

# Ultrathin Wood Laminae—Polyvinyl Alcohol Biodegradable Composites

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Novel polyvinyl alcohol (PVOH) based biodegradable composites were prepared by a hand lay-up process using ultrathin beech laminae cut by a specialized planer machine, and the resulting materials were thermo-mechanically characterized. Density measured showed how the adopted procedure led to laminates having a high porosity degree (about 50% by volume) and an elevated wood concentration (about 80% by weight). In fact, because the wood fibers were perfectly cut (not pressed and abraded), wood porosity was partially filled by the PVOH resin, as documented by field emission scanning electron microscope (FESEM) micrographs. The occlusion of wood porosity by the PVOH matrix resulted to be beneficial for the tensile mechanical properties of the composites. In fact, quasi-static tensile tests and DMTA analysis revealed how the stiffness ( $E$ ,  $E'$ ) and strength ( $\sigma_b$ ) values of the composites both along longitudinal and transversal directions were considerably higher than those of the constituents. On the other hand, the values of the specific energy adsorbed under impact conditions by the composites samples were rather low, if compared to the neat matrix. POLYM. COMPOS., 39:1116–1124, 2018. © 2016 Society of Plastics Engineers

## INTRODUCTION

In the last years, the scientific and industrial interest toward the use of polymer matrix composites (PMCs) as replacements of more traditional structural materials, such as metals and ceramics, has been continuously increasing [1]. PMCs offer several advantages over conventional materials, such as outstanding specific mechanical properties, easy processability and elevated chemical resistance. However, the use of high strength fibers (i.e., glass, carbon and aramid) as reinforcement for conventional plastics led to several environmental concerns, and current

environmental legislation encourages manufacturers to carefully evaluate the environmental impact of their products over their whole life cycle, including recycling and final disposal [2]. It is also widely demonstrated that life cycle analysis on traditional composite materials does not yield favorable results in terms of recyclability and energy requirements of the end-of-life processes [3]. A possible solution to these environmental issues is represented by the use of natural fibers as alternatives to inorganic reinforcements [4]. In fact, they can be compounded with polymers to produce reinforced materials, retaining in the most cases the more desirable properties of conventional plastics [5–7]. However, if these fillers derive from renewable resources and can be incinerated, natural fiber-based thermoplastic composites are generally not mechanically recyclable, because the limited thermal stability of natural fillers represents a severe limit in the subsequent recycling or reprocessing steps [8].

Polyvinyl alcohol (PVOH) is the only known carbon-carbon backbone polymer that is biodegradable under both aerobic and anaerobic conditions [9]. It has been recently applied in a wide range of sectors as water-soluble biodegradable polymer and as biodegradable segment in the polymer chain, because of its high tensile strength, excellent adhesive properties, abrasion resistance, chemical resistance and gas barrier properties [10]. Therefore, PVOH is widely applied in many industrial applications, such as films, fibers, adhesives, textile sizing, emulsifiers, paper coating, etc. Furthermore, PVOH is one of the few polymers which can be prepared via non-petroleum route, i.e., by using natural gas as raw materials [11]. In a recent study, novel PVOH hydrogels with small amounts of polyvinylpyrrolidone (PVP) were synthesized by a repeated freezing-thawing method, and their effectiveness as potential articular cartilage prosthesis was assessed through fatigue tests [12]. Even if plastic items based on polyvinylalcohol are mainly obtained using casting techniques, the increasing interest in the production of PVOH films stimulated the development of

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new melt processing technologies [13]. For instance, the microstructural and thermo-mechanical behavior of novel fully biodegradable PVOH-based single-polymer composites (SPCs), prepared through a melt compounding process, was recently studied by our group [14].

Among natural reinforcements available for the production of fully biodegradable composites, wood fibers and their derivatives represent one of the most promising candidates [15]. One third of the wood is industrially used for the production of structural materials or in the paper industry, and the remaining part is utilized in the coke production or as fueling material [16]. From a chemical point of view, wood is generally composed by a combination of carbon, hydrogen and oxygen, to form cellulose (40–50 wt%), hemicellulose (20 wt%), lignin (about 35 wt%) and limited fractions of pectic substances [17].

The most important microstructural characteristics which affect the mechanical properties of wood are its anisotropy and heterogeneity. The mechanical response of wood based material strongly depends of the direction of the applied load, and it can be approximatively concluded that wood is an orthotropic material with a linear elastic behavior, at least at low deformation levels [18]. Even if the same direction is considered, the properties of wood can be influenced by the presence of nodes and defects. Furthermore, considering that under equilibrium conditions wood can generally absorb until 25–30 wt% of water, it is also clear that the mechanical performances of the wood will be strongly dependent by the environmental conditions. In particular, beech plants present a quite regular morphology of the anatomical structure. The wooden tissues are in fact described as diffuse-porous to semi-ring-porous, providing in the cross section a regular distribution of cellular lumen with very numerous solitary and clustered pores and thick-walled fibers. The large parenchymal rays generally distended along growth ring boundaries provide the typical and well known visual pattern of beech. Gum tyloses or gum inclusions potentially interacting with PVOH are extremely rare, and neither salt crystals nor extractives such as resins or lattices can occur in this wood [19].

From a technological point of view, the interest on wood reinforced composite materials was mainly related to Wood Plastic Composites (WPCs), in which short wood fibers or wood flour are compounded with thermoplastic matrices (especially polyethylene [PE], polypropylene [PP], polyvinylchloride [PVC]) [20]. They can be transformed with the traditional techniques of thermoplastics (i.e., extrusion, injection moulding), and they generally present a good resistance to corrosion. However, even by adding 70 wt% of reinforcement, the mechanical performances of these products are very far from that of the structural wood. Also the weathering effects due to the environmental conditions and to the fungal activity play a key role on the long term performances of WPCs. For instance, in a recent study of Srimalanon et al. the mechanical, physical and weathering properties and anti-

fungal efficacy of polyvinyl chloride (PVC) and wood flour/polyvinyl chloride composites (WPVC) were investigated [21]. In that work, 2-hydroxypropyl-3-piperazinyl-quinoline carboxylic acid methacrylate (HPQM) in propylene glycol was used as an anti-fungal agent.

Interestingly, less attention was devoted to the possibility of producing thin wood laminae to prepare thermo-plastic wood composites laminates. Considering that the performances of the wood are strongly influenced by the dimensions of the samples, a key point is the comprehension of the correlation with the microstructural features of the reinforcing laminae and the macroscopic properties of the resulting composites.

On the basis of the above considerations, the objective of the present paper is to evaluate the potential of novel PVOH based fully biodegradable composites, reinforced with ultrathin wood laminae. The thermo-mechanical behavior of the resulting materials will be evaluated and compared with the properties of the constituents, in order to correlate the obtained results with the microstructural features of the laminates.

## EXPERIMENTAL

### *Materials*

Polymer granules of Mowiflex TC 232, supplied by Kuraray Specialities Europe GmbH (Frankfurt, Germany), were used as PVOH matrix (density 1.28 g/cm<sup>3</sup>, melt flow index (MFI) at 190°C and 21.6 kg = 39 g/10 min). This resin is specifically designed to be processed with the techniques traditionally used for thermoplastics. The reinforcing laminates were obtained from a beech plant, whose density after conditioning at 23°C and relative humidity (RH) = 50% is about 0.73 g/cm<sup>3</sup>. This wood species was selected for the quite regular morphology of the anatomical structure; the wooden tissues are in fact described as diffuse-porous to semi-ring-porous, providing in the cross section a regular distribution of cellular lumen with very numerous solitary and clustered pores and thick-walled fibers. The large parenchymal rays generally distended along growth ring boundaries provide the typical and well known visual pattern of beech. Gum tyloses or gum inclusions potentially interacting with PVOH are extremely rare, and neither salt crystals nor extractives such as resins or lattices can occur in this wood [19].

### *Samples Preparation*

PVOH granules at a constant concentration of 16.5 wt% were dissolved in distilled water at 80°C under magnetic stirring for 2 h, and then the solution was cooled down in 1 h at 30°C, in order to favor bubble removal before pouring it in silicon molds. Neat PVOH films having a width of 10 cm and a thickness of 1.5 mm were obtained. Water removal was conducted for 48 h at room



FIG. 1. Representative image of (a) a ultrathin wood lamina (thickness = 159  $\mu\text{m}$ ) and (b) Comp-L laminate after hot pressing. [Color figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

temperature followed by a thermal treatment in an oven at 120°C for 1 h.

Ultrathin wood laminae (UWL) were prepared at the CNR Ivalsa Institute (San Michele all'Adige, Italy) cutting them from beech boards conditioned at 23°C and RH = 60%. By using a Marunaka Super Meca-s planer, supplied by Marunaka Tekkosho Inc. (Shizuoka, Japan), UWL with a width of 11 cm and a thickness of about 150  $\mu\text{m}$  were obtained (see Fig. 1a).

For as the preparation of the composite laminates is concerned, UWL were immersed in the PVOH solution, and then left to rest on an inclined (20°) Mylar plate in order to remove the resin in excess. The laminae were then manually stacked together and finally hot pressed at 120°C for 60 minutes under a pressure of 2.5 MPa, by using square Teflon plates. With this procedure, it was possible to prepare unidirectional composites with five UWL, and symmetric and balanced crossply laminates by using seven UWL (see Fig. 1b), as described in Table 1. In the following sections, the neat matrix was designated as PVOH, while the reinforcing ultrathin wood laminae

TABLE 1. Lamination sequence of the investigated composites.

Sample	Number laminae in L direction	Number laminae in T direction
Comp-L	5	0
Comp-T	0	5
Comp-LT	4	3

were indicated as UWL, unidirectional composites were indicated as Comp-L and Comp-T, while crossply laminate was denoted as Comp-LT.

### Experimental Methodologies

**Density Measurements.** Density measurements were performed in order to determine the volume and the weight fractions of the constituents in the composites. A Micro-metrics AccuPyc 1330 helium pycnometer, connected to a thermostatic bath at 25°C, was utilized. 100 repetitions were performed for each measurement. Before testing, both UWL and the relative composites were conditioned under vacuum at 70°C for 24 h. In this way, it was possible to determine the real density values of the wood laminae ( $\rho_f$ ), of the neat PVOH matrix ( $\rho_m$ ), and of the composites ( $\rho_c^*$ ).

First of all, the volume fraction of the solid component of the wood laminae (i.e., cellulose, hemicellulose and lignin, i.e.,  $V_f$ ) was determined, by using the following equations:

$$\rho_w = \rho_f V_f + \rho_v V_v \quad (1)$$

$$V_f = \frac{\rho_w - \rho_v}{\rho_f - \rho_v} \quad (2)$$

where  $\rho_w$  is the apparent density of the beech (i.e., 0.52  $\text{g}/\text{cm}^3$  from literature data [19]),  $\rho_v$  is the density of the air in the voids (1.205  $\text{kg}/\text{m}^3$  at 25°C and 1 atm), and  $V_v$  is the volume concentration of the voids. The apparent density of the composite ( $\rho_c$ ) is an unknown value, and it can be expressed in the following way:

$$\rho_c = \rho_c^* V_c^* + \rho_v V_v = \rho_c^* (1 - V_v) + \rho_v V_v \quad (3)$$

$$\rho_c^* (1 - V_v) + \rho_v V_v = \rho_f V_f + \rho_m (1 - V_v - V_f) + \rho_v V_v \quad (4)$$

where  $V_c^*$  is the volume fraction of the solid part of the composite. With this procedure, it is possible to determine the volume fraction of the voids ( $V_v$ ), and therefore the volume fraction of the matrix as  $V_m = 1 - V_f - V_v$ .

For as concerns the weight fraction of the PVOH matrix ( $W_m$ ) and of the wood ( $W_f$ ), it is possible to rely on the traditional rule of mixture of the composites to derive the following expressions [22]:

$$\rho_c = \frac{1}{W_f/\rho_f + W_m/\rho_m + W_v/\rho_v} \quad (5)$$

$$W_f = \frac{\rho_f}{\rho_c} \left( \frac{\rho_c - \rho_m}{\rho_f - \rho_m} \right) \quad (6)$$

where the weight fraction of the voids ( $W_v$ ) represents a negligible term, and  $W_m = 1 - W_f$ . It is important to underline that in *Eqs. 5, 6* the apparent density of the composite ( $\rho_c$ ) must be replaced by the real density values ( $\rho_c^*$ ), because pycnometric technique allows to measure the real density of the solid part of the composite.



**Electron Microscopy.** Field emission scanning electron microscope (FESEM) analysis was used to evaluate the morphological features of the constituents and of the composites. FESEM micrographs of cryofractured specimens were collected at different magnifications by using a Carl Zeiss AG Supra 40 microscope.

**Thermal Properties.** Differential scanning calorimetry (DSC) measurements were carried out with a Mettler DSC30 machine under a nitrogen flow of 100 ml/min. Samples were tested from 0°C to 240°C at a heating rate of 10°C/min (first heating); then cooled down from 240°C to 0°C at a rate of -10°C/min (cooling) and re-heated at the same rate from 0°C to 240°C (second heating).

Dynamic mechanical thermal analysis (DMTA) was carried out to determine the temperature dependency of the storage ( $E'$ ) and loss ( $E''$ ) moduli and of the loss tangent ( $\tan\delta$ ). DMTA tests were performed on a TA Instruments Q800 machine in tensile mode on rectangular specimens with a gage length of 11 mm. Samples were tested from -30°C to 150°C at a heating rate of 3°C/min, a frequency of 1 Hz, and a strain amplitude of 32  $\mu\text{m}$ .

**Mechanical Properties.** Quasi-static tensile tests were conducted by an Instron 4502 testing machine. The tests on the PVOH matrix were carried out on ISO 527 1BA dumbbell specimens with a gage length of 30 mm. Elastic modulus ( $E$ ) was measured at a cross-head speed of 0.25 mm/min measuring the deformation by a resistance extensometer having a gage length of 12.5 mm. A secant

TABLE 2. Results of density measurements on the prepared samples, with the weight and volume fractions of the components of Comp-L laminate.

Sample	Density [ $\text{g}/\text{cm}^3$ ]	$V_f$	$V_m$	$V_v$	$W_f$	$W_m$
PVOH	$1.28 \pm 0.01$	—	1	—	—	1
UWL	$1.48 \pm 0.01$	1	—	1	1	—
Comp-L	$1.44 \pm 0.01$	0.39	0.10	0.51	0.82	0.18

modulus between deformation levels of 0.05% and 0.25% was determined as an average values on at least five specimens. Tensile properties at break ( $\sigma_b$ ,  $\epsilon_b$ ) were determined at a testing speed of 10 mm/min, without using the extensometer. Tensile tests on wood laminae in longitudinal direction (UWL-L) and in transversal direction (UWL-T) were determined on rectangular laminae 170 mm long and 10 mm wide (the nominal lamina thickness is about 150  $\mu\text{m}$ ) at a testing speed of 5 mm/min. Sample were tested applying wood tabs on the grips, with a gage length of 140 mm. At least 5 specimens were tested for each sample. Composite materials (Comp-L, Comp-T and Comp-LT) were tested according to ASTM D3039 standard at 5 mm/min on rectangular specimens 250 mm long and 15 mm wide, applying wood tabs (the resulting gage length was 200 mm). Even in this case, 5 specimens were tested for each sample.

Tensile impact tests were carried out by a CEAST instrumented pendulum at an impact speed of 1 m/s and at an impact energy of 1.82 J. Tensile impact tests on neat

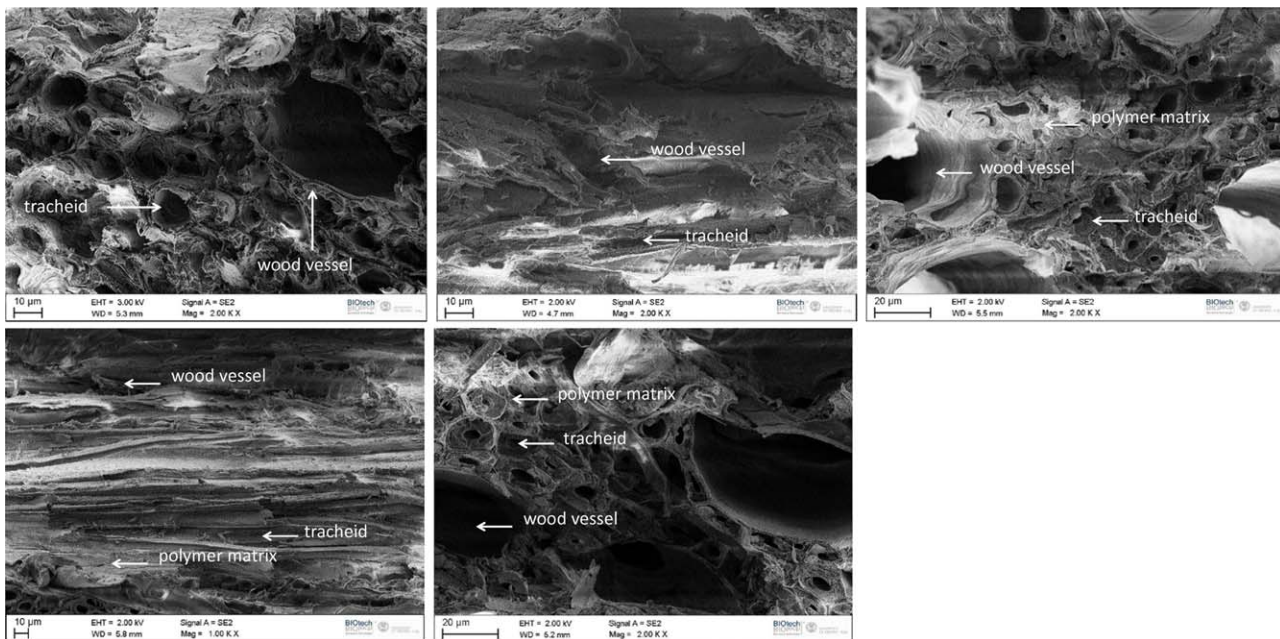


FIG. 2. FESEM micrographs of the cryofractured sections of the prepared samples. (a) ultrathin wood lamina sectioned in transversal direction, (b) ultrathin wood lamina sectioned in longitudinal direction, (c) Comp-L sample sectioned in transversal direction, (d) Comp-L sample sectioned in longitudinal direction and (e) Comp-LT sample sectioned in transversal direction.

## RESULTS AND DISCUSSION

### Density and Microstructure

In Table 2 the results of the density measurements on the prepared samples, with the weight and volume fractions of the constituents of the Comp-L laminate are summarized. It is important to underline that in the case of wood laminae a real density value was determined with pycnometric measurements because the probe gas (helium) certainly penetrates in the macroscopic pores of beech wood. The density values determined both for wood laminae and neat PVOH are very close to those reported in literature [19]. It is interesting to note that the final concentration of the polymeric matrix in the composite (i.e.,  $W_m$  or  $V_m$ ) is quite limited, and that about 50% of the composite volume is constituted by voids. This is probably due to the high wood porosity, and it is reasonable to think that part of the polymeric matrix could enter wood pores. It is also interesting to note that the weight fraction of the reinforcement (about 82%) is higher than that generally obtainable for traditional composite materials. These results were confirmed by thermogravimetric analysis (not reported for the sake of brevity).

In Fig. 2a and b FESEM micrographs of the wood laminae cut in the transversal and in the longitudinal direction are respectively reported. In the longitudinal direction it is clearly visible the typical structure of the wood, with tracheids, wood fibers and vessels, while the parenchymal cells are less clearly visible. Tracheids and wood fibers have a mean diameter of about 10  $\mu\text{m}$ , while wood vessels have a mean size of 40  $\mu\text{m}$ . In the transversal section it is detectable the presence of some tracheids in radial direction. An interesting microstructural feature is visible in Fig. 2c and d, where the micrographs of the Comp-L sample taken in transversal and in the longitudinal directions are respectively reported. It is clear that part of the PVOH matrix penetrated in the wood structure, partially filling the voids inside the wood fibers and the tracheids, while matrix interpenetration seems to not involve wood vessels. Also the radial tracheids seems to be partially filled by the resin. These micrographs can explain the high void content determined through pycnometric measurements on the composite materials (see Table 2). Also in the Comp-LT sample the penetration of

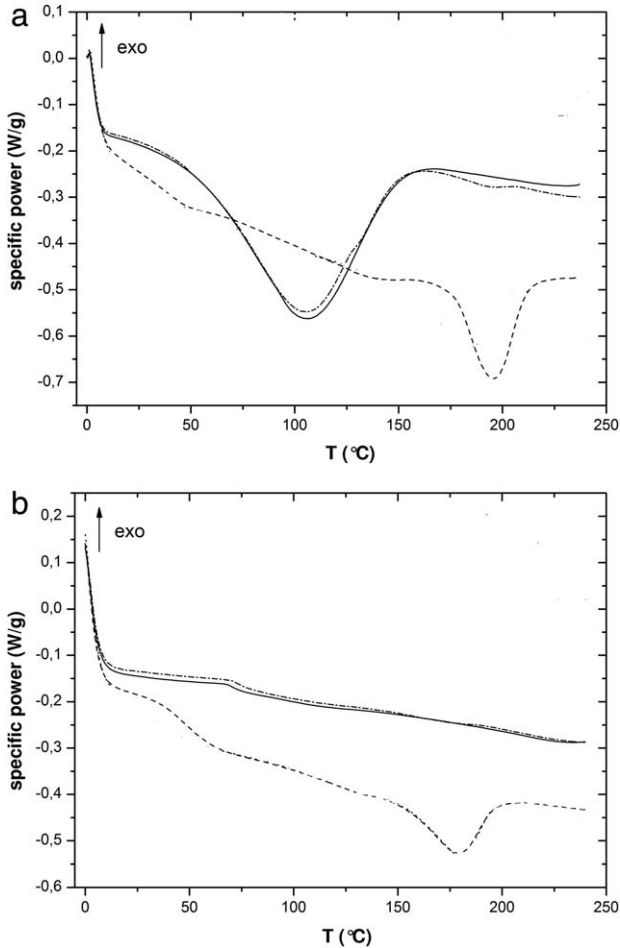


FIG. 3. DSC thermograms of the prepared samples: PVOH (dashed line), UWL (continuous line), Comp-L (dash-dotted line). (a) First heating stage, (b) second heating stage.

PVOH samples were conducted on ISO 527 1BA dumbbell specimens, while tests on Comp-L and Comp-LT samples were carried out on rectangular specimens 75-mm long and 5-mm wide, with a gage length of 40 mm. Due to the small force required to break them it was not possible to test UWL-L, UWL-T and Comp-T samples. The elastic modulus ( $E$ ), the stress ( $\sigma_i$ ), the strain ( $\varepsilon_i$ ) and the specific energy ( $U_i$ ) for fracture initiation, the specific energy for fracture propagation ( $U_p$ ), the total specific energy absorbed ( $U_{TOT}$ ), and the ductility index (i.e., the ratio between  $U_p$  and  $U_i$ ) were determined.

TABLE 3. Results of DSC measurements on the prepared samples.

Sample	First heating				Second heating			
	$T_g$ (°C)	$T_m$ (°C)	$\chi_c$ (%)	Water content (%)	$T_g$ (°C)	$T_m$ (°C)	$\chi_c$ (%)	Water content (%)
PVOH	46	192	19,0	—	38	177	15	—
UWL	—	—	—	5.3	69	—	—	—
Comp-L	—	192 <sup>a</sup>	—	4.7	71	177 <sup>a</sup>	—	—

<sup>a</sup>Melting temperature of the PVOH matrix.

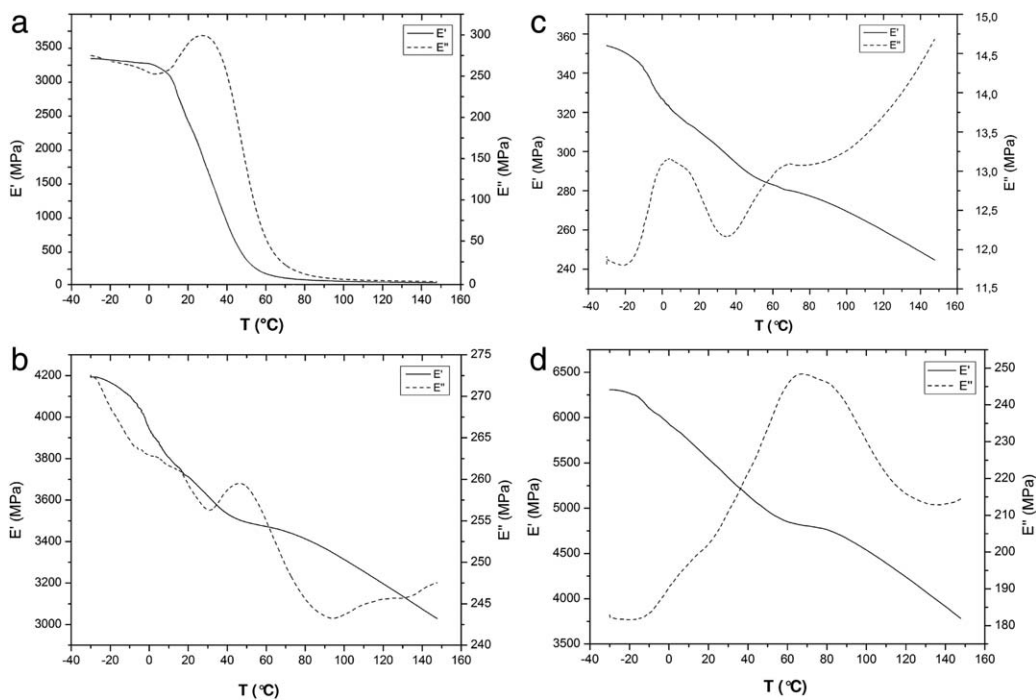


FIG. 4. DMTA thermograms with storage ( $E'$ ) and loss ( $E''$ ) moduli as a function of temperature for (a) PVOH, (b) UWL-L, (c) UWL-T and (d) Comp-LT samples.

the PVOH matrix inside the wood porosity is clear, and the filling degree seems to be similar to that observed for Comp-L specimens (see Fig. 2e). According to the micrographs, it appears that the greatest part of the PVOH matrix penetrated the wood porosity, and only a small fraction of the polymer remained in the interlayer region. It is evident that such a peculiar microstructure can strongly influence the mechanical behavior of the resulting composites.

### Thermal Properties

In Fig. 3a and b DSC thermograms of the prepared samples during the first and the second heating stages are respectively reported, while the most important results are summarized in Table 3. From the first DSC scan, it is clear that the neat PVOH matrix shows a melting temperature ( $T_m$ ) of 192°C and a glass transition temperature ( $T_g$ ) of 46°C, while no thermal signals around 100°C due to water evaporation were detected. This means all the

water loss at 100°C detected for the Comp-L sample is due to the water content in the wood reinforcement. As it could be expected, the measured water content in the Comp-L is slightly lower than that detected in the reinforcement. For as concerns the thermal properties of the prepared samples in the second DSC scan, an evident decrease of both the  $T_m$  and  $T_g$  values can be noticed. This is probably due to the fact that during the cooling stage less homogeneous crystals with lower size nucleate. It is also interesting to note that in the second DSC scan a thermal transition around 70°C is detectable in both the neat wood and the composite samples.

Even if the values of the thermal transitions of the lignin are still debated in literature because they are strongly dependent on the adopted techniques and on the testing time scale [23], this signal is called  $\alpha_1$  transition, and can be associated to the glass transition temperature of the lignin component in the wood. In fact, some studies by differential thermal analysis (DTA) on eucalypt and pine samples conducted by Irvine showed that the glass transition of lignin in water-saturated wood occurred over the approximate temperature interval 60-90°C [24].

In Fig. 4a–d the DMTA thermograms of the neat PVOH, of the wood reinforcement and of the prepared composites are reported, while the most important results are collected in Table 4. The  $T_g$  value detected for the neat resin is similar to that determined in DSC tests, while wood samples show an  $\alpha_2$  transition at the temperature  $T_I$ , followed by an  $\alpha_1$  transition at a temperature  $T_{II}$ . As reported in literature [23],  $\alpha_2$  transition is due to a thermal transition in the hemicellulose, while  $\alpha_1$  is a

TABLE 4. Results of DMTA measurements on the prepared samples.

Sample	$E'_{25}$ (MPa)	$E''_{25}$ (MPa)	$T_g$ (°C)	$T_I$ (°C)	$T_{II}$ (°C)
PVOH	2023	298	52	—	—
UWL-L	3668	257	49	19	49
UWL-T	306	12	67	14	67
Comp-L	9675	249	92	—	92
Comp-T	1688	123	124	30	124
Comp-LT	5445	205	83	67	83

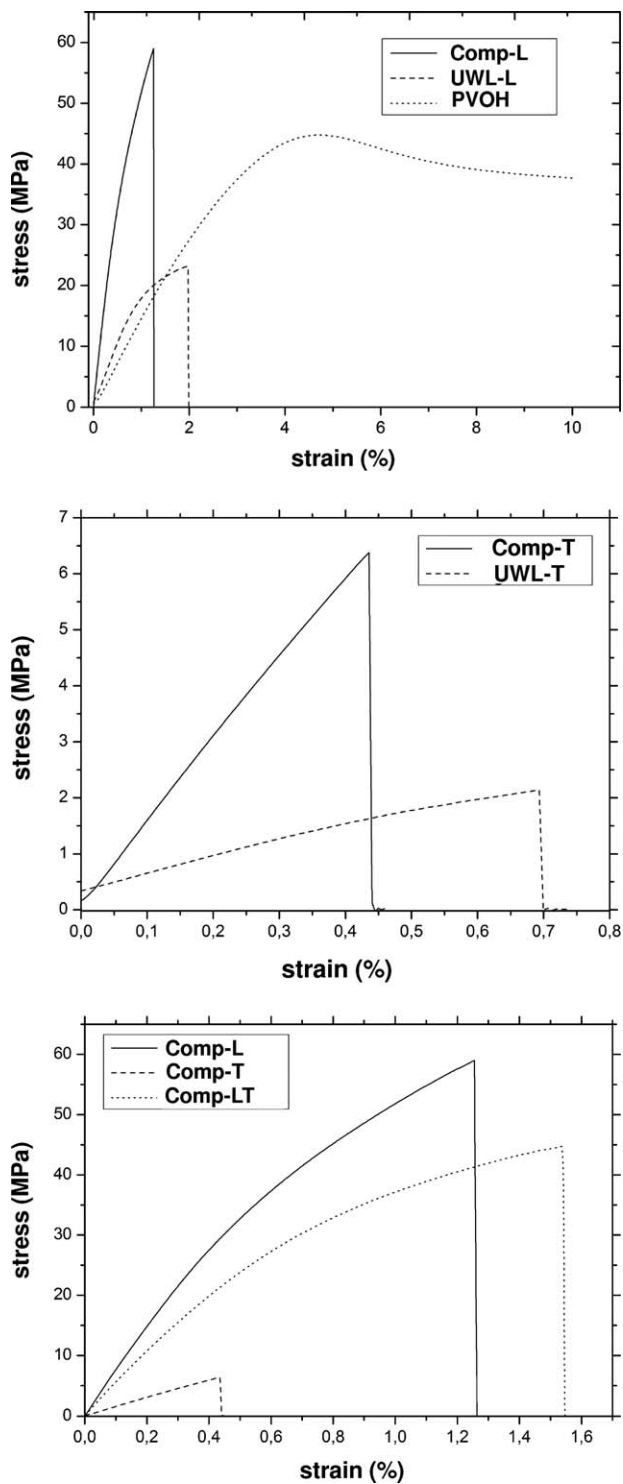


FIG. 5. Representative stress–strain curves from quasi-static tensile tests of the prepared samples. (a) Comparison between the neat PVOH matrix and the longitudinal properties of the UWL and the composites, (b) comparison between the transversal properties of UWL and the composites, (c) comparison between the properties of the laminates.

thermal transition of the lignin, and it is generally considered as the glass transition of the wood. Also in the composite samples both these transitions are visible, but for these materials they seem to be shifted at higher temperatures. It is possible that the thermal treatment at which

TABLE 5. Results of quasi-static tensile tests on the prepared samples.

Sample	$E$ (MPa)	$\sigma_b$ (MPa)	$\epsilon_b$ (%)
PVOH	$1009 \pm 133$	$49.0 \pm 10.0$	$214.0 \pm 90.0$
UWL-L	$2214 \pm 477$	$25.0 \pm 5.0$	$2.2 \pm 0.4$
UWL-T	$320 \pm 36$	$2.0 \pm 0.3$	$0.6 \pm 0.1$
Comp-L	$7567 \pm 582$	$60.0 \pm 6.0$	$1.2 \pm 0.2$
Comp-T	$1517 \pm 263$	$5.9 \pm 2.0$	$0.4 \pm 0.1$
Comp-LT	$5179 \pm 631$	$45.0 \pm 10.0$	$1.6 \pm 0.4$

the composites are subjected during the manufacturing process could affect the transition temperatures of the reinforcement. However, further studies will be required to have a deeper comprehension of this aspect. But what is interesting to note is that the  $E'$  values of the composite samples in the longitudinal direction are noticeably higher than those detected both for the reinforcement and for the wood (see Table 4). This is probably due to the fact that the greatest part of the matrix was entrapped in the wood porosity (see Fig. 2). It is therefore reasonable to think that the real reinforcing capability of the wood laminae with a partially occluded porosity is completely different from that of the neat wood laminae.

### Mechanical Properties

In Fig. 5a–c representative stress–strain curves from quasi-static tensile tests of the prepared samples are reported, while the results of the most important mechanical properties are summarized in Table 5. The tensile properties of the neat resin are very close to those reported in literature for these materials [25]. On the other hand, it is clear that the measured stiffness and strength values of the wood thin laminae are considerably lower than those reported for bulk wood (see Fig. 5a). In fact, a flexural modulus of 14 GPa and an ultimate flexural stress of 120 MPa is reported in the literature for massive beech [19]. This discrepancy is probably due to the fact that cutting

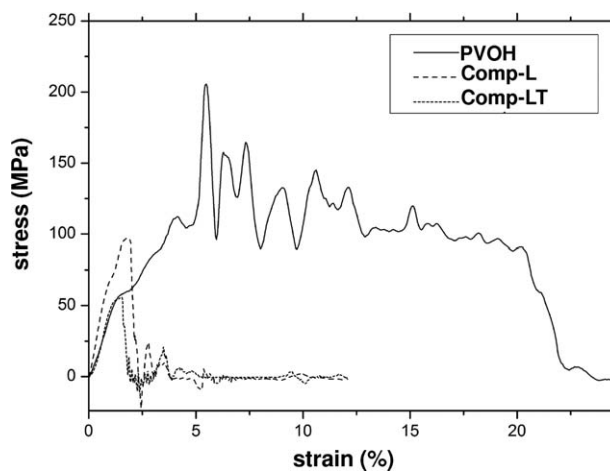


FIG. 6. Representative stress–strain curves from tensile impact tests on the investigated samples.



TABLE 6. Results of tensile impact tests on the prepared samples.

Sample	$E$ (MPa)	$\sigma_i$ (MPa)	$\varepsilon_i$ (%)	$U_i$ (J/mm <sup>2</sup> )	$U_p$ (J/mm <sup>2</sup> )	$U_{tot}$ (J/mm <sup>2</sup> )	ID <sup>a</sup>
PVOH	4964	191 ± 13	5.54 ± 0.44	0.130 ± 0.020	0.430 ± 0.100	0.560 ± 0.120	3.30 ± 0.57
Comp-L	8100	102 ± 9	1.97 ± 0.27	0.044 ± 0.011	0.008 ± 0.002	0.052 ± 0.013	0.18 ± 0.05
Comp-LT	6500	55 ± 15	1.51 ± 0.31	0.018 ± 0.007	0.004 ± 0.002	0.023 ± 0.009	0.24 ± 0.14

<sup>a</sup>ID: ductility index =  $U_p/U_i$ .

ultrathin wood sheets implies that the original cellular morphology of the wood is largely destroyed, and the stiffness of the pristine bulk material is completely compromised. The same situation can be found if the transversal properties of the wood are considered (Fig. 5b), and it is also evident that the properties of the cross-ply laminae are intermediate to those of the Comp-L and Comp-T samples. The obtained results are completely opposite to those predictable by using the rule of mixture traditionally used to predict the elastic constants of composite materials. According to FESEM micrographs, it is evident that the matrix interpenetration within wood laminae induces the occlusion of the wood porosity. In these conditions, the loss of the mechanical properties of the original reinforcing phase due to the ultrathin cut is partially recovered by the void filling performed by the PVOH resin.

Finally, tensile impact tests were carried out, in order to evaluate the resistance of the prepared composites under impact loadings. Unfortunately, it was not possible to test wood laminae, because of their intrinsic brittleness. In Fig. 6 representative stress–strain curves from tensile impact tests on the prepared samples are shown, while the most important results are summarized in Table 6. It is well known that the impact properties of the PVOH matrix are strongly affected by the testing speed. Therefore, both the elastic modulus and the ultimate strength are considerably higher than that measured in quasi-static conditions, while the ultimate stress is considerably reduced. In the case of the composites, the increase of the testing speed leads to a slight enhancement of the materials stiffness and strength, accompanied by an heavy reduction of the ultimate strain. However, comparing the values of the specific energy adsorbed and the ductility index values it is clear that the impact resistance of the prepared composites is rather low.

## CONCLUSIONS

Ultrathin beech laminae were cut through an innovative liner and used to prepare fully biodegradable laminates with a PVOH matrix. Density measured indicated that the prepared composites are characterized by a very high porosity and by an elevated reinforcement weight concentration. Interestingly, the resulting materials had a peculiar microstructure, in which the original porosity of the wood laminae are almost entirely occluded by the polymer matrix. The obtained microstructure strongly affects the thermo-mechanical behavior of the composites.

Even if the ultrathin laminae manifest mechanical properties lower than that of the corresponding massive wood, the occlusion of macroscopic porosity caused by matrix penetration led to fully biodegradable composites having stiffness and strength values considerably higher than those of their constituents.

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## ABBREVIATIONS

DMTA	Dynamic mechanical thermal analysis
DSC	Differential scanning calorimetry
FESEM	Field emission scanning electron microscope
MFI	Melt flow index
PE	Polyethylene
PP	Polypropylene
PVC	Polyvinylchloride
PVOH	polyvinyl alcohol
PVP	Polyvinylpyrrolidone
RH	Relative humidity
UWL	Ultrathin wood laminae
WPVC	Wood flour/polyvinyl chloride composites

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