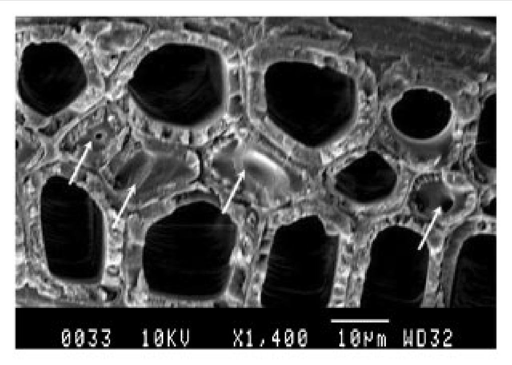
Summary: In order to improve the dimensional stability of end-grained wood upon environmental humidity variations, a two-step procedure was thoroughly studied which involved the osmotic impregnation of native poplar wood by PEG, followed by the reactive impregnation with HMDI, leading to polymer chain extension and polyurethane formation. It came out that the efficiency of PEG and/or polyurethane grafting within ligno-cellulosic cell walls was intimately related to parameters such as concentration of the PEG impregnation bath, PEG molar mass, time and temperature of impregnation steps. Based on the different sample characterizations, Soxhlet extraction and density measurements, it came out that adequate experimental conditions are to carry out osmotic impregnation at 20 °C for 24 h starting from an aqueous solution of PEG ($[\text{PEG}] = 0.5\ \text{mol} \cdot \text{L}^{-1}$ and $\overline{M}_{\text{n PEG}} = 400$ or 1 000) and reactive impregnation in bulk with a large excess of HMDI at 20 °C for 2 h. Combining scanning electron microscopy and mercury porosimetry demonstrated the selective impregnation of cell wall and wood rays which were collapsed in native wood and expanded in wood polyurethane composites.



SEM of an end-grained wood transversal cross-section after Soxhlet extractions successively with water and THF.

End-Grained Wood-Polyurethane Composites, 1

Synthesis, Morphology and Characterization

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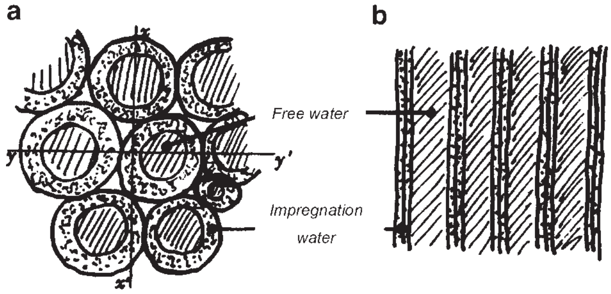
Introduction

Wood is a natural composite material which mainly combines cellulose, lignin and hemicellulose. Extended chains of cellulose form semi-crystalline microfibrils surrounded by a mixture of amorphous cellulose and hemicellulose. Bundles of microfibrils are organized within a matrix of lignin as a lamellar macrostructure which is at the origin of cell wall. Tubular wood cells present a width ranging from 20 to 35 μm and a length depending on the wood variety. They are placed side by side so that a transversal cross section looks like an assembly of vessels (Scheme 1).[1–3] As a result of such a supramolecular architecture, wood displays its best mechanical properties when employed in its natural direction of growth, i.e. with the wood vessels perpendicular to the ground, so-called end-grained wood. For instance, the ratio of Young's moduli in longitudinal (E_L) and radial (E_R) directions reached 11 for poplar wood.[4] The main limitation to the development of new applications using end-grained wood for timber, floor covering, etc., is its poor dimensional stability upon humidity variation. Indeed, it is in the radial and especially tangential directions that the dimensional variations are the more pronounced.

In order to decrease shrinkage and swelling of end-grained wood, several treatments have been developed which can be categorized into chemical modifications and impregnation methods. Chemical modifications aim to reduce wood hygroscopicity through the reaction between available hydroxyl functions on wood surface and such



Scheme 1. Representation of wood structure.

chemicals as anhydrides,[5] isocyanates,[6] formaldehyde,[7] alkoxysilane[8] or epoxides.[9,10] Osmotic wood impregnation consists in bulking wood cell or more selectively cell wall with unreactive chemicals by immersion into an aqueous solution of salts,[11] sugars,[12] glycerol[13] or poly(ethylene glycol) (PEG).[14] In order to prevent or at least to limit leaching due to environmental water content fluctuations, osmotic impregnation is adequately followed by a covalent grafting reaction, also referred as reactive impregnation. Typical wood polymer composites (WPCs) have been stabilized by phenol-formaldehyde,[15,16] melamine-formaldehyde or urea-formaldehyde resins.[17] Impregnation with vinylic monomers such as styrene,[18] methyl methacrylate,[19–21] 2-hydroxyethyl methacrylate,[20] acrylonitrile,[22] or allyl alcohol,[23] followed by radiation-initiated polymerization has also been reported. The efficiency of this technique is closely related to the nature of the monomer and its ability to penetrate wood cell. Other WPCs have been prepared by osmotic impregnation with functional (pre)polymers such as PEG[24] or hydroxyethyl methacrylate-based copolymers,[25,26] followed by reactive impregnation with diisocyanates, usually performed using organic solvents. Reactive impregnation can also been achieved using polyglycerol as prepolymer followed by maleic anhydride treatment.[27] In the same way, α,ω-protected isocyanate perfluoropolymers have been used for impregnation and directly cured to give rise to WPCs with a low interfacial tension.[28] More recently, impregnation of wood with aqueous solution of poly(glycerol methacrylate) has been performed through a vacuum-pressure process in the presence of a peroxide initiator, leading to the formation of a cross-linked polymer.[29]

The aim of the present paper is to report on the synthesis of end-grained wood-polyurethane composites using PEG for osmotic impregnation and 1,6-hexamethylene diisocyanate (HMDI) for reactive impregnation in bulk, i.e. in the absence of organic solvent unlike previously published data.[24] A thorough study of the relationship between molecular parameters and impregnation and grafting efficiencies has been carried out together with leaching experiences and morphological characterizations. A second paper within this series will then report on the improvement in dimensional stability of the so-obtained end-grained wood-polyurethane composites.

Experimental Part

Materials

α,ω-Dihydroxy-poly(ethylene oxide) characterized by different molar masses ($\bar{M}_n$) of 200, 400, 600 and 1 000, respectively, and HMDI were purchased from Fluka. α-Methoxy-ω-hydroxy-poly(ethylene oxide) (CH_3O-PEG-OH) with a $\bar{M}_n$ of 550 was purchased from Acros. All these reagents were used as received. End-grained poplar wood timber was cut into parallelipedic specimens $18 \times 18 \times 10$ mm^3 by using a band-saw.

Synthesis of Wood-Polyurethane Composites

End-grained poplar specimens were first immersed into a water bath heated up to 100 °C and cooled down to 20 °C. They were then transferred into a bath containing a PEG aqueous solution for 24 h at either 20 or 50 °C. After osmotic impregnation, the samples were dried overnight in a ventilated oven at 100 °C. At this stage, the residual water content (as checked by gravimetry after a further extensive drying at 100 °C under high vacuum) was estimated to be in the range of 0.3 wt.-%. The resulting PEG-impregnated wood samples were introduced into a double jacket heating reaction vessel and added with a large excess of HMDI so that they were completely immersed into the liquid. The reactive impregnation temperature was varied from 20 to 65 °C. After a reaction time of 2 h, the samples were taken off and sponged up before being cured at 100 °C in a ventilated oven for 18 h. PEG and HMDI contents were determined by gravimetry.

Characterization

Scanning electron micrographs were taken on a gold coated surface of previously washed and dried native poplar wood and wood-polymer composites by using a JEOL JSM 6100 apparatus working at 10 kV. Mercury porosimetry measurements were performed with a Carlo Erba porosimeter 2000 covering a volume range from 0 to 400 mm^3 (± 0.5) and a pressure range from 0.01 to 200 MPa ($\pm 2\%$). The samples density was determined by measuring both weight and volume. Weights were accurately determined by using a Mettler AE 200 balance after extensive drying in a ventilated oven at 100 °C while specimen dimensions were measured using a Mitutoyo digital caliper.

Results and Discussion

Synthesis by Reactive Impregnation

Osmotic Impregnation

End-grained poplar samples were first immersed into a water bath heated up to 100 °C (for 15 min) and cooled down to 20 °C. Such a pre-treatment aims at enhancing the

Table 1. Dependence of PEG molar mass on PEG content during osmotic impregnation ([PEG] = 0.5 mol · L^{-1}, at 20 °C for 24 h).

Entry	$\overline{M}_{n\,PEG}$ g · mol^{-1}	n_{PEG} mmol · g^{-1}
1	200	0.70 ± 0.20
2	400	1.00 ± 0.15
3	600	1.20 ± 0.05
4	1 000	1.32 ± 0.10

osmotic impregnation efficacy, i.e. the amount of PEG that can be incorporated into native wood.[30] Once fully swollen with water, the wood specimens were immersed into aqueous solutions of α,ω-dihydroxy-poly(ethylene oxide) with molar masses ranging from 200 to 1 000 for an initial concentration in PEG of 0.5 mol · L^{-1}, an impregnation temperature of 20 °C and an impregnation time of 24 h. Table 1 shows the PEG uptake by the end-grained poplar samples in function of PEG molar mass ($\overline{M}_{n\,PEG}$). The content in PEG (n_{PEG} expressed in mol · g^{-1}) was determined by gravimetry according to Equation (1).

$$n_{PEG} = \frac{m_{iw} - m_{nw}}{m_{nw} \times \overline{M}_{n\,PEG}} \tag{1}$$

where m_{nw} and m_{iw} denote the weights of dried native wood and dried PEG-impregnated wood, respectively.

The result was that the total amount of PEG incorporated into the wood structure increases with $\overline{M}_{n\,PEG}$. It thus attests that longer PEG chains are more effectively incorporated and trapped in the wood structure. This can be explained by the formation of more favorable hydrogen bonding interactions between the polyether chains and the hydroxyl groups of the cellulosic wood cells as $\overline{M}_{n\,PEG}$ increases. Note that extending the impregnation time up to 400 h does not significantly modify PEG uptake.

In a second series of experiments, the concentration of the PEG impregnation bath was varied from 0.25 to 0.75 mol · L^{-1} for a $\overline{M}_{n\,PEG}$ of 400. All other experimental conditions were kept unchanged. As might be expected from the osmotic pressure theory, an increase in PEG concentration leads to higher amounts of incorporated PEG. Figure 1 shows the dependence of the PEG weight fraction in the wood polymer composites ($F_{w\ PEG} = \frac{m_{iw} - m_{nw}}{m_{nw}}$ expressed in %) on the initial concentration of PEG aqueous solution. A linear relationship is obtained with a slope of 89.9 and a very good confidence (>99.9%).

Finally, the effect of the temperature on the PEG uptake has been investigated for a $\overline{M}_{n\,PEG}$ of 400, a PEG concentration in water of 0.5 mol · L^{-1} and an impregnation time of 24 h. Conducting the impregnation at a higher temperature decreases the PEG weight fraction within the composite. $F_{w\,PEG}$ reaches 48% at 20 °C while it levels off at 37% when the impregnation is carried out at 50 °C. Such a behavior might be explained by the decrease of PEG solubility in water as temperature increases. Indeed, the PEG phase diagram in water is characterized by a lower critical solubility temperature.[31] These observations prompted us to carry out further wood impregnation experiments at 20 °C.

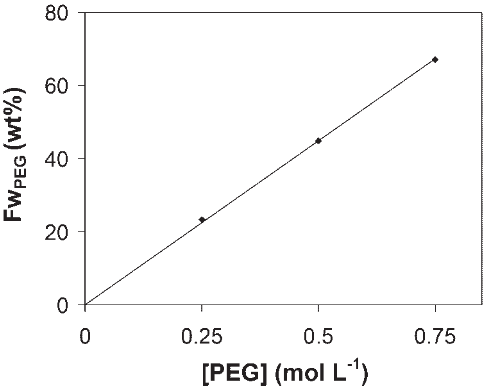


Figure 1. Influence of the initial PEG concentration on the PEG weight fraction in the wood polymer composite ($F_{w\ PEG}$) (impregnation conditions: 24 h at 20 °C with $\overline{M}_{n\,PEG} = 400$).

Reactive Impregnation

Typical PEG-impregnated wood specimens were obtained after immersion in an aqueous solution of PEG ([PEG] = 0.5 mol · L^{-1}, $\overline{M}_{n\,PEG} = 400$) at 20 °C for 24 h. They were dried in a ventilated oven at 100 °C until reaching a constant weight. Then, they were introduced in a double jacket heating reaction vessel and immersed in a large excess of HMDI at 20 °C. After immersion for 2 h, the sample surface was sponged before curing the specimens in a ventilated oven at 100 °C for 18 h. The HMDI content in mol · g^{-1} was determined by weighing the dried PEG-impregnated wood (m_{iw}) and wood-polyurethane composite (m_{WPC}) taking into account the molar mass of HMDI (MM_{HMDI}) [Equation (2)].

$$n_{HMDI} = \frac{m_{WPC} - m_{iw}}{m_{iw} \times MM_{HMDI}} \tag{2}$$

For a sake of accuracy, impregnation and curing experiments were carried out on several wood specimens (18 × 18 × 10 mm^3 in radial, tangential and longitudinal directions) cut from a same section of end-grained poplar wood (60 × 60 × 10 mm^3 in radial, tangential and longitudinal directions). A good reproducibility was obtained with values for n_{PEG} and n_{HMDI} of 1.00 ± 0.15 mmol · g^{-1} and 1.98 ± 0.25 mmol · g^{-1}, respectively. It demonstrates the reliability of the method and shows that a two-fold molar excess of HMDI is trapped into the wood structure, at least for such a PEG content. A two-fold molar excess of reactive HMDI is actually essential in order to graft PEG and/or in situ formed polyurethane chains to the lignocellulosic matrix of wood through covalent urethane linkages. It is also worth mentioning that the effect of HMDI impregnation temperature was checked as well, by increasing

Table 2. Dependence of the initial concentration of PEG on impregnated PEG and HMDI relative contents (PEG impregnation at 20 °C for 24 h and HMDI reactive impregnation at 20 °C for 2 h).

Entry	[PEG]	n_{PEG}	n_{HMDI}	n_{HMDI}/n_{PEG}	F_w
	$mol \cdot L^{-1}$	$mmol \cdot g^{-1}$	$mmol \cdot g^{-1}$		%
1	0.25	0.45	2.45	5.4	59.3
2	0.50	1.00	1.98	2.0	67.3
3	0.75	1.33	2.05	1.5	87.7

Table 3. Dependence of PEG molar mass on impregnated PEG and HMDI content ([PEG] = 0.5 mol · L^{-1}, 20 °C for 24 h; reactive impregnation at 20 °C for 2 h).

Entry	$\overline{M}_{n\,PEG}$	n_{PEG}	n_{HMDI}	n_{HMDI}/n_{PEG}
	$g \cdot mol^{-1}$	$mmol \cdot g^{-1}$	$mmol \cdot g^{-1}$	
1	400	1.00	1.98	2.0
2	1 000	1.32	2.56	1.9

the impregnation temperature from 20 to 65 °C. After 2 h at 65 °C, n_{HMDI} reaches an average value of 1.78 ± 0.25 mmol · g^{-1}. Extending the HMDI impregnation time to 7 h did not substantially enhance diisocyanate incorporation ($n_{HMDI} = 1.89 \pm 0.25$ mmol · g^{-1}). Consequently, it was decided to run all further experiments at 20 °C for 2 h. In order to investigate whether PEG content might affect HMDI uptake and subsequent reactions, PEG-impregnated wood samples were prepared by osmotic impregnation at 20 °C for 24 h, starting with various concentrations of PEG and then treated with HMDI for reactive impregnation (Table 2). As the PEG content decreased, the relative amount of HMDI increased while the polymer weight fraction in the impregnated composite (F_w) decreased. Last but not least, the effect of $\overline{M}_{n\,PEG}$ on HMDI content entrapped in the poplar wood specimens was examined (Table 3). There is no substantial increase of the relative content of impregnated HMDI when the PEG molar mass increases from 400 to 1 000. In an attempt to correlate the reactive impregnation conditions and the efficiency of the covalent grafting of PEG and/or in situ formed polyurethane chains onto the wood cell walls, Soxhlet extractions were carried out for 48 h on the WPCs using water or tetrahydrofuran (THF) as solvent. It is worth recalling that both water and THF are good solvents for PEG chains while THF is better suited to dissolve PEG-based polyurethanes. Different WPCs specimens were tested together with a PEG-impregnated wood specimen (without reactive impregnation with HMDI) and a WPC initially impregnated with monofunctional PEG chains, i.e., CH_3O-PEG-OH and HMDI. The interest of impregnating poplar wood with monohydroxyl-polyether chains relies upon the impossibility to form a polyurethane by chain extension. Rather, a simple covalent grafting of PEG chains onto the lignocellulosic cell walls can be achieved by reaction between the available hydroxyl groups and HMDI. Table 4 shows the dependence of the polymer weight fraction in composites on Soxhlet extractions. As expected, PEG is quantitatively leached out by water extraction in the absence of reaction with HMDI (entry 1, Table 4). In contrast, after reactive impregnation with HMDI, the polymer weight loss undergone by the WPC after water extraction is limited to 15.5% (entry 2, Table 4). When the same sample was further extracted with THF, a very limited weight loss (less than 1%) is recorded and more likely corresponds to the leaching of non-grafted PU chains (entry 3, Table 4). A decrease of PEG content to the benefit of HMDI content decreases the polymer weight loss from 15.5 to 5.4% (entries 2,4 and 5, Table 4). As far as $\overline{M}_{n\,PEG}$ is concerned, the polymer weight loss is enhanced when PEG molar mass increases from 400 to 1 000 (entries 2 and 6, Table 4). Substituting CH_3O-PEG-OH for PEG significantly increases the polymer weight loss up to 29.7% undergone by the WPC after water extraction even though a higher relative excess of HMDI is incorporated into the wood structure (entries 2 and 7, Table 4). All these observations are thus consistent with the beneficial effect of combining flexible α,ω-dihydroxy-poly(ethylene oxide) pre-polymers and HMDI to favor the PEG/PU grafting reactions onto cell walls and to reduce leaching of polymer chains. Furthermore, it must also be emphasized

Table 4. Dependence of reactive impregnation on polymer weight fraction in WPCs (F_w) and extraction conditions: Soxhlet extraction with water (a) or THF (b).

Entry	Polyether	$\overline{M}_{n\,PEG}$	[PEG]	n_{PEG}	n_{HMDI}	F_w before extract.	F_w after extract.	Δm[a]
		$g \cdot mol^{-1}$	$mol \cdot L^{-1}$	$mmol \cdot g^{-1}$	$mmol \cdot g^{-1}$	%	%	%
1(a)[b]	PEG	400	0.50	1.02	0.00	40.1	0.0	100.0
2(a)	PEG	400	0.50	1.00	1.98	67.3	56.9	15.5
3(b)	PEG	400	0.50	1.00	1.98	56.9	56.4	0.9
4(a)	PEG	400	0.25	0.45	2.45	59.3	56.1	5.4
5(a)	PEG	400	0.75	1.33	2.05	87.7	74.9	14.5
6(a)	PEG	1 000	0.50	1.32	2.56	143.8	114.0	20.7
7(a)	CH_3O-PEG-OH	550	0.50	0.97	2.81	92.7	65.2	29.7

[a] Δm represents the relative weight loss in polymer due to Soxhlet extraction.
[b] Impregnation of PEG without HMDI.

that the formation of allophonate bridges by reaction between urethane functions and isocyanate groups likely occurs in the prevailing experimental conditions.[32] In other words, this two-step reactive impregnation might not only favor the grafting of polyurethane chains to the lignocellulosic cell walls but also the formation of a polyurethane network directly within the wood structure as will be discussed in the next section.

Characterization

Scanning Electron Microscopy

End-grained wood can be sketched as vessels joined side by side so that a transversal cross section shows empty lumen areas separated by cell walls (Scheme 1). Both the lumen and the cell wall contain water but the poor dimensional stability of wood is known to be due to variation of the water content localized in the cell wall rather than in the lumen.[33] Indeed, no substantial shrinkage of the lumen is observed when the environmental humidity degree is reduced. Moreover, it has been demonstrated that lumen-filled wood-polymer composites expand as much as untreated wood when placed in a high humidity environment.[34] In order to determine whether polyurethane impregnated wood samples are cell wall-bulked wood-polymer composites, the microstructure of native poplar wood compared to wood-polyurethane composites before and after Soxhlet extraction (entries 2 and 3 in Table 4) was investigated by scanning electron microscopy. Figure 2 shows microphotographs of transversal cross sections as obtained from the central part of the specimens ($18 \times 18 \times 10$ mm^3 in radial, tangential and longitudinal directions) by Stanley knife cutting. It is worth mentioning that the microstructure is similar all along the 10 mm depth of the sample attesting for the homogeneity of the reactive impregnation. The average cell wall thickness (*CWT*) increases from 1.0 to 2.5 μm for untreated poplar wood and wood-polyurethane sample, respectively. After Soxhlet extraction with water, a small shrinkage of the cell wall is observed ($CWT = 1.5$ μm) while subsequent extraction with THF induces a significant swelling of the cell wall thickness ($CWT = 3.0$ μm). This can be explained by the fact that, in contrast to water, THF is capable to dissolve PEG-based polyurethane and in the present compositions to swell cell wall grafted and/or cross-linked polyurethane. It must also be emphasized that THF extraction triggers a partial lumen obstruction by a very thin film of dissolved polymer chains. This film can be formed by the 0.9 wt.-% of extracted polyurethane (entry 3, Table 4). Figure 3 shows micrographs of longitudinal sections in native end-grained poplar wood compared to wood-polyurethane composite (entry 2, Table 2) as obtained by cryogenic fracture after immersion in liquid nitrogen. As far as untreated wood is concerned (Figure 3a), the micrograph shows the inside of the vessels meaning that the fracture propagates specifically in the lumen region (localization of the fracture propagation shown by a V in Scheme 2). In contrast, the fracture of wood-polyurethane composite also

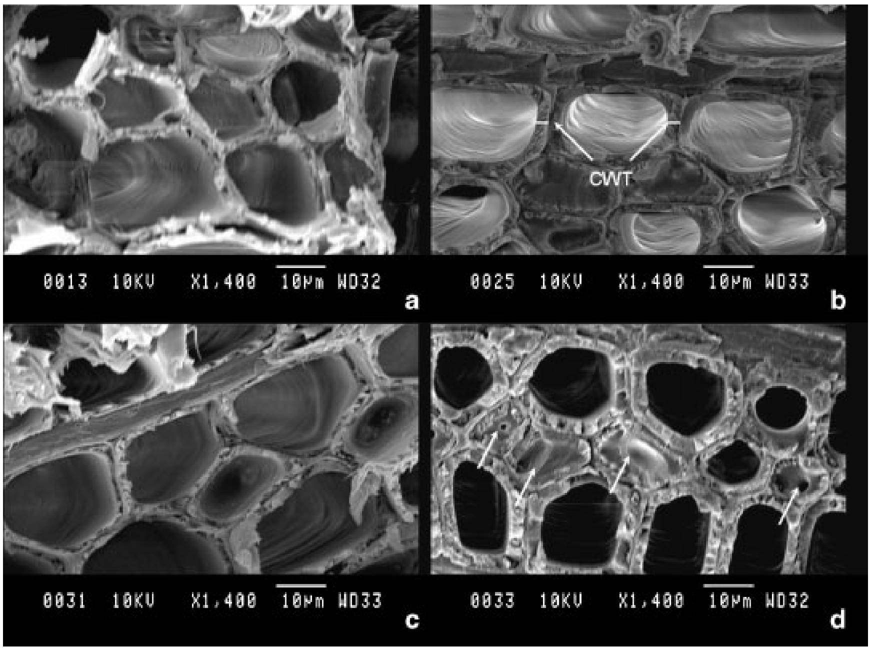


Figure 2. Scanning electron micrographs of end-grained wood transversal cross-sections: (a) untreated poplar, (b) WPC (entry 2, Table 2), (c) WPC after Soxhlet extraction with water (entry 2, Table 4) and (d) WPC after Soxhlet extractions successively with water and THF (entry 3, Table 4).

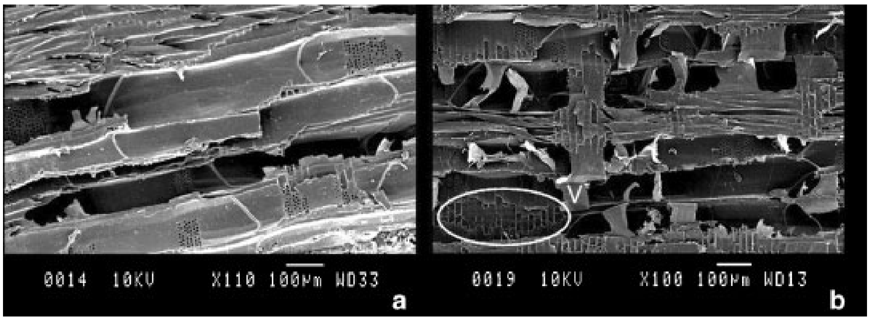


Figure 3. Scanning electron micrographs of end-grained wood longitudinal cross-sections: (a) untreated poplar wood and (b) WPC (entry 2 in Table 2).

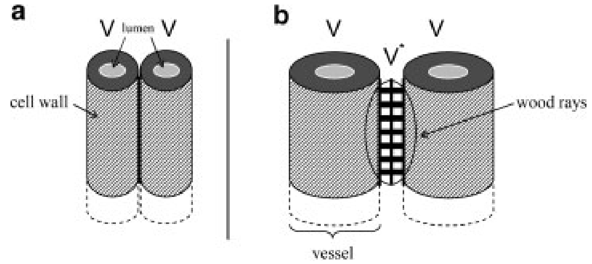
occurs in between two adjacent vessels in the region containing swollen wood rays bridging the parallel vessels (shown by V* in Scheme 2). These observations are initially consistent with the impregnation of cell wall and wood rays which are collapsed in untreated wood and expanded in wood-polyurethane composites. Interestingly, Figure 4 shows a linear relationship between the average *CWT* and polymer weight fraction in composites (entries 1–3, Table 2). Such a behavior is in agreement with cell wall-bulked wood-polymer composites in which the volume of a macroscopic sample is directly proportional to the volume of chemicals incorporated.[35]

Mercury Porosimetry

To characterize further the wood-polyurethane composites, mercury porosimetry analyses were performed. Weighing before and after measurements demonstrates that mercury penetrates the pore volume and that the material is not crushed by mercury pressure.[36] In these conditions, analyses provide reliable data on the porous volume distribution in function of pore size by using the Washburn's equation [Equation (3)].

$$p = \frac{-2\gamma \times \cos\theta}{r} \tag{3}$$

where p is the pressure required for mercury intrusion into the wood structure, r is the porous radius, γ is the mercury surface tension (480 $\text{mN} \cdot \text{m}^{-1}$) and θ is the contact angle between mercury and wood (140°). Figure 5 shows the dependence of the cumulative porous volume per weight unit on the pore size for an untreated poplar wood sample compared to a representative wood-polyurethane composite (entry 2, Table 2). First of all, it is worth noting that the total volume available for mercury is lower in the WPC sample. Both samples are characterized by two well-separated pore size distributions. The large pores (ca. 35 µm) likely correspond to the lumen while the smaller ones (ca. 0.9 µm) might reflect the size of longitudinal and radial perforations present in the vessels. The cell walls grafting and/or cross-linking polyurethane chains would thus lead to a decrease of the vessels internal volume as a result of the cell wall swelling and to a partial occlusion of the junction pores inside and between the vessels.



Scheme 2. Representation of two adjacent wood vessels in untreated wood (a) compared to WPC (b) and localization of the fracture propagation V and V*.

Density Measurements

Cell wall filled-WPCs present two major advantages compared to lumen filled composites. Indeed, they preserve the wood aspect and their density remains lower at least starting from softwood and low density hardwood such as poplar. This second advantage is a result of the relatively low weight fraction in polymer within the WPCs. The measurement of the density was carried out on both untreated wood and representative WPCs (entries 2 and 3, Table 2) after either 1) drying in a ventilated oven at 100 °C for 18 h, or 2)

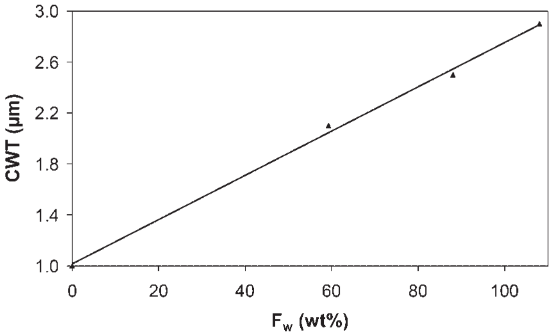


Figure 4. Effect of the on polymer weight fraction (F_w) on the cell wall thickness (CWT).

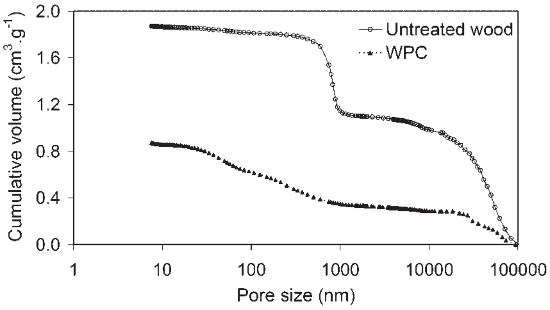


Figure 5. Relationship between the porous volume per weight unit and pores size for untreated poplar wood and WPC (entry 2, Table 2).

conditioning in 90% relative humidity for 41 h, or 3) immersion in water at 25 °C for 41 h (Table 5). It comes out that the density of a WPC containing 87.7 wt.-% of impregnated PEG-based polyurethane remains rather low and below 1 (entries 1 and 3, Table 5). Whatever the polymer weight fraction, the densities are increased by ca. 0.05 $g \cdot cm^{-3}$ when the samples are conditioned under 90% relative humidity. In contrast, a more significant difference is observed after immersion in water. Indeed, the water uptake is actually more pronounced for untreated wood than for WPCs as evidenced by the relative increase in density. Moreover, the density increase is clearly dependent on the polymer weight fraction of WPCs. Such a limited fluctuation in density observed for WPCs is expected to reflect improved dimensional stability as will be reported elsewhere.

Conclusion

This study has demonstrated the ability to prepare end-grained wood polyurethane composites according to a reliable two-step method involving the osmotic impregnation with PEG aqueous solutions, followed by the reactive impregnation with HMDI in bulk. Impregnation parameters have been tuned to reduce polymer leaching during Soxhlet extractions with both water and THF while keeping an initial polymer weight fraction in the composite close to 60–65%. Combining scanning electron microscopy and mercury porosimetry together with the covalent grafting of monohydroxyl-polyether chains/HMDI as a model system allows to demonstrate that polyurethane chains are selectively anchored to the lignocellulosic matrix of cell wall without bulking the lumen. As a result, the density of wood polyurethane composites remains low, displaying limited fluctuation with environmental conditions. The expected improvement of the dimensional stability and mechanical properties of these polyurethane-wood composites will be reported separately in a forthcoming paper.

Table 5. Density of untreated poplar wood compared to WPCs after different treatment: (1) ventilated oven at 100 °C for 18 h, (2) 90% relative humidity for 41 h and (3) water immersion for 41 h.

Entry	F_w	ρ_a	ρ_b	ρ_c
	%	$g \cdot cm^{-3}$	$g \cdot cm^{-3}$	$g \cdot cm^{-3}$
1	0.0	0.34	0.38	0.85
2	67.3	0.59	0.64	0.96
3	87.7	0.64	0.70	0.93

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