Nondestructive Measurement of Dynamic Modulus for Cellulose Nanofibril Films

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Abstract

Nondestructive evaluation of cellulose nanofibril (CNF) films was performed using cantilever beam vibration (CBV) and acoustic methods to measure dynamic modulus. Static modulus was tested using tensile tension method. Correlation analysis shows the data measured by CBV has little linear relationship with static modulus, possessing a correlation coefficient (R^2) of 0.282. However, the data tested by acoustic method correlated well with the static modulus, approaching a correlation coefficient of 0.6. Irregular sample shape largely contributed to these obtained results. The dynamic modulus, especially measured by acoustic method, is likely an effective tool in non-destructive evaluation of mechanical properties for CNF nanomaterials.

Keywords: Cellulose nanofibril films, Cantilever beam vibration, Acoustic method, Tensile test

1. Introduction

As the most abundant biopolymer on the earth, cellulose and its derivations are attracting a high level of attention. In the 1980s, cellulose nanofibrils were created by subjecting plant pulp fibers to repeated mechanical defibrillation (Herrick et al., 1983; Turbak et al., 1983). Compared to conventional natural fibers, these nanofibrils exhibit a diameter less than 100 nm, and approach several micrometers in length. Abundant and eco-friendly, cellulose nanofibrils have other unique advantages, such as outstanding mechanical strength, excellent visible light transmittance, low thermal expansion, and desirable barrier capability for low molecular substances (Siró and Plackett, 2010). Until now, many attempts were dedicated to seeking industrial applications of cellulose nanofibils in a broad variety of fields like special packaging, engineered polymeric composites, medical carriers, flexible conductive substrates, and energy storage (Nyström et al., 2010; Olsson et al., 2010; Okahisa et al., 2009).

Theoretically, it was calculated that nanofibrils have a Young's modulus of approximately 150 GPa (Iwamoto et al., 2009). However, due to their superfine dimensions, measurement of mechanical properties of nanofibrils using traditional approaches is still challenging. A testing method via atomic force microscopy (AFM) was successfully applied to measure mechanical strength of individual

nanofibrils at the nanoscale level (Cheng and Wang, 2008; Iwamoto et al., 2009). Similar to a three-point bending test, the samples were initially suspended on a silicon wafer possessing several regular micro-grooves. A cantilever tip was used to apply a small test load on the nanofibrils at an appropriate position. The deflection and load obtained were used to estimate the exact mechanical strength. However, determination of deflection and distinguishing the test position are complicated and sensitive. Static mechanical properties tested from nanofibril films, on the other hand, indirectly provide evaluation of such individual nanofibrils.

Many nondestructive methods involving vibrational and acoustic assessments have been used to predict the mechanical properties of forest products (Ross et al., 2004; Wessels et al., 2011). The measured dynamic modulus is reported correlating highly to the static modulus tested by bending or tensile tension (Wang et al., 2007; Wang et al., 2012). Hunt and Turk (2008) developed a cantilever beam vibration apparatus for thick wood fiber composites such as fiberboard and particleboard. However, to the best of our knowledge, there is scant literature regarding dynamic modulus measurement of cellulose nanofibril films or its composites. Here, the dynamic modulus of various cellulose nanofibril films prepared from different species of cellulose nanofibrils was tested by means of cantilever beam vibration and acoustic method. Based on the statistical analysis of correlation between obtained dynamic and tensile modulus, an optimized approach was selected which provides an alternative in estimating the mechanical properties of cellulose nanofibrils and CNF composites nondestructively.

2. Materials and methods

2.1 Materials

Five species of cellulose nanofibrils denoted as R, RM, ER, ERM, and TEMPO were used in the study to prepare different films. The TEMPO nanofibril was produced by chemical treatment at neutral condition (Saito et al., 2009), involving 2, 2, 6, 6-tetramethylpiperidinyl-1-oxyl (TEMPO) mediated oxidation with hypochlorite and chlorite as common reactants. The R and RM nanofibrils were mechanically refined in a stone grinder for 6h, and RM was followed by 20 times microfiluidization pass-through. While, ER and ERM nanofibrils were previously treated by enzyme hydrolysis for 1.5h, and subsequently treated by mechanical fibrillation like the R and RM variants. Detailed descriptions for above mentioned nanofibrils were offered in our previous work (Qing et al., 2013).

2.2 Preparation of CNF films

The CNF films were prepared by filtrating CNF suspensions, followed by air- and then oven-drying of wet films. The nanofiber solution, diluted into 0.2% solid concentration, was filtrated using a 142 mm Milipore ultrafiltration System (Millipore, Millipore Corporation, USA) under 0.55 MPa air pressure. OmniporeTM filter membranes with micropore size of 0.1 μm (JVWP14225, JV, Millipore Corporation, USA) were used in the apparatus, and were supported by the filter paper. The wet films were peeled from the membrane and stacked first between waxed paper and then filter paper, and maintained between two metal plates. The package was air dried at room temperature for 24h and then oven dried at 60 ^{o}C for 8h under a load of approximately 250 N. These films were then conditioned in a 50% relative humidity chamber at a temperature of 23 ^{o}C until tested. The final tensile test, dogbone-shape specimens (seen in Figure 1) were cut to conform to ASTM D638-10 type V by means of a special die.

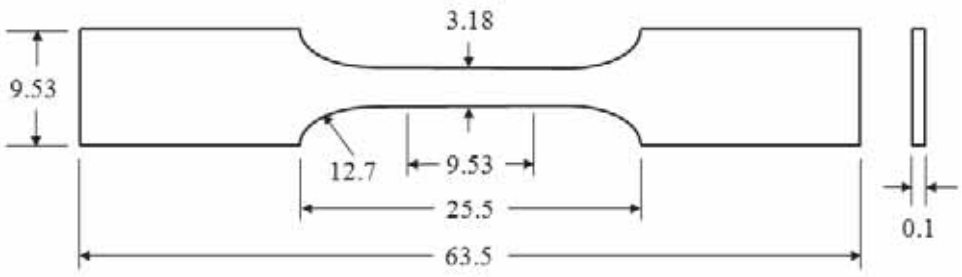


Figure 1—Dimensional profile of ASTM tensile specimens. (Unit: mm)

2.3 Cantilever beam vibration (CBV) measurement

Cantilever beam vibration (CBV) modulus was measured using a USDA Forest Service, Forest Products Laboratory (FPL) designed apparatus, a general profile of which was given in Figure 2. A specific description including mechanism, manual instruction, and applications is available in the reference (Turk et al., 2008). As shown in Figure 2a, the ASTM tensile specimens were clamped at three different positions and subjected to a free vibration which was induced by an initial displacement of 6, 7 and 8mm, respectively. The clamped lengths were 10, 19, and 32 mm, respectively. A laser detector automatically collected the vertical displacement with a sampling frequency of 1000 Hz. More than 5 replicate tests were conducted at each condition. Figure 3 illustrates a representative specimen vibration response, exhibiting typical free-vibration damping.

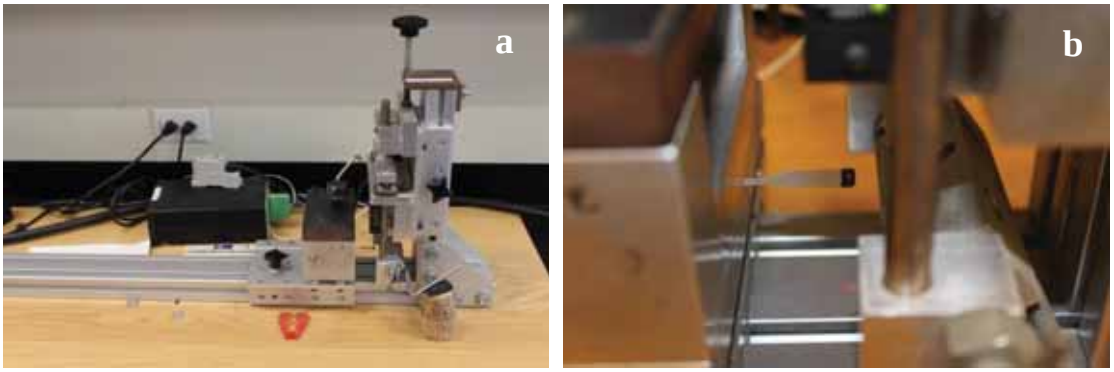


Figure 2—Cantilever beam vibration apparatus (a) and specimens clamped at the grip (b)

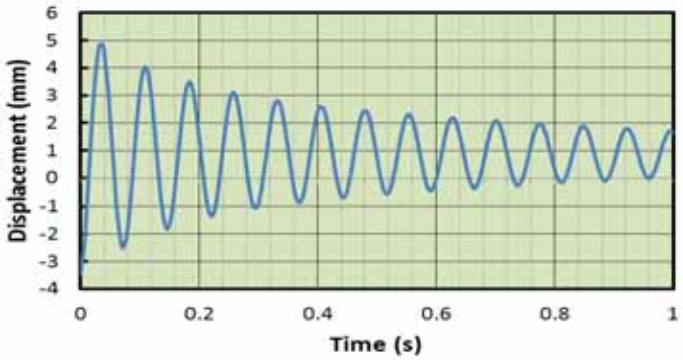


Figure 3—A typical specimen free-vibration response

The frequency of the first model of free vibration of a cantilever beam is given in the following equation (Harris 2002).

$$\omega = 2\pi f = \left(\frac{1.875}{l}\right)^2 \sqrt{\frac{EI}{\rho_A A}}$$

Where f is detected frequency (Hz), l is unclamped length of cantilever beam (m), E is dynamic modulus (Pa), I is area moment of inertia of the vibration beam (m^4), ρ_A is density of vibration beam (kg/m^3), and A is the cross area of vibration beam (m^2).

2.4 Acoustic modulus measurement

The acoustic modulus was calculated based on the equation $DMOE_{aco} = v^2 \rho$, where v is the acoustic velocity transmitted in the testing material, and ρ is the actual density of testing material (Ross et al., 2004). To measure the acoustic velocity, a JAMES v-meter (seen in Figure 4) was used. The transmit times of regenerated ultrasonic pulses traveled in a defined distance which ranged from 20, 30, 40 to 50mm were determined, respectively. The acoustic velocity was defined as slope of the distance scatter data and its corresponding time. At each condition, more than 5 specimens were tested.

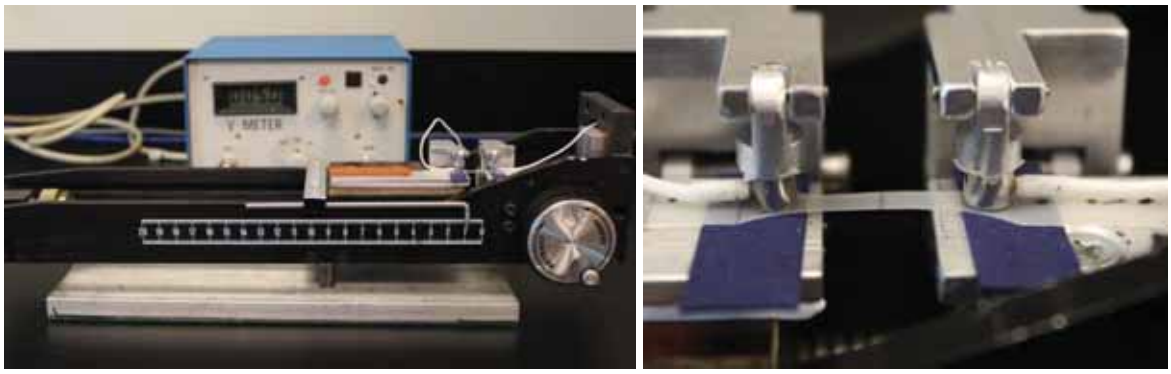


Figure 5—Profile of acoustic velocity testing apparatus

2.5 Tensile tests (static modulus)

The tensile properties of different CNF films were tested by an Instron 5865 universal material testing apparatus (Instron Engineering Corporation, MA, USA) with a 500 N load cell, according to ASTM D638-10. The specimens were cut to conform to ASTM D638-10 type V dog bone shape using a special cutting die (Qualitest, FL, USA) and were subsequently conditioned for a minimum of 1 week at 50% RH and 23 °C prior to testing. Testing was performed within the conditioned chamber in order to maintain specimen equilibration. The specimens were pre-loaded with 5 N of force to remove slack, and the tests were performed with a crosshead speed of 1 mm/min. At least 6 specimens were tested for each condition. An LX 500 laser extensometer (MTS Systems Corporation, MN, USA) was used to determine the displacement with sampling frequency of 10 Hz. The laser recorded the displacement between two strips of reflective tape initially placed approximately 8 mm apart on the necked-down region of the dog-bone specimens. Strain was calculated from the determined displacement and initial gage length. Tensile modulus was calculated as the slope of the stress-strain curve in the stress region of 30-70 MPa.

3. Results and Discussion

3.1 Cantilever beam vibration

Table 1 gives dynamic modulus of various nanofibril films measured by cantilever beam vibration. It is clearly seen that there were significant differences in dynamic modulus as the clamp length varied. However, the tested values differed slightly when the samples were clamped at the same length, even with different initial displacements to induce free vibration. Considering the cellulose nanofibril films were homogeneous, apart from the nanofibril itself, the clamp length appears to play an important role in the evaluation of dynamic modulus.

Unlike conventional forest product samples such as fiberboard and plywood, the test samples here had unique shape, and were extremely light. It was thought these factors would affect the natural free vibration. The hypothesis was supported by a similar test of aluminum strips (64L×9.53W×0.1mmT). When clamped at three different lengths of 10, 19, and 32mm, the measured dynamic modulus varied largely, even though the homogeneous aluminum has a reported theoretical dynamic modulus of 65-70 GPa. It is believed the clamped length would influence the stiffness of test samples with such dimension and weight. As a result, the measured dynamic modulus varies widely.

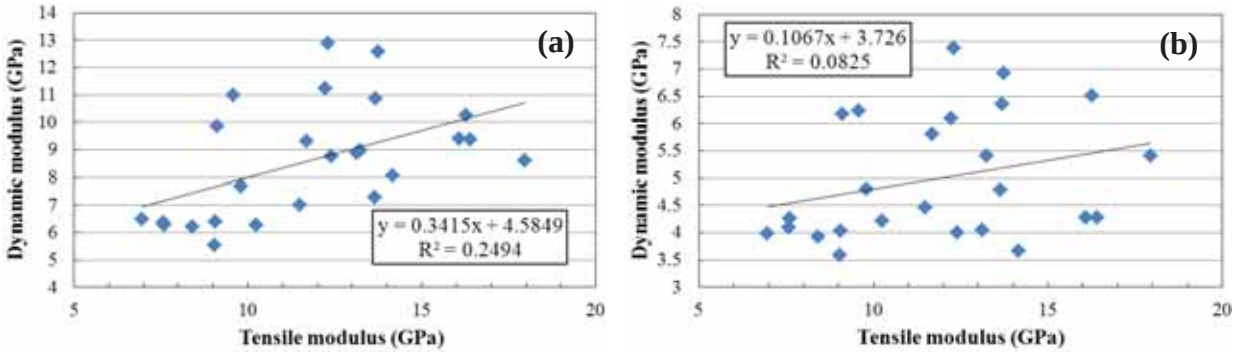
Additionally, the tested cellulose nanofibril films were not perfectly flat because of residual growth stress and unique sizing. The warping originated naturally from the above factors and contributed to the difference in measured dynamic modulus.

Table 1—Tensile and CBV dynamic modulus for various nanofibril films.

Materials	Tensile modulus (GPa)	Dynamic modulus (GPa)		
		Clamped at10 mm	Clamped at19 mm	Clamped at 32 mm
TEMPO	11.71 (1.56)	10.46 (1.62)	6.17 (0.74)	17.58 (1.99)
R	8.29 (1.34)	6.37 (0.09)	4.12 (0.12)	11.47 (0.96)
RM	10.48 (2.11)	6.75 (0.86)	4.31 (0.53)	11.89 (1.57)
ER	14.25 (3.17)	10.66 (1.44)	6.29 (0.56)	17.65 (1.48)
ERM	14.43 (1.76)	8.89 (0.55)	4.05 (0.25)	14.31 (0.40)

Values in parenthesis represent standard deviation

To figure out how well the measured CBV dynamic modulus can be correlated to static modulus, the nondestructive samples were then subjected to tensile testing. The specific values are displayed in Table 1. The correlation between CBV dynamic and static modulus are shown in Figure 5. The correlation coefficient of these data sets is relatively low, approaching R^2 values less than 0.3. This indicates a huge, existing challenge in predicting mechanical properties of cellulose films using conventional CBV methods. As illustrated above, improvement of sample preparation and enhancing the accuracy of displacement and free vibration detection are warranted for future investigations. However, this CBV testing provides valuable insight into nondestructive prediction of cellulose nanofibril properties.



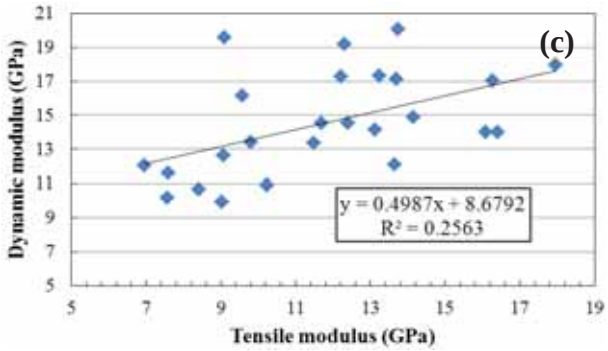


Figure 5—Correlation between CBV dynamic and tensile modulus. (a), (b), and (c) represents clamped length at 10, 19 and 32 mm, respectively.

3.2 Acoustic dynamic modulus

As comparison, the acoustic approach was also applied in testing dynamic modulus. The measured values are shown in Table 2. Because this dynamic modulus is simply equal to density times the acoustic velocity squared, one should be pay more attention to the determination of such velocity transmitted in testing samples. Therefore, 6 different methods, denoted as Method 1 to 6 respectively, were developed to compute acoustic velocity. Method 1 was that which the velocity is identical to the slope of a linear trendline of transmitted distance against time. When considering the initial state should be at the coordinate origin, in Method 2 the linear trendline started at zero. However, the correlation coefficient (R^2) is less than 0.6, which is relatively low. Velocity in Method 3 is an average value calculated from four different predetermined transmitted distances. Due to small tested distance (not more than 50 mm), Methods 4 to 6 attempted to decrease interruption of transverse waves in the least distance and thus improve the accuracy of intrinsic velocity. Method 4 is a simple velocity calculated from greatest testing distance of 50 mm. Similar to Method 1, the velocity measured from Method 5 is the slope of the linear trendline of transmitted distance against time. However, the first two distances were subtracted from corresponding intercepts which are obtained from Method 1. In Method 6, the velocity is equal to the slope of the linear trendline of such data sets with the greatest two distances and coordinate origins.

Table 2—Tensile and acoustic dynamic modulus for various cellulose nanofibril films

Materials	Tensile modulus (GPa)	Dynamic modulus (GPa)					
		Method 1	Method 2	Method 3	Method 4	Method 5	Method 6
TEMPO	11.71 (1.56)	5.12 (0.37)	12.08 (0.83)	20.40 (1.33)	11.40 (1.03)	13.58 (1.00)	10.73 (0.75)
R	8.29 (1.34)	3.84 (0.29)	8.75 (0.49)	13.92 (0.40)	8.18 (0.36)	9.87 (0.57)	7.78 (0.43)
RM	10.48 (2.11)	4.02 (0.26)	9.63 (0.50)	16.37 (1.07)	8.82 (0.65)	10.77 (0.60)	8.49 (0.46)
ER	14.25 (3.17)	5.03 (0.19)	12.59 (0.50)	22.40 (2.10)	11.62 (0.28)	14.08 (0.46)	11.09 (0.36)
ERM	14.43 (1.76)	5.10 (0.19)	12.14 (0.40)	21.03 (0.81)	11.41 (0.60)	13.57 (0.47)	10.80 (0.40)

Values in parenthesis represent standard deviation.

The correlation between acoustic dynamic and tensile modulus is shown in Figure 6. Interestingly, the coefficient of correlation is approximately 0.6, much greater than was calculated in CBV dynamic modulus measurement. The result indicates that nondestructive measurement using acoustic approach is better than CBV testing in the prediction of mechanical properties of cellulose nanofibril film materials. As interpreted above, these nanofibril films are of unique dimension which would block an intrinsic free vibration. On the contrary, such characteristics might have little effect on the transmission of ultrasonic waves. However, the determination of velocity is another challenge. As comparison, Method 6 appears to provide a more effective and efficient approach to detect an exact transmitted velocity in such testing samples. Figure 7 gives a comprehensive comparison of dynamic and tensile modulus.

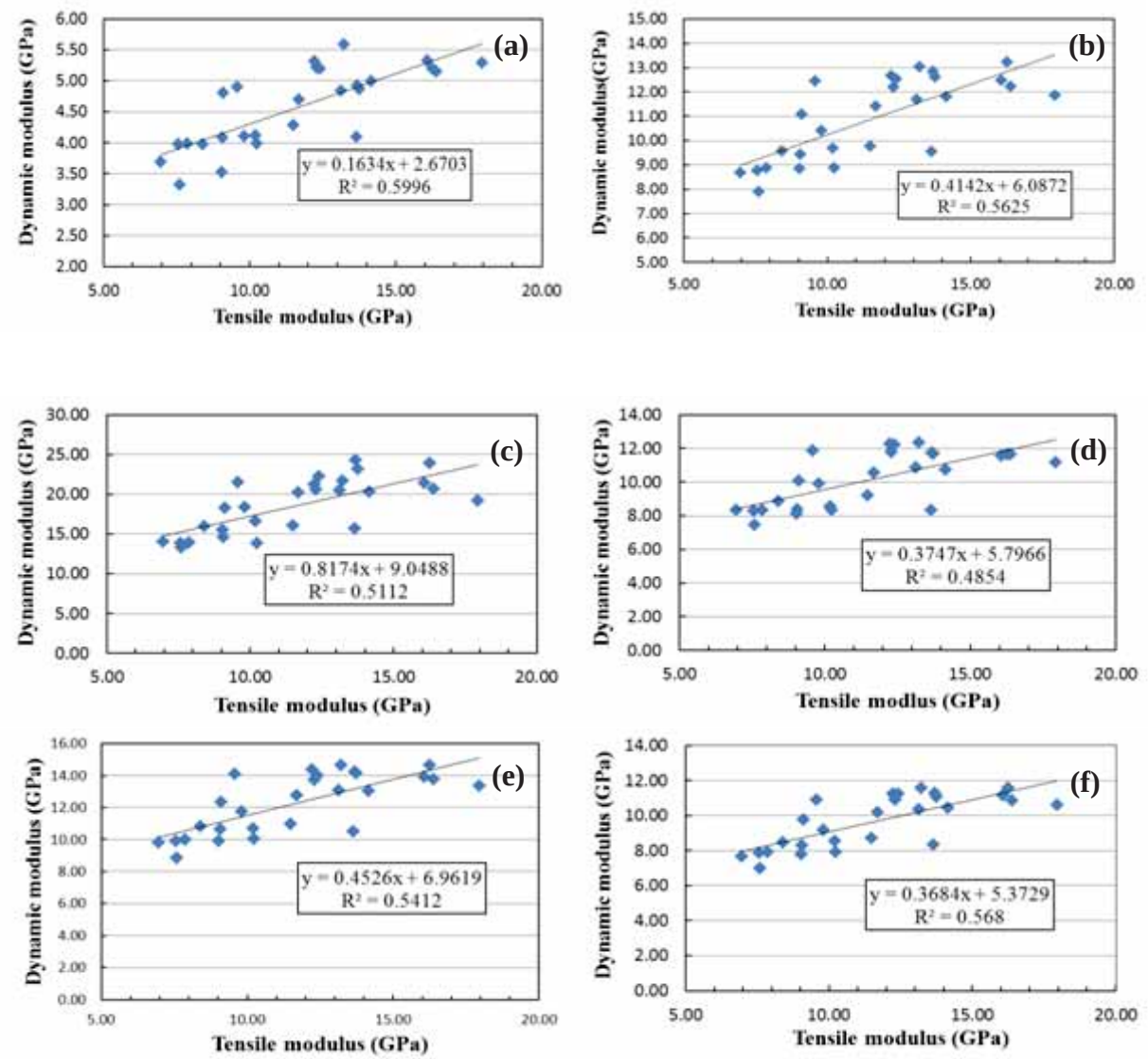


Figure 6—Correlation between acoustic dynamic and tensile modulus. (a), (b), (c), (d), (e), and (f) represents dynamic modulus calculated from method 1, 2, 3, 4, 5, and 6, respectively.

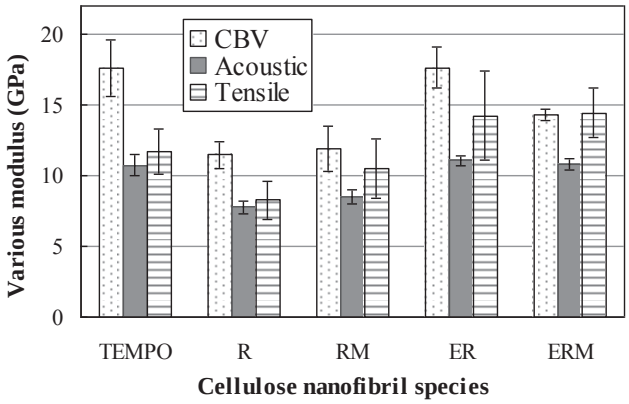


Figure 7—Comprehensive comparison of dynamic and tensile modulus.

Conclusions

Nondestructive evaluation involving cantilever beam vibration and acoustic methods was performed to measure the dynamic modulus of cellulose nanofibril films. The comparison of resulting dynamic modulus and static modulus tested using tensile tension was investigated. Results show a correlation coefficient (R^2) of 0.282 and indicate the data measured by CBV has little linear relationship to static modulus. However, the data tested by acoustic method correlated well with the static modulus, approaching a correlation coefficient of 0.6. The irregular and special sample shape could contribute largely to the obtained result. The dynamic modulus, especially measured by acoustic method, is likely an effective indictor to evaluate the mechanical properties of cellulose nanofibril materials in nondestructive testing.

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18th International Nondestructive Testing and Evaluation of Wood Symposium

Madison, Wisconsin, USA 2013

Abstract

The 18th International Nondestructive Testing and Evaluation of Wood Symposium was hosted by the USDA Forest Service's Forest Products Laboratory (FPL) in Madison, Wisconsin, on September 24–27, 2013. This Symposium was a forum for those involved in nondestructive testing and evaluation (NDT/NDE) of wood and brought together many NDT/NDE users, suppliers, international researchers, representatives from various government agencies, and other groups to share research results, products, and technology for evaluating a wide range of wood products, including standing trees, logs, lumber, and wood structures. Networking among participants encouraged international collaborative efforts and fostered the implementation of NDT/NDE technologies around the world. The technical content of the 18th Symposium is captured in this proceedings.

Keywords: International Nondestructive Testing and Evaluation of Wood Symposium, nondestructive testing, nondestructive evaluation, wood, wood products

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