood-flour content × surface treatment interaction is defined as half of the difference of the effects at the different wood-flour contents. Milling the surfaces of the composites increased the moisture content at both wood-flour contents but the effect was greater at 50%.

Removing the resin-rich surface layer increases the accessibility of the wood-flour particles near the specimen surface to moisture. Furthermore, wood particles swell with moisture and may damage the plastic matrix especially at high wood content, providing more pathways for moisture penetration.[26] Also, milling can more easily damage the more brittle composites containing 50% wood-flour and the dispersion of the wood-flour may not be as good as composites containing 25% wood-flour and lead to greater moisture penetration. Generally, we observed higher variability in moisture content as wood-flour content was increased.

At 85% RH, all possible main effects and interaction terms were significant for diffusion coefficient. As with moisture content, the wood-flour content had by far the largest influence and the diffusion coefficient increased with increasing wood-flour content. Since our unfilled PP specimens took up less than 0.23% moisture, we assume that the wood-flour absorbs nearly all of the moisture. Since the average moisture content of the composites containing 50% wood-flour is about twice that of those containing 25% wood-flour, the average moisture content in the wood-flour is roughly equal. This suggests that the diffusion coef-
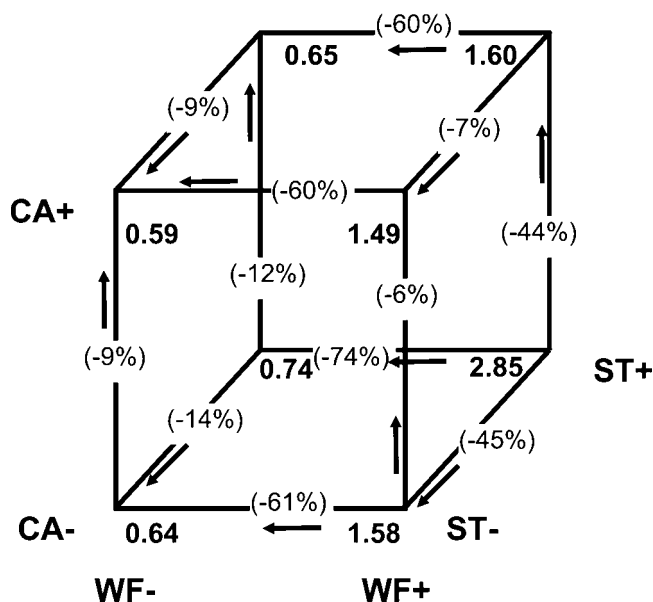
Figure 6 Cube plot representing the wood-flour content × coupling agent × surface treatment interaction for the response diffusion coefficient of the diffusion experiment at 85% RH. The effect of particle size is averaged. All values in units of 10^{-10} m²/s. Values in parentheses are the differences between corners in percent.
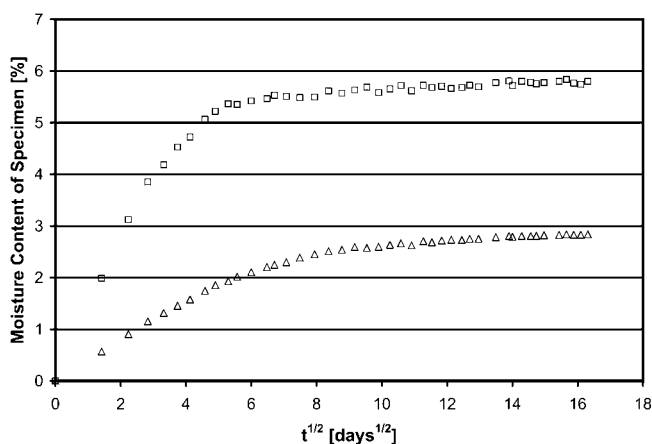
Figure 7 Sorption curves (single data points) from sorption experiments at 85% RH for specimens with 25% (triangular symbols) or 50% (square symbols) coarse wood-flour, no MAPP, and milled surfaces.

ficient in the wood component is likely similar in all composites despite its dependence on moisture content. However, the wood particles in composites containing 50% wood-flour are closer together than in composites with 25% wood-flour allowing moisture to more easily percolate through the composite.

Also, there might be damage of the composite due to moisture sorption. Peyer and Wolcott[26] reported the expansion of cracks and debonding at the wood–plastic interface caused by swelling of the wood particles at or near the surface of the specimens. Thus pathways for further water penetration are created. Furthermore, swelling of wood particles inside the composite might result in spaces where diffusion of

water vapor in air is possible, which is much faster than diffusion of water vapor in solids and atmospheric pressure ($D_{\text{water vapor}} = 2.62 \times 10^{-5}$ m^2/s at 20°C).[27]

The other main effects and interactions were also significant at 85% RH. Many of these were large, even the three-factor interaction among wood-flour content, coupling agent, and surface treatment, suggesting significant and complex relationships among these factors. Figure 6 shows the cube plot representing this interaction. The values of each corner are averaged over both particle sizes.

One way of looking at the three-factor interaction is as a measure of the consistency of the wood-flour content × coupling agent interaction for the two levels of surface treatment.[25] The interaction between wood-flour content and coupling agent is represented by the front face of the cube for the unmilled composites and by the back face for the milled ones. In unmilled composites, the change in diffusion coefficient when adding coupling agent differed by only 3% between the two levels of wood-flour. However, the effect of coupling agent was larger when the surfaces were milled, especially at high wood-flour content. Thus, the magnitude of the wood-flour content × coupling agent interaction depends on the surface treatment, i.e., all of these three factors interact.

Generally, the diffusion experiments at 65% RH showed similar trends as the diffusion experiments at 85% RH. However, particle size had a larger influence and coupling agent had a smaller influence on the diffusion coefficients at the lower RH. Values derived from steady state methods for similar composites or for bound water diffusion in wood are not available in

TABLE III
Average Results of the Sorption Experiments at 85% RH and Soaked in Distilled Water

Specimen type	Moisture content (%) of specimens after 238 days		D_{sorp} (10^{-14}) (m^2/s) at 85% RH
	85% RH	Soak	
25% Coarse wood-flour, no MAPP, unmilled	2.57 (0.11)	5.08 (0.03)	—[a]
25% Coarse wood-flour, no MAPP, milled	2.82 (0.01)	6.33 (0.21)	2.89 (0.11)
25% Coarse wood-flour, MAPP, unmilled	2.43 (0.02)	4.42 (0.16)	—[a]
25% Coarse wood-flour, MAPP, milled	2.60 (0.05)	5.75 (0.05)	2.59 (0.27)
25% Fine wood-flour, no MAPP, unmilled	2.45 (0.04)	4.76 (0.17)	—[a]
25% Fine wood-flour, no MAPP, milled	2.40 (0.05)	5.73 (0.04)	—[a]
25% Fine wood-flour, MAPP, unmilled	2.40 (0.02)	4.43 (0.06)	—[a]
25% Fine wood-flour, MAPP, milled	2.49 (0.09)	5.19 (0.20)	—[a]
50% Coarse wood-flour, no MAPP, unmilled	5.72 (0.07)	13.33 (0.34)	—[a]
50% Coarse wood-flour, no MAPP, milled	5.83 (0.11)	14.12 (0.43)	7.44 (1.81)
50% Coarse wood-flour, MAPP, unmilled	5.18 (0.19)	10.92 (0.27)	—[a]
50% Coarse wood-flour, MAPP, milled	5.68 (0.07)	12.56 (0.16)	3.98 (0.42)
50% Fine wood-flour, no MAPP, unmilled	5.12 (0.04)	11.51 (0.16)	—[a]
50% Fine wood-flour, no MAPP, milled	5.47 (0.03)	12.41 (0.07)	4.25 (0.20)
50% Fine wood-flour, MAPP, unmilled	5.06 (0.01)	10.77 (0.17)	—[a]
50% Fine wood-flour, MAPP, milled	5.27 (0.04)	11.51 (0.10)	3.26 (0.12)

Values in parentheses are one standard deviation.
[a] It was not possible to measure D_{sorp} because equilibrium was not reached.

the literature making comparisons with our values difficult.

Moisture sorption experiments

Specimens were exposed to 20°C and 85% RH or soaked in distilled water. For both experiments, adding more wood-flour, removing the surface layer, employing coupling agent, and increasing particle size reduced the time required to reach equilibrium. While all immersed specimens reached equilibrium, most specimens exposed to 85% RH did not reach equilibrium within our time schedule, i.e., 238 days, and diffusion coefficients could not be calculated for them.

Figure 7 shows the composite moisture content versus square root of time for the sorption experiment at 85% RH. The curves increase linearly until ~60% of the equilibrium moisture content are reached and then approach a saturation value, suggesting Fickian behavior.[1] Using the initial slope and the equilibrium moisture content, diffusion coefficients D_{sorp} were calculated with Boltzmann's form of Fick's general diffusion equation [see eq. (8)].[6,16,24] Diffusion coefficients were not calculated for the immersion experiment because it was not possible to determine an accurate

initial slope due to high variability resulting from the difficulty of consistently removing surface moisture prior to weighing.

Table III shows the moisture contents of the specimens soaked in water or exposed to 85% RH as well as the diffusion coefficients, where possible. Table IV shows the results of the statistical analyses. The sign of the main effects and interactions for moisture content were similar in all experiments of both types, i.e., sorption and diffusion, but the terms that were significant and their relative magnitude occasionally differed. For example, adding 25% more wood-flour had by far the largest influence on moisture content in both experiments. However, particle size had the second largest effect in the sorption tests at 85% RH, whereas surface treatment was the second largest in the water soak tests. Particle size was also involved in the largest interaction term for moisture content at 85% RH in the sorption experiment, suggesting an increased role compared with the other experiments. The reason for this increased importance is not clear.

The highest moisture content measured for all specimens exposed to 85% RH after 238 days was 5.8% (Table III). These specimens had reached equilibrium. Assuming that all moisture was absorbed by the wood-flour, the average moisture content of the wood

TABLE IV
Complete List of Significant Main Effects and Interaction Terms for Both Sorption Experiments

	Variable[a]	Moisture content (%) of specimens at day 238 (85% RH)	Equilibrium moisture content (%) of specimens (Water soak)
		Responses	
Main effects[b]	WFC	2.91	6.93
	PS	−0.29	−0.77
	CA	−0.14	−0.96
	ST	0.18	1.05
Interactions[c]	WFC × PS	−0.12	−0.41
	WFC × CA	−0.06	−0.44
	WFC × ST	0.07	
	PS × CA	0.09	0.34
	PS × ST	−0.04	−0.20
	CA × ST		
	WFC × PS × CA		0.25
	WFC × PS × ST	0.06	
	WFC × CA × ST		
	PS × CA × ST		−0.16
	WFC × PS × CA × ST	−0.08	
Overall mean		*3.95*	*8.68*
Standard deviation		*0.06*	*0.20*
Coefficient of variation (%)		*1.51*	*2.32*

[a] WFC is wood-flour content, PS is particle size, CA is coupling agent, ST is surface treatment.
[b] Change in property resulting from the particular variable, averaged over all other variables.
[c] $X \times Y$ interaction = ½ (average effect of X at first level of Y − average effect of X at second level of Y); $X \times Y \times Z$ interaction = ½ the difference between the $X \times Y$ interactions at the two levels of X.[25]

particles was 11.7%. However, when wood-flour alone was exposed to 85% RH, it reached an EMC of about 15%, suggesting that the moisture sorption of wood-flour may be reduced and not just delayed when combined with plastic. This could be partly due to reduced hygroscopicity of wood when exposed to elevated temperatures during processing.[28] Mechanical restraints exerted by the PP matrix on the wood particles may be another reason for reduced EMC of the wood-flour inside the composites. However, further research needs to be performed to support these assumptions and identify other factors influencing moisture uptake.

The calculated average moisture content of the wood component of specimens exposed to 85% RH was about 10.3% regardless of wood-flour content. However, in the immersion experiments, the average EMCs depended on the wood-flour content. EMCs of 20.9 and 24.3% were found for specimens with 25 and 50% wood content and the average standard deviation was 2.5%. This inconsistency between the immersion tests and those in humid environments was also found in our diffusion tests as well in other research on injection-molded WPCs.[8] However, all wood moisture content values are averages over the specimen cross section, since the moisture distribution inside the composite is unknown. Further research should explore the moisture distribution and its relationship to climate and composition.

D_{sorp} had values of about 3–7 $\times$ 10^{-14} m^2/s. The comparison of D_{sorp} with values from literature is difficult due to variations of composites and conditions. Mohd. Ishak et al.[16] calculated diffusion coefficients for injection-molded composites of rice husks and PP from sorption tests in water at 30°C. They found a diffusion coefficient of 15.9 $\times$ 10^{-15} m^2/s for composites containing 30% filler at an EMC of 1.9% and of 8.8 $\times$ 10^{-14} m^2/s for composites containing 40% filler at

an EMC of 4.2%. These values are of similar magnitude as ours and also increase with increasing lignocellulosic filler content. Segerholm et al.[29] prepared injection-molded composites of PP and 50% pine-wood fibers. After 140 days of exposure at 22°C and 80% RH, the specimens had a moisture content of 5.6%. The authors calculated a diffusion coefficient of 4.27 $\times$ 10^{-14} m^2/s. This supports our findings, since the material and test method were very similar.

Comparison between methods: Sorption experiments and diffusion experiments

Table V compares the two coefficients, D_{diff} and D_{sorp}, from the diffusion and the sorption experiments. D_{diff} was calculated using Fick's law in the form of eq. (4) and D_{sorp} was calculated with Fick's law in Boltzmann's Form [see eq. (7)]. Because only milled sorption specimens at 85% RH reached equilibrium within our time schedule, comparisons are limited.

Both D_{sorp} and D_{diff} increased with wood-flour content. However, D_{diff} is orders of magnitude higher than D_{sorp}. Since wood, unlike PP, shows large interactions with water, it seems appropriate to assume that wood and wood-related mechanisms dominate moisture uptake and transport properties of our composites and it is useful to discuss these and their relevance to our experiments.

Stamm[6] used sorption experiments and Boltzmann's form of Fick's law to obtain diffusion coefficients of wood cell wall material. The author concluded that deviations of the sorption curve from the ideal shape are due to the concentration-dependent diffusivity of wood but are not critical since they do not occur at the parts of the curve used for calculation of diffusion coefficients (i.e., initial slope and EMC). However, moisture sorption causes swelling of the wood particles. Swelling changes the cell wall struc-

TABLE V
Average Coefficients and Moisture Contents of Wood Component from Diffusion and Sorption Experiments at 20°C and 85% RH

Specimen type	D_{diff} at 20°C and 85% RH at steady state (10^{-10}) (m^2/s)	Moisture content (%) of wood component at steady state	D_{sorp} at 20°C and 85% RH at equilibrium (10^{-14}) (m^2/s)	Moisture content (%) of wood component at equilibrium
PP, nonmilled	0.25 (0.02)	–	–[a]	–
PP + MAPP, nonmilled	0.25 (0.01)	–	–[a]	–
25% Coarse wood-flour, no MAPP, milled	0.82 (0.04)	6.26 (0.03)	2.89 (0.11)	11.29 (0.04)
25% Coarse wood-flour, MAPP, milled	0.70 (0.01)	5.81 (0.02)	2.59 (0.27)	10.39 (0.20)
50% Coarse wood-flour, no MAPP, milled	3.56 (0.31)	6.27 (0.14)	7.44 (1.81)	11.66 (0.21)
50% Coarse wood-flour, MAPP, milled	1.77 (0.08)	5.18 (0.17)	3.98 (0.42)	11.35 (0.14)
50% Fine wood-flour, no MAPP, milled	2.15 (0.18)	5.52 (0.11)	4.25 (0.20)	10.94 (0.05)
50% Fine wood-flour, MAPP, milled	1.43 (0.04)	5.56 (0.01)	3.26 (0.12)	10.54 (0.08)
Average 25% wood-flour	0.70	6.03	2.71	10.84
Average 50% wood-flour	2.23	6.18	5.56	11.12

Values in parentheses are one standard deviation.
[a] D_{sorp} could not be calculated because the moisture uptake was too low.

ture and thus the amount of accessible sorptive sites. Several researchers have suggested that time-dependent processes, such as mechanical relaxation of the cell wall material (e.g., during swelling) might control moisture uptake instead of diffusion.[4,30] Therefore, results from sorption tests may result in coefficients that are dominated by processes other than diffusion.

Considering these findings, our results for D_{diff} and D_{sorp} suggest that different phenomena were measured by the two methods. This is supported by the observation that the diffusion experiments reached steady state after about 40 days, whereas most sorption specimens took more than 200 days to reach equilibrium. During the unsteady state of our diffusion experiments, water molecules occupy the accessible hydroxyl groups in the wood. However, measurements were made at steady state, i.e., when the sorption processes are completed and the permanent moisture gradient drives diffusion. In our sorption experiments, data were used both from equilibrium and from the unsteady state. Initially, a gradient exists between the dry specimen and the surrounding climate, and the specimen takes up moisture until equilibrium is achieved. Initial moisture sorbed by the wood is strongly bonded to the sorptive sites, e.g., the accessible hydroxyl groups of the cellulose, whereas further sorbed moisture is not as tightly bonded and diffuses more readily.

For systems without strong interactions (e.g., bonding and swelling) between the solid material and the diffusing molecules, a sorption experiment might yield the same results as a diffusion experiment. However, it seems debatable whether D_{sorp} is a true diffusion coefficient in our experiments. To find appropriate models and methods to determine the diffusional properties of our composites, further investigations are needed. Our approach shows that different methods might yield different values that have been both called "diffusion coefficients." This is important to consider when comparing results of different studies, and when applying these values to determine actual material behavior.

CONCLUSIONS

A two-level, full-factorial experimental design and analysis were applied to determine how wood-flour content, particle size, coupling agent, surface treatment, and their interactions affect the moisture uptake and transport behavior of injection-molded wood-flour/PP composites. Moisture uptake, water-vapor transmission rate, and diffusion coefficients were determined by conducting diffusion and sorption experiments.

Many effects and interactions were significant at 95% confidence, indicating that not only did the varia-

bles chosen influence the moisture transport properties but that they often interacted with each other. The wood-flour content had by far the largest influence on all responses of both experiment types but the effects of other variables were also significant. Increasing wood-flour content or removing the surface always increased moisture uptake and transport. These results were not surprising, since wood was the only component in our composites that sorbed much moisture and surface milling increased the accessibility of the wood particles by removing the resin-rich layer formed during injection molding. Generally, increasing particle size increased the moisture content and transport coefficients of the composites but adding coupling agent reduced them.

However, significant interactions between the variables were also found. The wood-flour content × surface treatment interaction was often the largest. Removing the surface almost always increased moisture content and moisture transport coefficients more when the wood-flour content was increased. Though smaller, other two-factor interactions were also significant and need to be considered to adequately describe moisture transport behavior.

The average moisture content of the wood component inside the sorption specimens was mostly below the EMC that wood-flour alone would reach in the same climate. This suggests that PP can be an effective barrier to moisture or that the hygroscopicity of the wood particles is lowered due to the high temperatures applied during processing. In humid climates, the average moisture content of the wood-flour phase generally did not depend on the amount of wood-flour added. However, specimens immersed in water showed higher moisture uptake of the wood phase in specimens with increasing wood-flour content.

D_{diff} was 3–4 orders of magnitude higher than D_{sorp}, and the diffusion experiments reached steady state at least five times faster than the sorption experiment reached equilibrium. These differences probably indicate that different phenomena are measured by the two methods. The diffusion experiments may yield more appropriate values of actual diffusion coefficients than the sorption experiments, since steady state data is used to calculate the coefficients. Thus time-dependent processes (i.e., swelling of wood) that might control moisture uptake and transport instead of diffusion are excluded. However, sorption experiments are valuable in predicting moisture uptake regardless of the mechanisms.

There is still considerable work yet to be performed on exploring in detail the mechanisms of moisture sorption and desorption, moisture distribution and damage development, and their influence on transport coefficients in WPCs. Additionally, more complete models establishing relationships among time, temperature, and exposure conditions need to be

developed to more accurately predict the performance of this rapidly growing class of composites.

References

1. Weitsman, Y. J. Comprehensive Composite Materials, Vol. 2: Polymer Matrix Composites; Elsevier: Amsterdam, 2000; Chapters 11.1–11.3.
2. Manson, J. A.; Sperling, L. H. Polymer Blends and Composites; Plenum: New York, 1976; Chapter 12.
3. Crank, J.; Park, G. S. Diffusion in Polymers; Academic Press: London, 1968.
4. van Krevelen, D. W.; Hoftyzer, P. J. Properties of Polymers: Their Estimation and Correlation with Chemical Structure; Elsevier: Amsterdam, 1976; Chapter 18.
5. Siau, J. F. Transport Processes in Wood; Springer-Verlag: Berlin, 1984.
6. Stamm, A. J. Forest Prod J 1959, 9, 27.
7. Raj, R. G.; Kokta, B. V.; Daneault, C. Polym Mater Sci Eng 1988, 59, 446.
8. Stark, N. J Thermoplast Compos Mater 2001, 14, 421.
9. Cantero, G.; Arbelaiz, A.; Mugika, F.; Valea, A.; Mondragon, I. J Reinforced Plast Compos 2003, 22, 37.
10. Bledzki, A. K.; Faruk, O. Compos Sci Technol 2004, 64, 693.
11. Raj, R. G.; Kokta, B. V.; Dembele, F.; Sanschagrain, B. J Appl Polym Sci 1989, 38 1987.
12. Lu, J. Z.; Wu, Q.; McNabb, H. S., Jr. Wood Fiber Sci 2000, 32, 88.
13. Raj, R. G.; Kokta, B. V. Polym Mater Sci Eng 1989, 60, 690.
14. Clemons, C. M.; Ibach, R. E. Forest Prod J 2004, 54, 50.
15. Stark, N. M.; Matuana, L. M.; Clemons, C. M. J Appl Polym Sci 2004, 93, 1021.
16. Mohd Ishak, Z. A.; Yow, B. N.; Ng, B. L.; Khalil, H. P. S. A.; Rozman, H. D. J Appl Polym Sci 2001, 81, 742.
17. Marcovich, N. E.; Reboredo, M. M.; Aranguren, M. I. Polymer 1999, 40, 7313.
18. Thoemen, H. Ph.D. Dissertation, Oregon State University, Corvallis, OR, 2000; p 188.
19. Deutsches Institut für Normung e.V. 2001 – DIN 53122-1: Prüfung von Kunststoff-Folien, Elastomerfolien, Papier, Pappe und anderen Flächengebilden: Bestimmung der Wasserdampfdurchlässigkeit, Teil 1: Gravimetrisches Verfahren; Beuth Verlag: Berlin.
20. ASTM. In Annual Book of ASTM Standards, Vol. 04.06 (Index 2003); American Society for Testing and Materials: West Conshohocken, PA, 2000; ASTM E 96-00.
21. Humphrey, P. E.; Bolton, A. J. Holzforschung 1989, 43, 199.
22. Deutsches Institut für Normung e.V. 1999 – DIN EN ISO 62: Kunststoffe: Bestimmung der Wasseraufnahme; Beuth Verlag: Berlin.
23. ASTM. In Annual Book of ASTM Standards, Vol. 15.03 (Index 2003); American Society for Testing and Materials: West Conshohocken, PA, 1992. ASTM D 5229/D 5229M-92.
24. Osswald, T. A.; Menges, G. Materials Science of Polymers for Engineers; Hanser/Gardner Publications: Cincinnati, OH, 1995; p 475.
25. Box, G. E. P.; Hunter, W. G.; Hunter, J. S. Statistics for Experimenters: An Introduction to Design, Data Analysis, and Model Building; Wiley: New York, 1978; p 653.
26. Peyer, S.; Wolcott, M. Engineered wood composites for naval waterfront facilities, 2000 Yearly Report, Washington State University for Office of Naval Research, 2000; p 13, Contract N00014-97-C0395.
27. Deutsches Institut für Normung e.V. 1987 – DIN 52 615: Wärmeschutztechnische Prüfungen: Bestimmung der Wasserdampfdurchlässigkeit von Bau- und Dämmstoffen; Beuth Verlag: Berlin.
28. Nakano, T.; Miyazaki, J. Holzforschung 2003, 57, 289.
29. Segerholm, K.; Bryne, L.-E.; Larsson Brelid, P.; Wålinder, M. E. P.; Westin, M.; Söderström, O. Presented at the 8th International Conference on Woodfiber–Plastic Composites, Madison, Wisconsin, May 23–25, 2005.
30. Christensen, G. N.; Kelsey, K. E. Holz als Roh- und Werkstoff 1959, 17, 178.