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ORIGINAL

Multivariate modeling of acoustomechanical response of 14-year-old suppressed loblolly pine (*Pinus taeda*) to variation in wood chemistry, microfibril angle and density

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Abstract The polymeric angle and concentration within the S_2 layer of the softwood fiber cell wall are very critical for molecular and microscopic properties that influence strength, stiffness and acoustic velocity of wood at the macroscopic level. The main objective of this study was to elucidate the effect of cellulose, hemicellulose, lignin, microfibril angle and density on acoustic velocity and material mechanical properties of 14-year-old suppressed loblolly pine. Cellulose, hemicellulose and density are consistently the most important drivers of strength, stiffness and velocity. Cellulose and lignin are the highest and lowest contributor to velocity, respectively, with lignin acting as a sound wave dispersant, while cellulose is the most important conductor of sound wave at the molecular level, while hemicellulose acts as a special coupling agent between these components. The polymeric constituents are thus important drivers of sound wave propagation at the molecular level, while density played a subsequent role at the macroscale.

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Introduction

Wood is a fibrous material made up of tubular cells that account for 90% of all softwood cells in the tree. These cells provide resistance to load-bearing forces caused by tree weight and wind loading (Marra 1979). At the macroscopic level, wood is an anisotropic material that can be used as solid lumber and in the reinforcement of advanced composite products (Bodig and Jayne 1982). At the molecular level, wood is composed of cellulose, hemicellulose and lignin. Cellulose is the stiffest polymer in wood due to its high degree of polymerization, crystallinity and linear orientation. Hemicellulose is a non-crystalline branched molecule composed of a linear backbone of galactoglucomannan and glucomannan, which is attached with side chains of pentose and hexose (Winandy and Rowell 2005). Winandy and Rowell (2005) stated that hemicellulose functions to connect the non-crystalline part of hydrophilic cellulose to the amorphous and hydrophobic lignin. Thus, hemicellulose acts to transfer stress between cellulose and lignin (Via et al. 2009). Lignin is a large hydrophobic tridimensional and highly branched phenolic molecule, which binds and holds other polymers together. It is also a stiffening agent for cellulose and provides resistance to compression forces (Winandy and Lebow 2001).

Researchers have hypothesized that these polymeric constituents influence the mechanical and acoustic properties of wood and wood products. These natural polymers are carefully engineered by nature to bear and distribute loads imposed on a growing tree. Several polymeric cross-sectional structural models exist to explain the morphology of this composite matrix, but most agree that the elementary fibrils of cellulose exhibit the least variation in dimension due to their high crystallinity, coupled with the interaction between the lignin and hemicellulose matrix. The hemicellulose matrix is sandwiched between lignin and the amorphous portion of the cellulose elementary fibrils and is thus defined as a coupling agent between cellulose and lignin (Winandy and Rowell 2005; Via et al. 2009). The highly hydrophobic lignin polymer acts as a sheath around the hydrophilic cellulose and hemicellulose matrix. The lignin polymer is entangled in the xylan portion of the hemicellulose, while the glucomannan of hemicellulose is attached to the non-crystalline portion of the cellulose elementary fibrils (or microfibrils). Cellulose has been shown to significantly influence the elastic phase, when the load is applied nearly parallel to the cellulose plane and thus is anticipated to impact modulus of elasticity (MOE) at the macroscale. Lignin and hemicellulose become dominant as the axis of the load is at an increased angle to the axis of the microfibrils. Strength is reduced by a factor of ten at the nanoscale level for loads applied at a transverse angle to the fiber axis (Via et al. 2009; Gindl and Schoberl 2004). At the macroscopic level, softwoods are composed of 90% longitudinal fiber elements specialized for fluid conduction and mechanical strength. These fibers have multilayered cell walls consisting of one primary cell wall layer and three secondary layers (S_1, S_2, S_3). These layers are differentiated by the degree of orderliness and orientation of the crystalline portion of the cellulose. The S_2 layer is considered most important for the acoustic, or elastic, response of wood because it is located at the middle portion of the cell wall and accounts for 83% of the overall secondary cell wall (Gindl and Schoberl 2004).

The acoustic properties of live trees have been of significant interest in recent years because stems currently being harvested without any knowledge of the internal stiffness quality affect the performance of the material. The velocity of acoustic waves propagating through the tissue of trees has been measured to estimate the stiffness of wood, but little is known about the influence of the polymeric constituents on acoustic velocity. It has been hypothesized that the acoustic response of wood varies as a function of wood chemistry, macrodensity and the angle of the aggregate polymers. To date, only isolated examples exist where a study considered only one trait at a time, while the effect of all other traits that might influence velocity was assumed to be held constant. For example, Hori et al. (2002) found a positive correlation between acoustic velocity and cellulose crystallinity and a negative relationship between crystallinity and microfibril angle (MFA). This was probably the result of increased acoustic velocity along the cellulose crystalline structure with MFA providing the primary direction of the fastest wave propagation. On the other hand, a polymer such as lignin is lower in density, is three dimensional in structure and is thus more likely to absorb or diffuse acoustic energy in multiple directions, resulting in some energy loss and a reduction in acoustic velocity. However, to the authors' knowledge, no studies have tested such a hypothesis, nor has the relationship between multiple polymeric constituents and velocity been reported within a single study. Thus, the main objective of this study was to explore the effects of polymeric constituents, density and microfibril angle (MFA) on the modulus of rupture (MOR), modulus of elasticity (MOE), and acoustic velocity of 14-year-old suppressed loblolly pine. Suppressed loblolly pine has been reported to contain less cellulose, more lignin and hemicellulose than the normal wood. It also has higher MFA, wider growth rings with higher proportions of latewood as compared to normal wood (Donaldson et al. 2004). Thus, it is suspected that these properties will significantly affect the relationship between the polymeric constituents versus velocity and mechanical properties.

Materials and methods

Materials

The materials for this study were selected from a plantation of genetically improved families of loblolly pine (*Pinus taeda*), located at Brantley County near Nahunta, Georgia, USA (latitude 31°12′16″N and longitude 81°58′56″W). The topography of site is relatively flat with slope <2% and 20 m altitude above sea level. The soil is very fine sandy loam, poorly drained and generally poor in nutrients, which was formed from loamy and silty coastal plain sediments. The mean annual temperature ranged from 17 to 19 °C, and the annual precipitation from 1981 to 2010 averaged 1315 mm (NOAA 2011). The total size of site was 6744 m^2, which was divided into fifteen blocks measuring 450 m^2. Eighty seedlings from eighty different genetically improved loblolly pine families were randomly planted on bed at 1.8 m × 3.6 m.

Eight out of the eighty genetically improved loblolly pine families were used for this study in spring 2014 when the trees were 14 years.

The stand had not received any commercial thinning since establishment. Eight trees were selected randomly from each family, with care taken to avoid trees with visible defects, such as leaning, forked stems, chlorotic needles, as well as other less significant growth defects. The diameters of the selected trees were measured at breast height and ranged from 8.8 to 12.6 cm with a mean of 10 cm.

Acoustic measurements

The selected trees were acoustically tested using the Director ST 300 acoustic tool (Fibre-gen, Christchurch, New Zealand), which relied on the time-of-flight (ToF) principle (Wang et al. 2001; Mora et al. 2009; Essien et al. 2016). Basically, the accelerometers (i.e., the transmitter and the receiver probes) were positioned on the same side of the tree, 120 cm apart, with the center of the path positioned at breast height. Both probes were deployed at a 45° to the tree axis, and the stress wave was generated by striking the transmitter probe with a steel hammer using a steady force. The generated wave was detected by the receiver, and the amount of time it took for the sound wave to travel the distance between the probes was recorded by the data logger, which displayed the velocity reading automatically (Mora et al. 2009; Essien et al. 2016). Acoustic measurements were taken on the north and south aspects of the tree using a compass to determine location. Three readings were taken on the north and south aspect of each tree, respectively, resulting in a total of six readings per tree.

The selected trees were then harvested and bucked into 180-cm logs and 10-cm-thick disks, alternately along the entire length, yielding 3–5 logs, depending on the length of the tree. All 34 logs obtained from the 8 trees were used to determine log acoustics. The log acoustic velocity was determined while they were still green using a Director ST300 tool, with the same operational procedure as described above. Six readings per log were taken from the north and south aspects of the logs. The 180-cm logs were crosscut into two equal parts, and four pairs of disks, measuring 2 cm thick, were taken from the freshly cut surfaces, with 2 pairs taken from each piece. Three pairs were used to determine the moisture content and basic disk density (referred to as “disk density” in this study). The dimensions of the disk were taken to the nearest 0.025 mm using a digital caliper, and weight was measured to the nearest 0.001 g. The remaining pair was used for the chemistry and MFA analysis.

Static MOE and MOR determination

Static MOE and MOR were determined using the small clear specimens measuring $2.5 \times 2.5 \times 41$ cm^3 (radial × tangential × longitudinal) prepared from the remaining log samples after the specimens were conditioned (at 65% RH, 23 °C for 3 month) to approximately 12% equilibrium moisture content (EMC). Four outermost specimens (the first 2.5 cm sample obtained from each log without the bark material of the tree) from the north, south, east and west directions around the circumference of each log—totaling 136 specimens—were used for the static bending tests following the protocols of ASTM D143 (ASTM D143 2007). The load was applied on the tangential–longitudinal face in a three-point configuration using a Z010 Zwick Roell Testing System (Zwick Roell, Kennesaw, GA, USA) at a loading rate of 1.3 mm/min. The linear portion of the load–deflection curve was used to determine MOE, while MOR was calculated using maximum bending moment at the maximum load borne by the specimen. The moisture content and outerwood density (referred to as outerwood density (ODW) in this study and it is the first 2.5 cm sample obtained without the bark material of the tree at test) were determined following the protocols described in ASTM D143. The outerwood density was determined by measuring the dimensions of the samples with calipers to the nearest 0.025 mm and the weight to the nearest 0.001 g, all at 12% EMC.

MFA determination

Strips measuring 1 cm in width were extracted through the pith of the pair of disk samples meant for the MFA measurement. One sample was prepared in the "south–north" direction, while the other was in the "east–west" direction. Two thin sections of wood samples measuring 0.2 mm were sliced from along the entire length of both 1 cm strips per log—one along the north–south and the other east–west directions. The thin samples were macerated using equal volumes of hydrogen peroxide (30%) and glacial acetic acid at 80 °C for 24 h for thorough maceration (Peter et al. 2003). Temporary slides were prepared from the macerated fibers and an MFA measured following the procedure described by Peter et al. (2003). The MFA measurements were taken on forty fibers selected from both the earlywood and latewood using differential interference contrast (DIC) microscope (Olympus BX53).

Chemistry

The remaining portion of the disks that were used for the MFA measurements were also used for chemistry, although the MFA measurements were extracted from subsamples of a smaller scale. The wood was ground to pass the 40-mesh screen sieve using a 3383L10 Wiley Mini Mill (Thomas Scientific, Swedesboro, NJ). Five grams of the ground sample was extracted with 150 ml of acetone for 6 h using a Soxhlet apparatus. The extractive-free samples were then used to determine the lignin, cellulose and hemicellulose content according to the NREL/TP 510-42,618. One half grams of the air-dried extractive-free sample was digested with 72% sulfuric acid and incubated in a water bath set at 30 °C for 2 h with intermittent stirring to ensure full and uniform hydrolysis. The solution was diluted with deionized water to a concentration of 4% and was then autoclaved at 121 °C for 1 h. The residue after hydrolysis was filtered and oven-dried to calculate the acid-insoluble lignin (AIL). In order to account for the total lignin content in the specimens, UV spectrophotometer was used to determine the acid-soluble portion of the lignin. Portions of the filtrate were used to determine the acid-soluble lignin (ASL) using UV spectrophotometer (Genesys 10-S Thermo Fisher Scientific, Madison, WI) set at the absorbance wavelength of 240 nm. The lignin content used in this study is the sum of the AIL and ASL. The remaining portion of the filtrate was used to determine the monosaccharide composition of the samples using high-performance liquid chromatography (Shimadzu LC-20A) equipped with an Aminex 87 P column and differential refractive index detector, operated at 85 °C for 35 min. The holocellulose, cellulose and hemicellulose contents of the samples were calculated using Eqs. (1), (2) and (3), respectively (Acquah et al. 2015; Jiang et al. 2014; Via et al. 2014)

$$\text{Holocellulose} = \text{Glucan} + \text{Xylan} + \text{Arabinan} + \text{Mannan} \tag{1}$$

$$\text{Cellulose} = \text{Glucan} - \left(\frac{1}{3} \times \text{Mannan}\right) \tag{2}$$

$$\text{Hemicellulose} = \text{Holocellulose} - \text{Cellulose} \tag{3}$$

The actual moisture content of the air-dried extractive-free samples used in this study was determined in order to calculate the dry weight of the samples used in the determination of the chemical composition of the samples, and hence, moisture was not included as weight during the computation of the cellulose, hemicelluloses and lignin. All experiments were performed in duplicate (Via et al. 2014).

Data analysis

The six acoustic measurements on each log were averaged to represent log velocity. The data gathered from the specimens of the same logs were collated, and the average used to represent that particular log and those from the same logs were pooled together to represent the tree. The data analysis was performed using SAS program version 9.4 (SAS 2014). Pearson correlation method was used to determine the level of relationship among the predictors and response variables. The response variables were MOR, MOE and velocity, while the predictors were cellulose, hemicellulose, lignin, MFA and density (outerwood and disk densities). The whole dataset was standardized by subtracting the mean and dividing by the standard deviation of each variable before the regression procedures were performed. Multiple linear regression and path analysis were performed to estimate the relative significance of the independent variables during the prediction of the response variables. The standard regression procedure in SAS was used to calculate the *p* values for the independent variables and to build regression models. It is worth noting that the relationship between MFA and stiffness is not a linear response and thus may be less sensitive to linear analysis than wood chemistry and density (Via et al. 2009, 2012). To ensure the independent variables were not highly correlated, the variance inflation factor (VIF) was used and a VIF value <6 was set as the constraint to determine whether the coefficient was stable while that >6 meant that the coefficient was inflated and not reliable for interpretation purposes (Via et al. 2009, 2012). The coefficient of determination (R^2) that demonstrates the proportion of variation within the response variable attributed to the predictor variables was reported (Via et al. 2009). The path analysis was then used to segregate the covariance coefficient into the direct and indirect components. Thus, the effect of the predictor variable on the response variable will be the sum of both the direct and the indirect paths relationships (Lachenbruch et al. 2010). The fitted model:

$$Y_i = \beta_0 + \beta_1 \text{density} + \beta_2 \text{cellulose} + \beta_3 \text{hemicellulose} + \beta_4 \text{lignin} + \beta_5 \text{mfa} + \varepsilon_i$$

where Y_i is the response variable, which can be MOR, MOE or velocity of the *i*th sample, β_0 is the intercept of the model, β_1, β_2, β_3, β_4, and β_5 are the coefficients associated with density (either disk or outerwood density), cellulose, hemicellulose, lignin and MFA, respectively. These parameters were tested whether they are significantly different from zero.

Results and Discussion

Mechanical properties and velocity

The summary statistics of all the parameters studied are presented in Table 1. Generally, there is a positive linear relationship between log velocity versus MOR and MOE with a coefficient of determination (R^2) of 52 and 69%, respectively (Fig. 1). A similar but statistically stronger relationship existed between tree velocity versus MOR and MOE with 66 and 84% R^2, respectively (Fig. 2). There is a highly significant correlation between the log velocity versus MOR (0.66) and MOE (0.79) with a $p < 0.001$ (Table 2). There are significant linear relationships with correlation of determination of 0.63 and 0.71 for tree velocity versus MOR and MOE, respectively (Fig. 2) at the tree level. There is a very tight positive relationship between MOR versus MOE (Figs. 3, 4; Table 2), indicating that trees can be segregated into strength and stiffness classes using acoustic ToF method (Wang et al. 2001; Mora et al. 2009).

The results of this study are in conformity with Vikram et al. (2011) who reported a correlation coefficient of 0.40 and 0.90 for the relationship between static MOE versus log velocity and static MOE versus tree velocity, respectively. In that study, 373 logs derived from 373 twenty-five-year-old Douglas fir trees (*Pseudotsuga*

Table 1 Descriptive statistics of log velocity, chemistry and wood properties

	Mean	SD	Minimum	Maximum
Disk density (DD) (g/cm^3)	0.57	0.06	0.47	0.73
Outerwood density (OWD) (g/cm^3)	0.56	0.08	0.42	0.76
Modulus of elasticity (MOE) (GPa)	7.97	2.37	2.71	13.30
Modulus of rupture (MPa)	74.47	16.42	37.10	112.25
Cellulose (%)	42.01	2.30	38.46	48.15
Hemicelluloses (%)	23.84	3.55	16.86	29.91
Lignin (%)	27.39	0.99	25.20	29.39
Log velocity (km/s)	4.44	0.44	3.40	5.18
MFA (°)	23.88	2.15	19.35	28.05

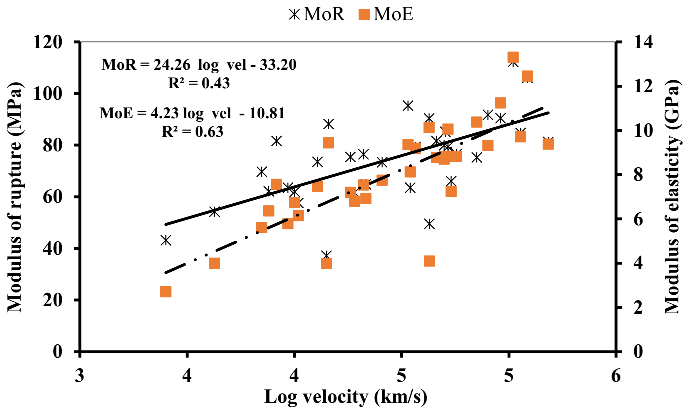

Fig. 1 Fitted linear relations between log velocity versus MOR and MOE

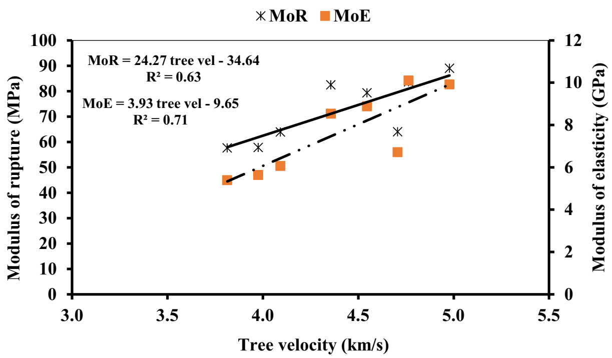

Fig. 2 Fitted linear relations between tree velocity versus MOR and MOE

menziesii) were tested. Ilic (2001) reported a correlation coefficient of 0.63 and 0.76 for the relationship between MOR versus velocity and MOE versus velocity, respectively, when small clear samples obtained from 52 boards of mature *Eucalyptus delegatensis* were studied. The linear relationship of MOE versus tree velocity result presented in this work is in agreement with earlier studies (Ilic 2001; Vikram et al. 2011). The correlation coefficient for MOE versus log velocity reported in the present paper is probably higher than other studies due to the type of the acoustic tool used to measure log velocity. In this study, Director ST 300 was used, while Vikram et al. (2011) used the Director HM200. The Director HM200 is reported to measure the weighted velocity of the whole log instead of only the outer wood as measured by the Director ST 300 in large diameter trees (Raymond et al. 2008; Vikram et al. 2011). This approach has been argued to result in a 30% reduction in velocity for the HM200 versus the ST 300 (Mora et al. 2009).

For 20-year-old Douglas fir, Lachenbruch et al. (2010) reported a correlation coefficient of 0.45 and 0.68 for the MOR versus tree velocity and MOE versus tree velocity, respectively. Ilic (2001) studied the relationship between MOR, MOE and

Table 2 Simple correlation coefficient among log velocity, chemistry and wood properties

	DD	OWD	MOE	MOR	Cellulose	Hemicellulose	Lignin	Log velocity	MFA
DD									
OWD	0.81***								
MOE	0.40*	0.72***							
MOR	0.54**	0.81***	0.92***						
Cellulose	−0.02^{ns}	0.27^{ns}	0.38*	0.22^{ns}					
Hemicelluloses	−0.17^{ns}	−0.08^{ns}	0.25^{ns}	0.22^{ns}	−0.38*				
Lignin	−0.27^{ns}	−0.32^{ns}	−0.04^{ns}	−0.11^{ns}	0.05^{ns}	0.21^{ns}			
Log velocity	0.39*	0.59***	0.79***	0.66***	0.48**	0.10^{ns}	−0.14^{ns}		
MFA	−0.14^{ns}	−0.11^{ns}	−0.04^{ns}	−0.09^{ns}	−0.05^{ns}	0.16^{ns}	−0.06^{ns}	0.16^{ns}	

DD disk density, *OWD* outerwood density, *MOE* modulus of elasticity, *MOR* modulus of rupture

* $p < 0.05$; ** $p < 0.01$; ***$p < 0.001$, *ns* not significant at $p > 0.05$

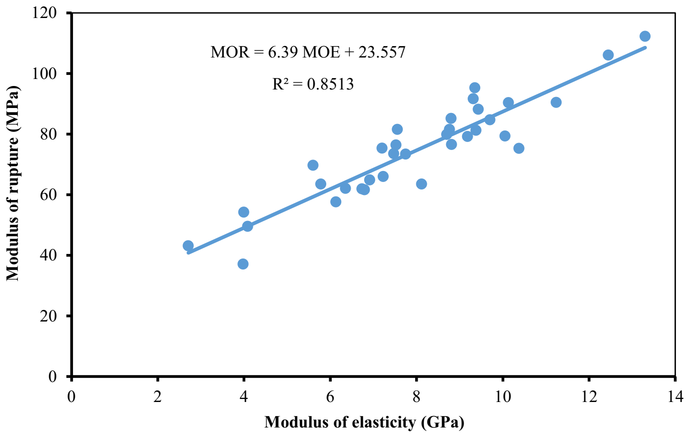

Fig. 3 Relations between MOR and MOE for the 34 logs

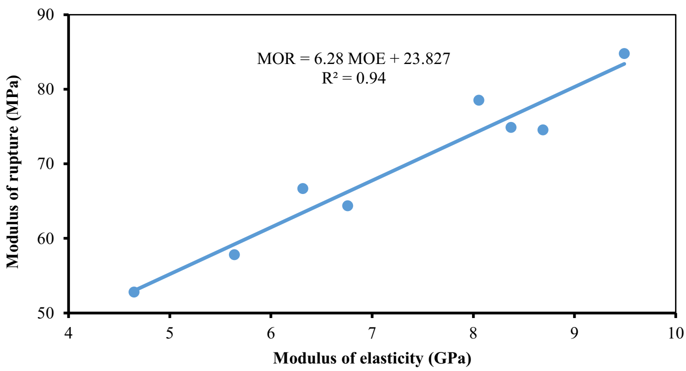

Fig. 4 Relations between MOR and MOE for the 8 trees

velocity of small clear samples and reported a 0.63 and 0.76 for MOR versus velocity and MOE versus velocity, respectively. Although their correlation coefficients were lower than that reported in the present study, it follows a similar trend where there is a strong linear relationship between velocity and MOE than that with MOR. Fundamentally, the report indicated that MOE had a stronger association with the cellulose (Via et al. 2009), while hemicellulose is strongly associated with MOR (Curling et al. 2000; Clausen and Kartal 2003). However, none of these studies used acoustic technique and therefore could not elucidate the relationship between the polymeric constituents versus velocity and MOE. The tight relationship between velocity and MOE observed in this study is due to the close association of both properties to cellulose at the molecular level (Tables 2, 3, 4). It is interesting to note that cellulose exerted stronger effect on velocity compared to density in both models (Tables 3, 4). This explains the stronger linear relationship between velocity versus MOE than MOR observed in this study.

Table 3 Full multiple linear regression models of chemistry, density and MFA for predicting MOR, MOE and velocity

	MOR			MOE			Log velocity		
	Coefficient	SE	R^2	Coefficient	SE	R^2	Coefficient	SE	R^2
Model 1	74.47***	1.49	76.39	7.97***	0.23	72.9	4.44***	0.05	59.13
Cellulose	1.95^{ns}	1.74		0.84**	0.27		0.22***	0.06	
Hemicelluloses	5.18**	1.72		1.00***	0.26		0.14*	0.06	
Lignin	1.41^{ns}	1.67		0.17^{ns}	0.25		−0.04^{ns}	0.05	
OWD	13.6***	1.68		1.62***	0.26		0.21***	0.06	
MFA	−0.89^{ns}	1.54		−0.05^{ns}	0.23		0.08^{ns}	0.05	
Model 2	74.47***	2.06	54.4	7.97***	0.29	56.4	4.44***	0.05	60.04
Cellulose	6.94**	2.29		1.44***	0.32		0.30***	0.06	
Hemicelluloses	8.29**	2.38		1.37***	0.34		0.19**	0.06	
Lignin	−1.06^{ns}	2.23		−0.12^{ns}	0.31		−0.06^{ns}	0.06	
Disk density	9.99***	2.13		1.15***	0.31		0.20**	0.06	
MFA	−1.06^{ns}	2.21		−0.07^{ns}	0.30		0.07^{ns}	0.05	

OWD outerwood density

* $p < 0.05$; ** $p < 0.01$; *** $p < 0.001$, *ns* not significant at $p > 0.05$

Table 4 Path analysis coefficients of models showing the relations among the predictors and the response variables

	MOR			MOE			Log velocity		
	Coefficient	SE	R^2	Coefficient	SE	R^2	Coefficient	SE	R^2
Model 1			76.21			73.23			59.94
Cellulose	0.105^{ns}	0.099		0.343**	0.110		0.481***	0.119	
Hemicellulose	0.306**	0.104		0.411***	0.113		0.302*	0.126	
Lignin	0.091^{ns}	0.096		0.082^{ns}	0.101		−0.055^{ns}	0.128	
MFA	0.016^{ns}	0.087		0.051^{ns}	0.092		0.212^{ns}	0.123	
OWD	0.841***	0.078		0.695***	0.096		0.475***	0.114	
Model 2			54.51			57.50			61.73
Cellulose	0.420***	0.130		0.604***	0.125		0.668***	0.119	
Hemicellulose	0.450***	0.136		0.566***	0.133		0.428***	0.128	
Lignin	−0.066^{ns}	0.126		−0.050^{ns}	0.122		−0.114^{ns}	0.116	
MFA	0.015^{ns}	0.120		0.048^{ns}	0.116		0.222^{ns}	0.111	
Disk density	0.621***	0.113		0.504***	0.119		0.470***	0.116	

OWD outerwood density

* $p < 0.05$; ** $p < 0.01$; *** $p < 0.001$, *ns* not significant at $p > 0.05$

There is a very tight positive linear relationship between MOR and MOE (Figs. 3, 4). A similar relationship was reported by Via et al. (2009). This tight relationship between the MOR and MOE is due to the same set of polymeric constituents driving these properties at the macroscale as observed in this study. Primarily cellulose, hemicellulose and density are the major drivers of MOR and MOE.

Velocity and density

Generally, there is a linear positive relationship between velocity and density (Figs. 5, 6; Table 2). However, outerwood density explained a higher variation in velocity than disk density (Fig. 7). The trend reported in the present study confirms the trends reported in previous studies (Wang et al. 2001; Ilic 2001; Lachenbruch et al. 2010; Vikram et al. 2011; Lenz et al. 2013). Vikram et al. (2011) studied the relationships among standing tree velocity, log velocity and basic density (calculated from whole disks) and reported significant correlations of 0.29 and 0.33, respectively, for tree velocity versus basic density and log velocity versus basic density, respectively. However, the same relations but with air-dried density (calculated from 5 × 10 cm stakes) yielded a correlation coefficient of 0.29 and 0.39 for tree velocity versus air-dried density and log velocity versus air-dried density, respectively (Vikram et al. (2011)). Lachenbruch et al. (2010) reported a significant tree velocity versus air-dried density correlation of 0.42 ($p = 0.02$). The correlation between velocity versus air-dried density for small clear samples was highly significant ($p = 0.0001$) (Ilic 2001). These trends, however, contradicted results presented by Hesegawa et al. (2011). Hesegawa et al. (2011) studied 60-year-old Japanese cedar (*Cryptomeria japonica*) and 28-year-old Japanese cypress (*Chamaecyparis obtuse*). They reported a highly significant negative correlation between velocity and air-dried density of these two species ($p = 0.01$). This negative correlation might be due to the decreasing density gradient from pith to the bark of their species. On the other hand, the density gradient increased from pith to the bark in most pine species including loblolly pine. These contrasting density gradients may be responsible for the positive relations between velocity and density reported in this study as compared to that reported by Hesegawa et al. (2011).

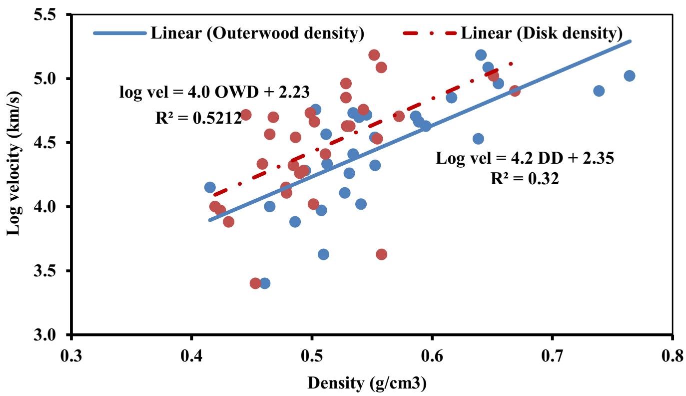

Fig. 5 Relations between log velocity and outerwood density (OWD) and disk density (DD)

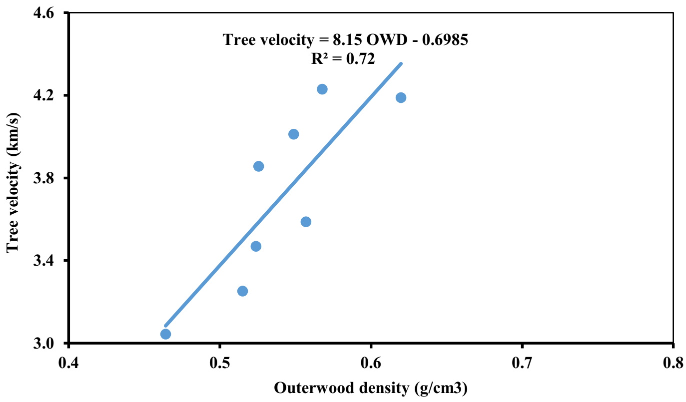

Fig. 6 Relations between tree acoustic velocity and outerwood density at 12% MC for the 8 trees

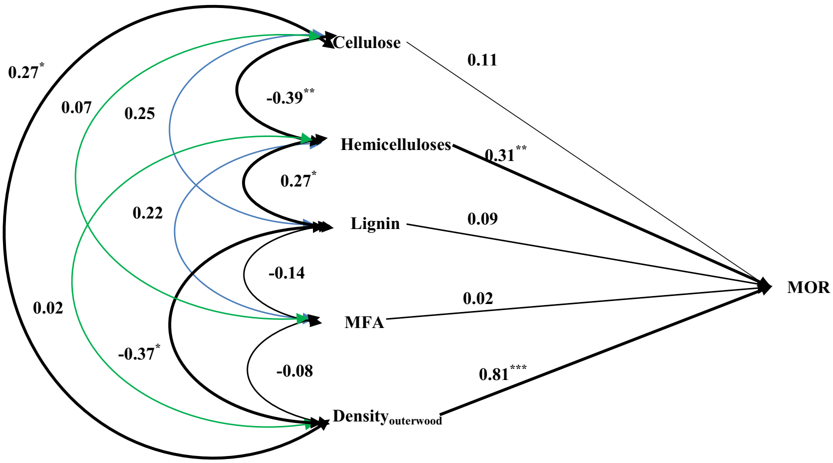

Fig. 7 Path analysis of the chemistry, MFA, outerwood density and MOR to examine the effect of outerwood density on the variables in the model. $*p < 0.1$; $**p < 0.01$;$***p < 0.001$, *ns* nonsignificant at $p > 0.1$

The observed high correlation between outerwood density and velocity (Fig. 5) may seem to indicate the path of flight of the time-of-flight (ToF) acoustic tool is limited to the outerwood portion of the stem of trees and logs as supported by Raymond et al. (2008) and Chauhan and Walker (2006). Those authors proposed that the one-dimensional wave equation is sufficient to estimate the stiffness of live tree when the ToF acoustic tool is used. However, other authors argue that the ToF stress wave is a tridimensional (dilatational) wave, and hence, it is probable that the propagated sound signal can collect some quality information of wood materials lying outside the path of flight. The one-dimensional equation is therefore not considered adequate to predict the stiffness of live trees (Mora et al. 2009; Wang 2013). It should be noted that most of these authors did not consider the complex relationships among the polymeric constituents and velocity that exist at the molecular level. In this study, cellulose and hemicellulose are found to be very important drivers of velocity at the molecular level (Tables 3, 4). At the molecular level, these polymeric components are tightly linked together to form a complex in wood; hence, it is plausible that the high-energy stress wave generated by the ToF tools probes resonates through adjacent materials beyond the path of flight of the stress wave. This molecular-level evidence supports the dilatational wave theory.

Also, one would expect that if the velocity follows the one-dimensional wave equation, then the outerwood density together with the polymeric constituents should explain higher variations within velocity than disk density as observed in Fig. 5. However, the results from both the multiple linear regressions and the path analysis indicated that disk density and the chemistry explained equal or higher variations in velocity than outerwood density and chemistry (Tables 3, 4). This trend confirms the heterogeneous nature of wood instead of isotropic material on which the one-dimensional wave equation is based.

Chemistry, MFA, density, velocity and mechanical properties

The influence of chemistry, MFA, and density on velocity, stiffness and strength is presented in Table 2. Cellulose had a positive relationship with MOE and velocity but a negative correlation with hemicellulose and MFA (Table 2). MFA and lignin had a nonsignificant negative relationship with density (both outerwood and disk), MOR, MOE and velocity (Table 2). Multiple linear regression analysis and path analysis conducted reveal consistently significant positive relationship between the response variables and cellulose, hemicelluloses and density (Tables 3, 4). On the other hand, MFA and lignin exhibit nonsignificant relationship with the entire response variables (Tables 3, 4). From Tables 3 and 4, cellulose, hemicellulose and density are required to estimate MOR, MOE and velocity. The results from the indirect path analysis indicate a significant positive and negative relationship between the outerwood density versus cellulose and lignin, respectively (Fig. 7). Also, there were significantly negative and positive relationships between the hemicellulose versus cellulose and lignin, respectively (Fig. 7). However, the relationship between the predictors when disk density was used in the indirect path analysis indicates a nonsignificant relationship among the predictor variables except a significant negative relationship between cellulose and hemicellulose (Fig. 8).

Density is the most influential predictor of MOR and MOE, while cellulose is slightly more important predictor of velocity than density (Table 3). The importance of hemicellulose and cellulose in predicting stiffness and strength confirmed several reports (Winandy and Rowell 2005; Via et al. 2009; Curling et al. 2000; Clausen and Kartal 2003). Via et al. (2009) reported that hemicellulose and cellulose associated wavelengths were very significant in predicting the stiffness and strength of 41-year-old longleaf pine using principal component regression and near-infrared reflectance (NIR) spectroscopy. Furthermore, Clausen and Kartal (2003) attributed the initial rapid loss of MOR (strength) to degradation of side chain sugars, especially arabinose and xylose associated with hemicellulose when the wood is subjected to bio-deterioration.

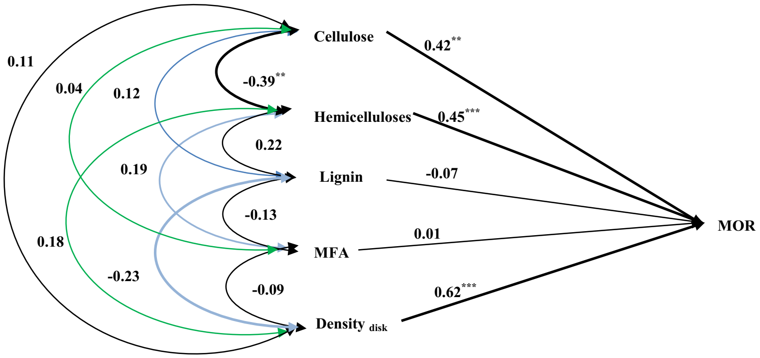

Fig. 8 Path analysis of the chemistry, MFA, disk density and MOR to examine the effect of disk density in the model. *$p < 0.1$; **$p < 0.01$; ***$p < 0.001$, *ns* nonsignificant at $p > 0.1$

Density, cellulose and hemicellulose are required for predicting velocity and MOE support the theoretical fact that the acoustic tools are capable of estimating the stiffness of wood. The major variables driving the wave propagation in order of importance are cellulose, density and hemicellulose, respectively. In softwoods, the S_2 layer accounts for 80–86% of the cell wall and is composed of 32.7, 18.4 and 9.1% for cellulose, hemicelluloses and lignin, respectively (Reiterer et al. 1999). Mark (1967) estimated the densities of the cell wall to be 1.5 g/cm^3 for cellulose, 1.49 g/cm^3 for hemicellulose and 1.4 g/cm^3 for lignin. The higher proportion and density of cellulose and hemicellulose may be responsible for their respective importance in driving the propagation of acoustic waves at the molecular level. Stamm (1964) asserted that more than 60% of the cellulose appeared as crystalline, which is much stiffer and stronger than the amorphous portion. The high crystallinity of the cellulose in the S_2 layer may be responsible for the sound conductance at the molecular level (Hori et al. 2002). Hori et al. (2002) found a positive correlation between the acoustic velocity and crystallinity of cellulose. From models 1 and 2 (Table 3), hemicellulose is less important as compared with cellulose and density in the transmission of sound waves. At the molecular level, the hemicellulose, which is linked to the non-crystalline portion of the cellulose and lignin, functions as a coupling agent for effective distribution of stresses (Winandy and Rowell 2005) just as couplants such as silicone grease functions in improving the transmission of sound waves during acoustics studies of wood (Beall 2002; Hesegawa et al. 2011). It is therefore plausible that hemicellulose acts as a coupling agent for the lateral sound transmission between lignin and cellulose. The velocity had a negative correlation with lignin. This negative coefficient is important because it supports the hypothesis that increased lignin slows the sound velocity. It was hypothesized that lignin has a highly branched tridimensional structure and hydrophobic in nature and hence may act as a sound dispersant or sink at the molecular level. Via et al. (2009) indicated that hemicellulose and lignin become very important when wood is loaded in the transverse direction. Similarly, when sound wave is transmitted in the transverse direction of wood, the less sound conductive hemicellulose and sound dispersant lignin become very important sound

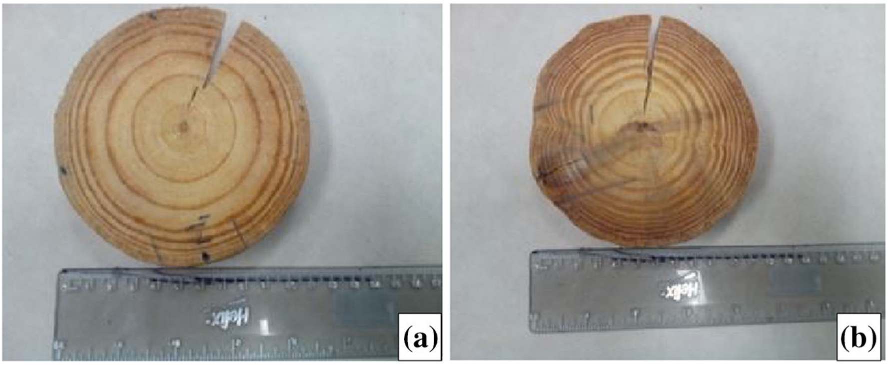

Fig. 9 Typical growth pattern of **a** normal and **b** suppressed 14-year-old loblolly pine

driver; hence, they can influence the magnitude of the incoming wave at the receiver probe. This observation explains the 2 and 3 times respective reduction in sound wave velocity in the radial and tangential directions as compared with sound propagation in the longitudinal direction as reported by Hesegawa et al. 2011. Lignin appeared to be nonsignificant predictor in the present study perhaps because the absorption of sound energy by lignin is passive compared to cellulose, which acts as a conductor of sound, resulting in a more direct influence on ToF. When lignin was investigated independently through the path analysis (Fig. 7), it has a significantly positive relation with hemicellulose. Notwithstanding however, since these polymeric constituents account for over 95% of the weight of southern pine (Via et al. 2009), their roles may overlap and therefore different constituents may assume critical influence contingent to the experimental methods, instrumentation and/or the statistical analytical procedure used.

The relationship between MFA and velocity, MOE and MOR is consistently nonsignificant as given in Tables 2, 3 and 4. This result is unexpected as it has been reported that a decrease in MFA will result in an increase in velocity because the sound wave travels through the axis of the cellulose along the MFA (Hesegawa et al. 2011). This unexpected result may be due to the sampling method used in the present study. Most studies investigating the effect of MFA on other wood properties optimize the range of MFA values through the use of matured wood (from 34 to 63 years) such that the MFA values cover wider range (Via et al. 2009; Hesegawa et al. 2011). In the present study, the random natural MFA range present in the 14-year-old samples was used; hence, there was no intention of selecting a wide range of MFA to optimize its variance. The MFA range of the suppressed wood used in the present study is from 19.3° to 29.6° (Table 1), which is narrower compared to the MFA range of 8°–46° used by Clark et al. (2006). The wood samples used for this study contained higher proportions of latewood, which is not typical of 14-year-old loblolly pine (Fig. 9a, b). The narrower range of MFA coupled with the higher density might have the potential to mask the importance of MFA on velocity, strength and stiffness as observed in this study.

Conclusion

Acoustic velocity and mechanical properties of the suppressed loblolly pine wood were predicted using the cellulose, hemicellulose, lignin, MFA and density. Both the multiple linear regression and path analysis indicate that the same set of variables is responsible for predicting the stiffness and velocity. This result provides a molecular-level evidence to confirm the capability of ToF acoustic tools to estimate stiffness. The results revealed that at the molecular level, cellulose is the most important molecular constituent responsible for the acoustic wave propagation; followed by the hemicelluloses, while lignin acts as a dispersant or sink, thereby reducing sound transmittance. Also, the fact that the polymeric constituents and disk density explained higher proportion of variations in velocity than with outerwood density provides molecular-level support that the ToF acoustic measurements on trees may rely on dilatational wave instead of the one-dimensional wave. It is possible that using matured trees may present a different picture, which may further help us understand the theoretical operations of the acoustic tools.

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