Poly(lactide acid) Composites Reinforced with Fibers Obtained from Different Tissue Types of *Picea sitchensis*

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ABSTRACT: Wood fibers vary in their properties across species, across trees of the same species, and within single trees. This work takes advantage of wood fibers reinforcing poly(lactic acid) composites that originate from different tissue types of the species Sitka spruce (*Picea sitchensis*). Fibers were prepared with high temperature thermo-mechanical processing (TMP) from juvenile, mature, and compression wood tissues of Sitka spruce. Composites were made by solution casting with subsequent hot-pressing. Thermal as well as mechanical properties were determined using differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), and tensile testing. The obtained results showed that the chemical and physical properties of different tissue-type Sitka spruce fibers have significant effects on the thermal and mechanical properties of the Polylactic acid (PLA)/Sitka fiber composites. To increase interfacial compatibility between the hydrophilic fibers and the hydrophobic polymer matrix, the fibers were treated with vinyltrimethoxysilane (VTMO), while PLA was modified with 4,4-methylene diphenyl diisocyanate (MDI). It was found that PLA/Sitka composites treated with VTMO and MDI exhibited improved thermal and mechanical properties, compared to the unmodified control. The work also demonstrates that there is potential to improve biobased composites by utilizing the natural variability of wood fibers.
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Key words: biopolymers; composites; mechanical properties; thermal properties; Sitka spruce [*Picea sitchensis* (Bong.) Carrière]

INTRODUCTION

During recent years, intensive research has been focusing on the development of biobased and biodegradable plastics with the intention to reduce environmental pollution and to replace petroleum-based plastics. Polylactic acid (PLA) is biodegradable hydrolysable aliphatic semi-crystalline polyester produced through direct condensation of its monomer, lactic acid, followed by a ring opening polymerization of the cyclic lactide dimmer. Lactic acid can be obtained from renewable resources such as saccharide-based materials.[1–3] PLA shows stiffness and strength properties comparable to petroleum-based plastics and can be processed by standard methods such as extrusion, injection molding, thermoforming, or compression molding.[4] Further, PLA is a readily compostable and degradable thermoplastic polymer. Despite these promising properties, its applicability is restricted by high production costs, brittleness, and a low softening temperature.[5] Brittleness can be lowered through incorporation of plasticizers,[6] while production costs can be reduced, and the mechanical performance of the material modified by the addition of various fillers. The use of renewable and biodegradable fillers such as starch, cellulose, kenaf, hemp, and wood fibers has been investigated intensively during the past years.[5,7–12]

Wood fibers attracted attention as fillers mainly in polyolefins in the first place because of their

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abundance, renewability, nonabrasiveness, low density, and low price. The use of wood fibers lowers production costs and has the potential to positively modify mechanical properties. However, there are drawbacks such as the high variability of the physical fiber properties as well as their low compatibility with hydrophobic thermoplastic polymers. Numerous coupling agents have been investigated to increase the interfacial compatibility between the hydrophilic fillers and the hydrophobic polymer matrix.[6,13–16] Pilla et al.[16] reported improved mechanical properties of PLA-recycled wood fiber composites with the fibers were treated with 0.5 wt % silane. Alternatively, methylenediphenyl diisocynate (MDI) was successfully as coupling agent to improve the interfacial interaction between the hydrophobic PLA matrix and the hydrophilic filler.[17–20] In addition, the increase of PLA hydrophilicity by chemical modification may promote biodegradation rate.[21]

As chemical modification trials of wood fibers have been frequently applied, no research was done so far on utilizing the natural variability of wood fibers for biocomposites. There are published data on the influence of different wood species on the physical properties of plastic (PVC)/wood-flour composites has been published.[22,23] Major factors influencing the physical properties of composite were reported to be the surface roughness, surface chemistry, and particle size. Although statistical significant differences were found between composites made from wood flours of different species, these influence was relatively small.

Wood fibers vary in their properties across species, across trees of the same species, and within single trees. Variations of the fiber properties with cambial age are well documented.[24–27] This knowledge is exploited in the pulp and paper industry where top logs (juvenile wood) and chips from saw milling (mature wood) are separated to adjust paper quality. Juvenile wood develops in early stages of tree growth. Cells in juvenile wood are shorter and have a smaller cell diameter as well as larger microfibril angles (up to 55°) as compared to mature wood. Juvenile wood has a lower density and strength than mature wood; it contains less cellulose, more hemicelluloses (in particular arabinoxylan), and also more lignin. Trees with normal wood grow form juvenile and mature wood, because it is purely a matter of the age. Reaction wood, as another type of wood tissue, is formed when a tree is forced out of its normal, straight growth to compensate for the abnormal growing conditions.[28,29] In softwoods, irregular cells develop on the underside of a stem or branch and are referred to as compression wood. This special type of reaction wood contains more lignin, less cellulose, and less galactoglucomannan compared to normal wood. Furthermore, β-1,3-linked glucan (callose) and β-1,4-linked galactan are also present in compression wood. The microfibril angle in the modified secondary cell wall layer of compression wood is high (>45°). The rounded and thick-walled compression wood fibers (tracheids) are 10–40% shorter than normal fibers. Compression wood is less stiff than normal wood and exhibits a higher strain at breakage.

The objective of this work was to assess the properties of PLA composites reinforced with fibers obtained from different wood tissue types of a Sitka spruce [lat. *Picea sitchensis* (Bong.) Carrière]. We hypothesize that (1) there is potential to optimize composites properties by utilizing the natural variability of fibers that originate from Sitka spruce, and (2) there is additional potential to improve property profiles through interaction between wood fibers coming from different tissue types and chemical fiber modification, i.e., silane and 4,4-methylene diphenyl diisocyanate treatment. There are no previously published reports on the effect of different wood fiber types of one tree species used with PLA composites.

EXPERIMENTAL PART

Materials

PLA 7000D pellets received from NatureWorks LLC (Minnetonka, MN), were used as matrix material. The PLA had a density of 1.24 g/cm^3. Wood fibers were prepared from a 36-year-old Sitka spruce [*P. sitchensis* (Bong.) Carrière] tree grown at Kershope (Northumbria, UK). Juvenile wood (JW), mature wood (MW), and severe compression wood (CW) were identified and isolated from the tree. The material was chipped using a hydraulic guillotine. Chips were defibrillated under mild conditions after saturated steam cooking for 4 min with 0.32 MPa pressure at 135.7°C, followed by 30 s mechanical defibrillation. Pulps were then refined at four refiner-plate distances (2 mm, 0.8 mm, 0.3 mm, 0.12 mm) and sorted through a 0.15 mm slit sieve. Centrifuged pulps at 30–40% moisture content were stored frozen until further processing. Splinter content was highest in JW (Table I). Vinyltrimethoxysilane (VTMO) used for fiber modification was obtained from Fluorochem (Derbyshire, UK), and 4,4-methylene diphenyl diisocyanate (MDI) was obtained from Sigma-Aldrich (Germany).

Fiber characterization

Extractive content was determined according to Tappi standard T264 om-88. The carbohydrate composition of the pulps was determined after Sinner et al.[30] and Sinner and Puls[31] applying a two-step hydrolysis with H_2SO_4. Subsequently, the monosaccharides were determined by borate complex anion exchange chromatography. The results were not

TABLE I
Designation of Sitka Spruce Fibers

Sitka spruce fibers	Source of fiber	Cambial age (Years)	Splinter content (%)
JW	Juvenile wood	<9	25.6
MW	Mature wood	>20	9.3
CW	Compression wood	10–15	18.0

corrected for sugar losses and water addition during hydrolysis. The hydrolysis residue was gravimetrically determined and denoted as lignin content analogous to the Klason method.

The fiber length was determined on a ZEISS Axioplan 2 optical microscope using the publicly available Scion Image software.[32] Averaged values were based on measurements of 50 complete, unbeaten fibers. Average microfibril angles (MFA) of JW, MW, and CW were measured on a representative radial profile (2 mm tangentially) by wide-angle X-ray scattering (WAXS). The diffraction patterns were obtained on a Rigaku R-AXIS RAPID image-plate diffractometer equipped with Cu radiation using a 0.8 mm collimator. Measurements were done at ambient temperature and relative humidity with the radiation passing through the sample in tangential direction. MFA was calculated according to the variance approach.[33]

Color of the Sitka spruce fibers was characterized using a Konica Minolta colorimeter calibrated to a white standard. The color parameters L^* , a^* , and b^* were determined by the CIELAB method,[34,35] where L^* indicates lightness, and a^* and b^* the chromatic coordinates on green–red and blue–yellow axes, respectively. Additionally, angle (h) and color saturation (C^*) were determined.

Fiber treatment

The mass of 0.3 g Sitka spruce fibers were stirred in distilled water for 8 h at room temperature. Fibers were sequentially dehydrated in 15 mL water-methanol (40/60 w/w) followed by pure methanol for 8 h each. For the following silane treatment, the 0.3 g of Sitka spruce fibers were stirred in 15 mL methanol with 0.5 wt % vinyltrimethoxysilane (weight percentage relative to the fiber dry mass) for 4 h. A few drops of acetic acid were added to adjust the mixture to pH 4. Weight percentage gain (WPG) was calculated to indicate the degree of chemical modification of the Sitka spruce fibers:

$$\mathrm{WPG} = \frac{W_2 - W_1}{W_1} \cdot 100[\%] \quad (1)$$

where, W_1 is the weight of the dry sample prior to modification, and W_2 the post modification weight.

Preparation of PLA/Sitka composites

Neat PLA and PLA/MDI were processed according to Li and Yang to prepare PLA/Sitka composites (detailed compositions are listed in Table II).[21] After complete dissolution of 1.2 g PLA in 50 mL chloroform, 0.3 g of wood fibers suspended in 15 mL methanol were added and stirred for 2 h. Mixtures were then casted on Teflon dishes and dried at room temperature for 1 day followed by 2 days at 40°C in vacuum. The obtained films were disintegrated into small flakes and hot pressed at 160°C for 2 min at a pressure of 10 MPa. Films were stored for 3 weeks at standard conditions (23 °C, 50% RH) prior to testing.

Differential scanning calorimetry

Thermal behavior of PLA and PLA/Sitka composites was characterized by differential scanning calorimeter (DSC 200 F3, Netzsch). Indium was used for calibration. Data were collected by heating from 30 to 200°C at a constant heating rate of 10°C/min under a constant nitrogen flow of 60 mL/min. Samples with a weight of ~ 10 mg were placed in aluminum pans. Values for glass transition temperatures, fusion enthalpies, and melting temperatures were

TABLE II
Composition of the PLA/Sitka Fiber Composites

Sample	PLA (wt %)	MDI/PLA in ratio 0.25% (wt %)	Sitka fibers (wt %)			Silane treatment of fibers
			JW	MW	CW	
PLA	100	–	–	–	–	–
PLA/JW	80	–	20	–	–	–
PLA/MW	80	–	–	20	–	–
PLA/CW	80	–	–	–	20	–
PLA/JW_silane	80	–	20	–	–	Yes
PLA/MW_silane	80	–	–	20	–	Yes
PLA/CW_silane	80	–	–	–	20	Yes
PLA_MDI/JW	–	80	20	–	–	–
PLA_MDI/MW	–	80	–	20	–	–
PLA_MDI/CW	–	80	–	–	20	–

TABLE III
Physical Properties and Color Parameters of Sitka Spruce Fibers

Sitka fibers	Average fiber length (mm)	Density (kg/dm^3)	Microfibril angle (°)	L^*	a	b	C^*	h
JW	2.1	0.361 (0.025)	17.8 (1.3)	67.86	2.73	14.71	13.98	78.73
MW	2.4	0.550 (0.075)	12.9 (0.2)	68.77	3.43	16.07	16.44	77.95
CW	1.7	0.475 (0.039)	33.1 (4.7)	62.04	6.66	22.59	23.55	73.58

Standard deviation in parentheses.

evaluated. Crystallinity was estimated following the equation,

$$Xc(\%) = \frac{\Delta H_m}{\Delta H_m^0} \times \frac{100}{w} \quad (2)$$

where, ΔH_m^0 is the enthalpy of melting for 100% crystalline PLA being equal to 93.7 J/g,[36] ΔH_m is the enthalpy for melting of the measured sample, and w is the PLA weight fraction of the measured sample.

Tensile testing

Tensile strength, elongation at break, and Young's modulus of the samples were determined on a 100 N Zwick, Type BZ1, universal testing machine. The rectangular films were 10 mm wide and a 25 mm grip clearance was used. The crosshead speed was 2 mm/min. All mechanical parameters were derived by averaging five experimental runs.

Gel content

The gel content of the composites was determined indirectly through xylene extraction at 110°C for 12 h. After xylene extraction, the samples were filtered, dried to constant weight, and re-weighed. The gel content (GC) of the samples was determined and calculated according to the following equation.

$$\mathrm{GC}(\%) = 100 - \left(\frac{\mathrm{W}_1 - \mathrm{W}_2}{\mathrm{W}_1} \times \frac{100}{\mathrm{w}}\right) \quad (3)$$

where, W_1 is the weight of the dry sample prior to xylene extraction, W_2 the dry sample weight after xylene extraction, and w is weight fraction of PLA in the sample.

Dynamic mechanical properties

The viscoelastic properties of neat PLA and the PLA/Sitka films including the storage modulus (E') as well as the mechanical loss factor ($\mathrm{Tan}\delta = E''/E'$) were determined using the dynamic mechanical analysis (DMA; 242 C, Netzsch) in tensile mode with strips having 10 × 6 × 0.18 mm cut from the films. Temperature ranged from −10°C to +100 °C, and oscillation frequency was kept at 1 Hz; the heating rate was 3°C/min.

RESULTS AND DISCUSSION

Sitka spruce fiber properties

Compression wood (CW) was easily defibrillated under the used mild thermo-mechanical pulping conditions. This was not the case for juvenile wood (JW), which did not readily imbibe. Reduced permeability of Sitka spruce heartwood, which contains also juvenile wood, is well documented.[37,38] Splinter content after refining for mature wood (MW), CW and JW was 9.3%, 18%, and 25.6 %, respectively (Table I). Physical properties of Sitka fibers and their color parameters are shown in Table III. Sitka spruce fibers originating from MW exhibited the highest density and the smallest microfibril angle (MFA) and the longest fibers. It is known that a larger MFA is essential for the pliability of young trees; MFA is also higher in CW. MFA in compression wood was over 33°, which was twice the value measured in MW. Fibers differed also with respect to color (Table III). Fibers originating from MW and JW woods were brighter and more yellow, while fibers from CW were darker and reddish. The chemical composition of the Sitka spruce fibers is presented in Table IV. Fibers originating from CW had the highest

TABLE IV
Chemical Composition of Sitka Spruce Fibers

Sitka spruce fiber type			
Chemical content (%)	JW	MW	CW
Extractives[a]	3.1	2.0	2.8
Lignin[b]	28.2	26.6	37.8
Xylose[b]	4.9	4.6	4.6
Glucose[b]	49.9	53.9	39.7
Mannose[b]	12.1	12.6	7.0
Galactose[b]	1.2	1.0	6.5
Arabinose[b]	0.7	0.7	0.5
Ramnose[b]	0.1	–	–
4-O- Methyl[b]	0.6	0.5	0.5

[a] Percentage based on weight of the unextracted Sitka fibers.
[b] Percentage based on weight of the extractive-free Sitka fibers.

lignin and galactose content in conjunction with the lowest glucose, mannose, and arabinose content. Data for CW were in accordance to literature.[29] Differences in chemical composition between JW and MW fibers were less pronounced, though significant. JW fibers exhibited higher xylose and lignin contents compared to those from MW, which was also in accordance to literature.[27,29,39]

Vinyltrimethoxysilane (VTMO) has been used to modify the hydrophilic character of the Sitka spruce fibers. Weight percentage gain (WPG) after silane treatment of the Sitka spruce fibers was 12.01% for JW fibers, 13.55% for MW fibers, and 7.46% for CW fibers. Lower WPG of CW in comparison with those of JW and MW might be explained by the fact that CW has thicker cell walls and fewer pits, which decreased accessibility and surface area and therefore reduced uptake of the silane coupling agent. The lower polysaccharide content of CW cell walls has also resulted in a lower amount of hydroxyl groups with allowed less silicate ester bonds to be available for the silane coupling agent.[40,41]

Thermal properties

DSC heating thermograms of PLA and PLA/Sitka composites recorded between 30 and 200°C are seen in Figures 1–3. Thermal properties such as glass transition temperature (T_g), melting enthalpy (ΔH_m), melting temperature (T_m), and degree of crystallinity (X_c) obtained from the DSC analysis are summarized in Table V. Pure PLA was characterized by a T_g of 46°C, a T_m of 150°C, and a crystallinity X_c of 18.2%. The 20 wt % addition of untreated Sitka spruce fibers raised T_g to 52–54°C, and X_c to 25.0–28.7% depending on the fiber type (JW, MW, CW). T_m did not change. The shift to a higher T_g could be explained by the restricted mobility of PLA chains due to the presence of reinforcing wood fibers and the increased crystallinity of the PLA. The observation that Sitka spruce fibers acted as nucleating agent and therefore has raised the crystallinity of the PLA matrix is in accordance with literature.[16,42] The PLA/JW and PLA/CW composites exhibited a slightly higher crystallinity than the PLA/MW composite. The surface characteristics of the fibers have most likely influenced their capability of acting as a nucleation point for the crystallization of the PLA matrix. The precipitation of hydrophobic extractives onto TMP fiber surfaces during processing has been reported.[43]

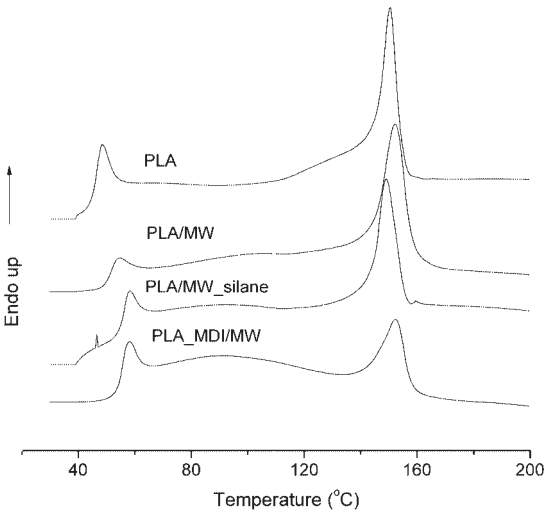

Figure 2 DSC heating thermograms for neat PLA and PLA/Sitka fiber composites made from mature wood (20 wt % fiber content).

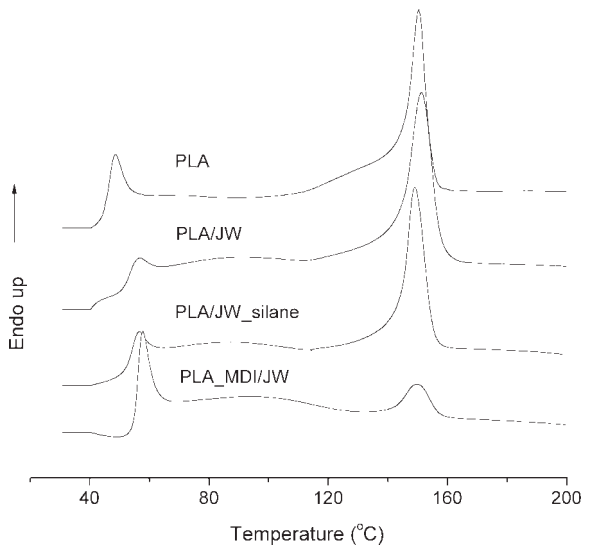

Figure 1 DSC heating thermograms for neat PLA and PLA/Sitka fiber composites made from juvenile wood (20 wt % fiber content).

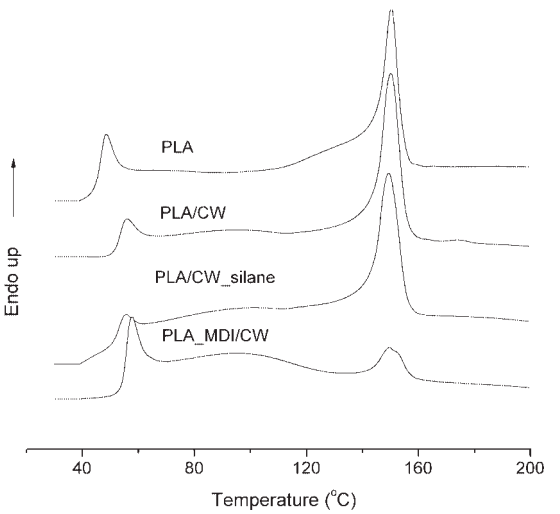

Figure 3 DSC heating thermograms for neat PLA and PLA/Sitka fiber composites made from compression wood (20 wt % fiber content).

TABLE V
Thermal Properties of Neat PLA and PLA/Sitka Fiber Composites

Sample	T_g (°C)	ΔH_m (J/g)	T_m (°C)	X_c (%)
PLA	46	17.1	150	18.2
PLA/JW	54	21.5	151	28.7
PLA/MW	52	18.7	150	25
PLA/CW	53	20.9	150	27.7
PLA/JW_silane	54	17.3	149	23.1
PLA/MW_silane	56	14.8	149	19.7
PLA/CW_silane	53	19.0	150	25.4
PLA_MDI/JW	55	4.4	150	6.0
PLA_MDI/MW	55	10.3	152	13.8
PLA_MDI/CW	55	4.8	150	6.4

From the data in Table V, it is evident that silane treatment of fibers slightly decreased the resulting crystallinity compared to those composites filled with untreated Sitka spurce fibers. This decrease in crystallinity was in agreement with literature, which reported that silane treatment of wood-flour increased the degree of crosslinking in HDPE/wood-flour composites. Crystallinity in turn was decreased.[44] The extent by which the crystallinity of the matrix decreased seemed to correlate with the WPG of silane of the individual fibers. Compared to the untreated PLA/Sitka composites, the silane treatment increased T_g only when MW fibers were used. No shift of T_g due to a silane treatment was recorded for JW and CW fibers. However, for better understanding, we determined glass transition temperature also with DMA since for semi-crystalline polymers higher sensitivity is reported.[45]

The MDI modified PLA/Sitka composites exhibited glass temperatures comparable to those treated with silane, although crystallinity was much lower. This could be attributed to a more branched molecular structures formed in PLA when mixed with MDI.[46] Investigation conducted by Li and Yang suggested that MDI as chain extender may disrupt PLA crystallization.[21]

Mechanical properties

Incorporation of 20 wt % untreated fibers into the PLA matrix slightly decreased tensile strength as well as elongation at break (Table VI). This indicated a low interfacial compatibility between the fibers and the PLA matrix. On the other hand, stiffness of PLA/Sitka composites was improved. The mechanical behavior of the Sitka composites depended on the fiber origin which can be explained by the present chemical differences and consequently different interfacial compatibility between the fibers and polymer matrix. The recorded different behavior of Sitka fibers was promoted by treatment with coupling agents. MW fibers were the most responsive to a silane or MDI treatment, possibly because of the differences in surface chemistry. Huda et al.[47] recorded an improvement of the mechanical properties of PLA/kenaf composites after alkali treatment of the fibers. It is well established that both silane and MDI react with the hydroxyl groups that are present in PLA as well as in the wood fibers.[48]

TABLE VI
Mechanical Properties of Neat PLA and PLA/Sitka Fiber Composites

Sample	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)
PLA	45.8 (4.7)	2.5 (0.7)	2620 (166)
PLA/JW	35.2 (4.0)	1.2 (0.2)	2930 (398)
PLA/MW	45.3 (7.3)	1.1 (0.2)	3390 (242)
PLA/CW	42.0 (5.2)	1.6 (0.2)	2920 (262)
PLA/JW_silane	38.0 (3.1)	0.9 (0.1)	3120 (405)
PLA/MW_silane	51.5 (6.6)	1.7 (0.1)	3940 (300)
PLA/CW_silane	47.8 (7.5)	1.4 (0.3)	3160 (437)
PLA_MDI/JW	39.6 (2.8)	1.4 (0.2)	2780 (220)
PLA_MDI/MW	55.0 (3.9)	1.3 (0.2)	3500 (230)
PLA_MDI/CW	46.2 (4.2)	1.5 (0.1)	3100 (230)

Standard deviation in parentheses.

The presence of a network in the matrix structure was measured indirectly as gel content after extraction in hot xylene. It is believed that the crosslinked part of the composite is insoluble in boiling xylene, while the non-crosslinked part is soluble. Figure 4 shows the determined gel content in PLA/Sitka composites. Composites treated with MDI and filled with fibers from MW exhibited the most extended network structure (32.1% gel content) what corresponded to the best mechanical properties.

Dynamic mechanical properties

Storage modulus and Tanδ dependent on temperature for neat PLA and untreated PLA/Sitka

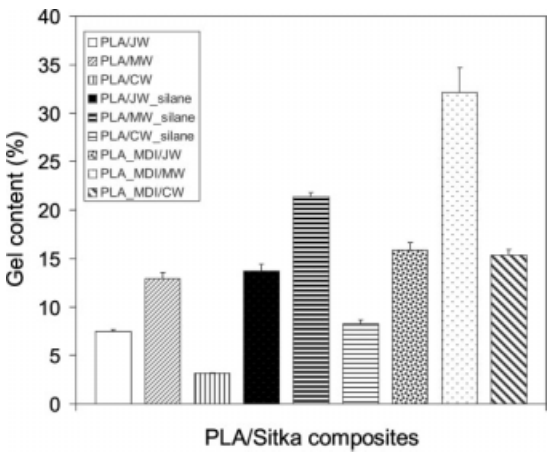

Figure 4 Gel content in PLA/Sitka composites after xylene extraction.

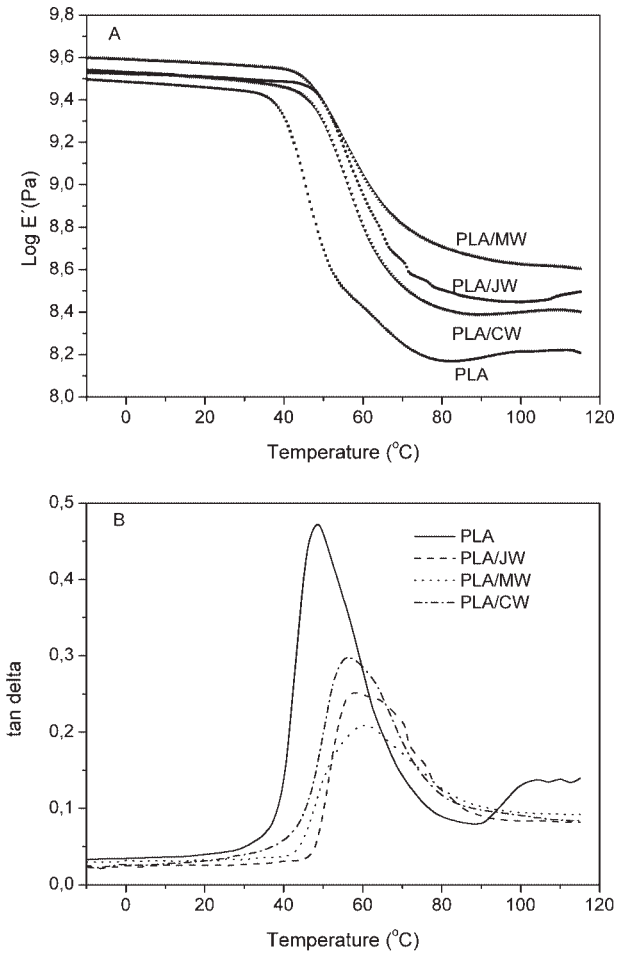

Figure 5 DMA curves for PLA and PLA/Sitka fiber composites containing 20 wt % of untreated fibers. (A) Dependence of storage modulus on temperature and (B) Dependence of Tanδ on temperature [juvenile wood (JW), mature wood (MW), compression wood (CW)].

composites are shown in Figure 5. The different fiber types improved stiffness of the PLA composites across the measured temperature range. Storage modulus of neat PLA dropped sharply at 38.3°C. The incorporation of 20 wt % of untreated Sitka spruce fibers shifted this storage modulus drop by ~ 10°C towards higher temperatures. Compared to neat PLA, the Tanδ peaks of the PLA/Sitka composites have decreased and they also shifted to higher temperatures. The intensity of the Tanδ peaks of PLA/Sitka fiber composites decreased and shifted to higher temperatures compared to neat PLA. This could be explained by a change in the molecular mobility of PLA molecules due to the incorporation of fibers. Table VII presents DMA data for PLA and PLA/Sitka composites at temperatures of 20, 40, 60, and 80°C, respectively. The storage modulus and T_g (deduced from the Tanδ peak temperature) increased after silane treatment of the fibers as well as after addition of MDI to the PLA matrix. Incorporation of untreated Sitka spruce fibers increased the storage modulus (stiffness) of the composites by 4–30% at 20°C depending on fibers origin. Fibers from MW embedded into a PLA/MDI matrix increased the storage modulus by 64% at 20°C. This indicated a significant improvement of the interfacial compatibility by the coupling agent. PLA_MDI/Sitka composites showed higher and broader Tanδ peaks compared to neat PLA, which suggested better damping of these samples. The increase of Tanδ was probably caused by a formation of branched molecular structures in the PLA/MDI matrix, which was also indicated by the more extended network structure (gel content).[49]

CONCLUSIONS

The thermal, mechanical, and dynamic mechanical properties of Sitka spruce fiber reinforced PLA composites have been investigated. Fibers originated from mature, juvenile, and compression wood of Sitka spruce.

Hypothesis 1 stating a potential for optimizing composite properties by utilizing the natural

TABLE VII
DMA Properties of Neat PLA and PLA/Sitka Fiber Composites at Different Temperatures

Sample	Storage modulus E' (MPa)				Tanδ	
	20°C	40°C	60°C	80°C	(°C)	Max. Intensity
PLA	2876	2175	270	147	48.4	0.474
PLA/JW	3018	2822	719	402	57	0.249
PLA/MW	3736	3504	1107	511	60.7	0.21
PLA/CW	3209	2880	641	261	56	0.297
PLA/JW_silane	3332	3061	1158	347	62.9	0.251
PLA/MW_silane	3928	3744	1704	615	62.1	0.201
PLA/CW_silane	3503	3197	1081	430	61.5	0.205
PLA_MDI/JW	3447	3281	473	123	59.1	0.526
PLA_MDI/MW	4720	4400	2106	663	65.8	0.621
PLA_MDI/CW	3853	3655	509	175	60	0.503

Oscillation frequency 1 Hz.

variability of fibers present in a single tree species (here *P. sitchensis*) was accepted. It was shown that mature fibers improved Young's modulus of the tested PLA composites by 30%, while juvenile fibers did so by 12% only. In contrast to the other fiber tissue types, who showed a decline, mature wood fibers kept the tensile strength of PLA/MW composites unchanged in comparison to neat PLA. The most effective reinforcing fibers originated from mature wood. They exhibited the highest content of glucose and lowest concentration of lignin, which could had an influence on better interfacial interaction with PLA matrix. However, physical characteristics such as high fiber length and surface area should not be ignored.

Hypothesis 2 claiming that fiber modification interacts with fiber type selection was also accepted. It was shown for Young's modulus that with silane treatment an improvement by 50% was possible. For tensile strength MDI treatment combined with mature wood fibers showed a 20% improvement, while silane treatment resulted in a 12% improvement only. The use of silane and isocyanate coupling agents had a positive influence on the thermal and mechanical properties of the composites. This is believed to be due to the improved interfacial compatibility between fibers and PLA matrix.

The variability of the fiber properties needs to be considered when wood fibers are to be used as reinforcing phase in biocomposite materials. The variability might even bear the potential of design materials with tailor-made properties.

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