Elastic Properties of Adhesive Polymers. II. Polymer Films and Bond Lines by Means of Nanoindentation

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ABSTRACT: Seven different polymers used frequently as adhesives and/or matrix polymers in wood, wood composites, and natural fiber-reinforced composites were studied by uniaxial tensile tests and nanoindentation. It was shown that the elastic modulus, the hardness, the creep factor, and the elastic-, plastic-, and viscoelastic work of indentation of the seven different polymers is essentially the same regardless whether the polymers were tested in the form of pure films or *in situ*, i.e., in an adhesive bond line with spruce wood. An excellent correlation was found between the elastic modulus measured by tensile tests and the elastic modulus measured by nanoindentation. In spite of the good correlation, the elastic modulus measured by nanoindentation is significantly higher than the elastic modulus measured by tensile tests. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 1234–1239, 2006

Key words: adhesives; mechanical properties; nanoindentation

INTRODUCTION

An adhesive bond in wood, and wood- or natural fiber-reinforced composites consists of zones of pure polymer and pure wood or fiber, a zone, termed interface, where the polymer and the wood/fiber mix with each other, and the interface between wood/fiber and polymer. The wood/fiber-polymer interface is mainly a matter of polymer- and surface chemistry and not the subject of the present study. The wood/fiber–polymer interface is generated by penetration of polymer into microscopic cavities of the cellular wood/fiber structure, or by diffusion of polymer into the wood/fiber cell wall. Both mechanisms may act in parallel. The penetration of polymer into microscopic cavities is widely observed.[1,2] Recently it was demonstrated that this type of interface formation significantly affects the distribution of strain across wood bond lines.[3] For melamine–urea–formaldehyde and phenol–resorcinol–formaldehyde resin it was shown that diffusion of polymer into the cell wall is significant[4–6] and results in a considerable increase in the hardness and elastic modulus of the cell wall.[5–7] To develop an understanding of the roles of different bond-line zones in transferring stress across the adhesive bond, the mechanical behavior of all components should be known as accurately as possible. For wood, wood fibers, and natural fibers, reliable mechanical data is available,[8,9] which is not always the case for polymers. In the first part of this study we showed how the elastic modulus and Poisson's ratio of thin polymer films may be accurately measured by means of electronic speckle pattern interferometry.[10] In the present article, we aim to characterize the mechanical properties of typical adhesive/matrix polymers used for adhesive bonds in wood and wood composites, and as matrix polymers in wood- and natural fiber-reinforced composites *in situ*, i.e., directly in the adhesive bond. Results from these measurements will be compared to previously obtained results from macroscopic tensile tests,[10] to evaluate the validity of macroscopic measurements on thin polymer films with regard to *in situ* mechanical behavior.

MATERIAL AND METHODS

Specimen preparation

Thin polymer films were prepared as described in detail in a previous paper.[10] The polymers used were four representative wood adhesives: polyvinyl-acetate (PVAc, PV/H Holzleim Standard, Henkel Austria GmbH, Vienna), melamine–urea–formalde-hyde (MUF, Dynomel L-435 with hardener H469,

Dynea Austria GmbH, Krems, Austria), phenol–rescorcinol–formaldehyde (PRF, Aerodux 185 with hardener HR150, Friebe, Mannheim, Germany), and one-component polyurethane (1K PUR, Purbond HB110, Collano AG, Sempach, Switzerland). In addition, the following polymers frequently used for producing wood- and natural fiber-reinforced composites were studied: epoxy (Epoxidharz L Nr. 236349 with hardener L Nr. 236357, Conrad Electronic, Hirschau, Germany), polyester (Polyester-Laminierharz VIPAL VUP 4782 BEMT with hardener MEKP M300, Gerber GFK-Systeme, Stuttgart, Germany), and polypropylene (PP, PP301460/14 film, Goodfellow Cambridge, Huntingdon, England). Pieces of adhesive film with dimensions of approximately 5 mm × 5 mm and a thickness of 0.2 mm to 0.5 mm were cut from the cast films and glued to metal discs with epoxy resin.

In addition to pure polymer films as described above, adhesive bonds with pieces of spruce wood were manufactured using all seven polymers. Pieces of spruce wood (*picea abies*) with a length of 100 mm, a width of 100 mm, and a thickness of 15 mm, were bonded by their radial anatomical planes (the inclination of annual rings was approximately 60–90°). For liquid polymer formulations, the procedure recommended by the manufacturer was followed and curing was done at ambient temperature. PP films were sandwiched between two pieces of wood in a hot press heated to 230°C for 20 min and then cooled under pressure for 2 h. For all specimens, the pressure applied was 0.8 MPa. Postcuring and conditioning was done by storing the specimens in a standard climate (20°C, 65% relative humidity) for 3 weeks. Pieces with a length of 2 mm, a width of 2 mm, and a thickness of 0.5 mm were taken directly from the adhesive bond region (Fig. 1), dried overnight in an oven at 60°C, and embedded in an epoxy resin[11] by alternating vacuum–pressure treatment. A smooth surface was cut using a Leica Ultracut-R microtome equipped with a Diatome Histo diamond knife. Same as pure adhesive films, the embedded and sectioned bond-line specimens were glued to metal discs with epoxy resin to be clamped magnetically to the nanoindenter sample stage.

Nanoindentation

Nanoindentation (NI) was chosen for the *in situ* characterization of polymers in adhesive bonds. NI was already used in a number of studies on polymers[12] and wood cell walls.[13] Usually, the elastic modulus and the hardness are evaluated from NI load–depth curves.[14] In this study, we also evaluated the amount of elastic, plastic, and viscoelastic energy spent during an indentation experiment,[15,16] and the indentation creep.[17]
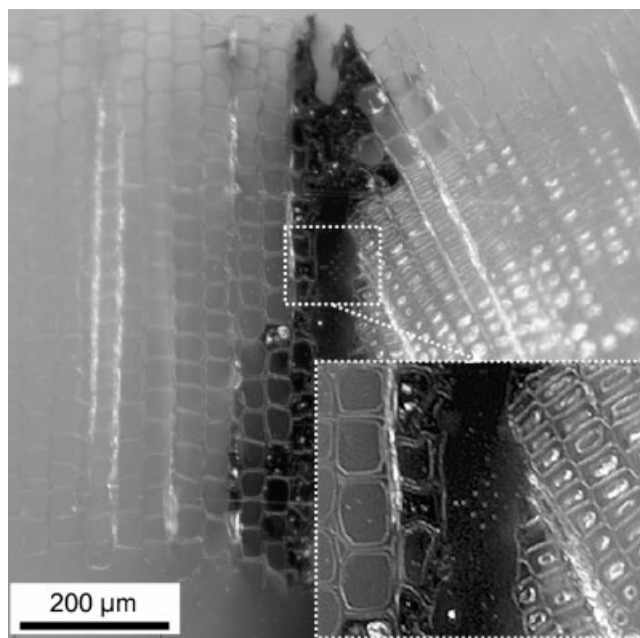

Figure 1 Incident light micrograph of an adhesive bond as it was used for nanoindentation. PRF polymer is recognized by its dark color. The inset shows nine visible indents in the PRF polymer (range of peak load from 500 μN to 1300 μN).

In theory, the elastic modulus should be size independent,[18] but analyzing polymers by NI causes a number of complications summarized under the term indentation size effect, which means that the elastic modulus tends to increase with decreasing penetration depth of the indenter pyramid. Also viscoelastic creep during unloading may affect the slope of the unloading curve, and thus the calculated elastic modulus. Comparing elastic moduli (E) of polymers from bulk measurements and indentation tests, results often show that $E_{bulk} < E_{surface}$.[12] Zheng et al.[19] tested an epoxy bond line of a carbon-reinforced polymer joint by NI and found that the epoxy adhesive performed uniformly throughout the bond-line thickness, but E determined from NI was 5–20% higher than that measured by uniaxial tests on bulk specimens.

All NI experiments were performed with a Hysitron TriboIndenter system (Hysitron, Minneapolis, MN) equipped with a three-sided pyramid diamond indenter tip (Berkovich type). The samples specified above were clamped magnetically to the indenter stage. Two different specimens for each pure polymer film and wood–polymer bond-line, respectively, were examined by performing 24 indents in films and 18 indents in bond-lines. In the case of PVAc, the number of bond-line specimens was increased to five, because of very high variability of measured properties. Experiments were performed in load-controlled mode using a preforce of 1.5 μN and a three
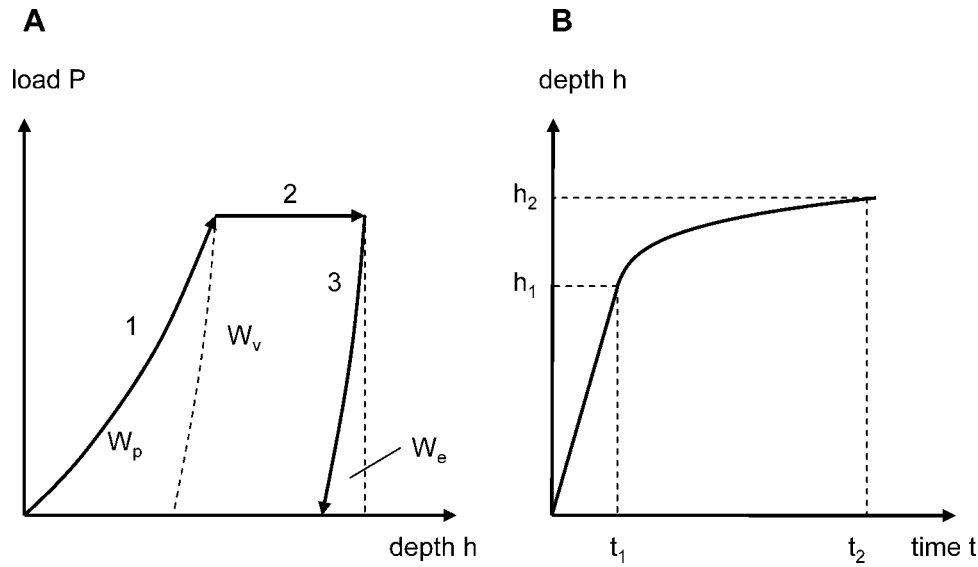
A

load P

B

depth h

Figure 2 Evaluation of the work of indentation and the indentation creep factor. A: schematic load depth graph from nanoindentation with loading (1), holding (2), and unloading (3) segments (continuous lines). The elastic (W_e), plastic (W_p), and viscoelastic (W_v) parts of the total work of indentation were calculated by integrating the respective areas under the load–displacement curve. B: schematic depth–time graph of a nanoindentation experiment indicating the relative change of indentation depth (creep) during the holding segment used to calculate the creep factor by means of eq. (3). The holding segment (Segment 2 on the left) starts at t_1 and ends at t_2.

segment load ramp: load application within 3 s, hold time 20 s, and unload time 3 s. The peak load was varied from 100 μN to 500 μN in steps of 50 μN and from 500 μN to 1300 μN in steps of 100 μN to monitor a possible influence of peak load and unloading rate on the elastic modulus.

Indentation depth is an important parameter in the testing of thin films. To avoid an influence of the substrate material, the indentation size has to be smaller than 10 to 30% of the film thickness.[16,20,21] In the present test series the thinnest film was a 0.2 mm PVAc film showing a maximum indentation depth of 1040 nm, which is equivalent to 0.5% of film thickness and thus much smaller than the maximum allowable depth.

The load–depth curves were evaluated according to the Oliver and Pharr method.[14] From the load–depth graph recorded during the experiment (Fig. 2) the peak load (P_{max}) and the contact area at the end of the holding segment (A) are determined and hardness is obtained by dividing P_{max} by A. From the initial slope of the unloading curve the unloading stiffness (S) is determined and the reduced elastic modulus E_r is calculated according to eq. (1).

$$E_r = \frac{1}{2}\sqrt{\pi}\frac{S}{\sqrt{A}} \qquad (1)$$

E_r is termed the reduced elastic modulus because it takes into account the compliance of the indenter tip according to eq. (2).

$$\frac{1}{E_r} = \left(\frac{1 - v_m^2}{E_m}\right)_{material} + \left(\frac{1 - v_i^2}{E_i}\right)_{indenter} \qquad (2)$$

The elastic modulus E_m of the specimen was calculated according to eq. (2) using Poisson's ratios v determined in a previous study.[10] E_i and v_i stand for the elastic modulus and the Poisson's ratio of the indenter. Since the compliance of diamond is very small compared with the tested polymers the term representing the indenter properties (subscript *indenter*) in eq. (2) was disregarded.

$$C_{IT} = \frac{h_2 - h_1}{h_1} \times 100 \qquad (3)$$

Indentation creep C_{IT} [eq. (3)][17] was defined as the relative change of the indentation depth while the applied load remains constant (Fig. 2). Finally, the elastic (W_e), viscoelastic (W_v) and plastic (W_p) parts of the work of indentation were calculated by integrating the respective area under the load–displacement graph as shown in Figure 2.

RESULTS AND DISCUSSION

The elastic modulus and the hardness of polymers measured by nanoindentation of polymer films and of adhesive bond lines made of the same polymers, respectively, are compared in Figures 3 and 4. For both parameters, an essentially good agreement between
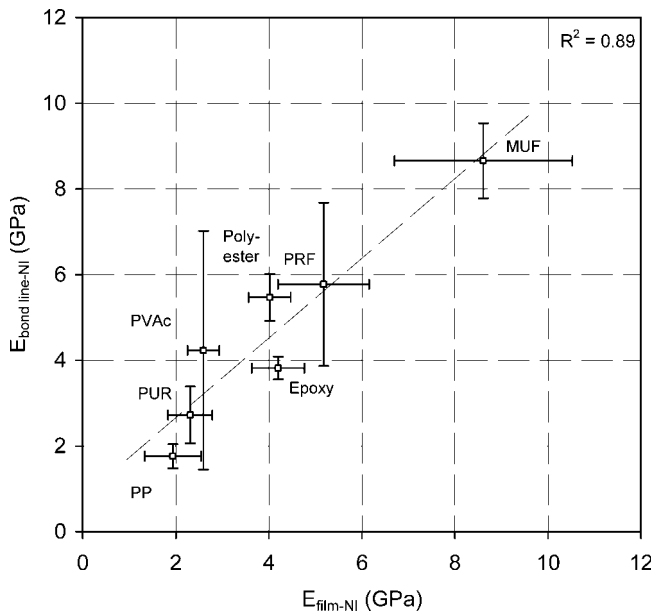
Figure 3 Comparison of the reduced elastic modulus from nanoindentation of pure polymer films and polymers in adhesive bond lines (error bars correspond to standard deviation).

measurements on films and bond lines is achieved, indicated by a highly significant coefficient of determination. The only exception from this overall trend is PVAc, which shows very high variability for both the elastic modulus and the hardness measured in the bond line. While the coefficient of variation varies between 10 and 30% throughout all measurements, it is 70% for the elastic modulus and 100% for the hardness of PVAc measured in the bond line. In view of this unusually high variability, additional experiments were performed with varying unloading rates to monitor a potential influence of viscoelastic effects on the measured parameters, but no statistically significant effect was found. It seems therefore possible that PVAc is less homogeneous in terms of mechanical properties in an adhesive bond line bonding two pieces of wood, than in a pure polymer film.

The tendency of the polymers to creep in an adhesive bond is shown in Figure 5, considering results of two indents per polymer performed at a peak force of 800 µN. Such measurements were also performed on pure adhesive films, but not displayed here, since no significant difference was found in the results apart from PVAc which showed an indentation creep factor of 0.8. The indentation creep factor in the adhesive bond varies from 0.1 for MUF, which showed lowest creep, to 0.2 for PVAc, which showed highest creep. Polymer creep is probably beneficial to the stability of adhesive bond lines in wood, because the polymer easily adapts to local stress concentrations by locally limited viscoelastic deformation. Through this process, microcracking is avoided

and long term stability of the bond is secured. On the other hand, creep has a more and more negative effect on composite properties with increasing polymer volume ratio. Creep is a distinct problem in classic wood composites such as particleboard,[22,23] and also in wood plastic composites.[24–26]

The capability of polymers to absorb elastic, plastic, and viscoelastic deformation work, respectively, is presented in Figure 6. Again this evaluation is based on two indents per polymer taken in an adhesive bond with a peak load of 800 µN. It is shown that MUF is the polymer with the lowest capability to absorb total deformation work, which is the sum of W_e, W_p, and W_v. This is perfectly in agreement with the thermosetting behavior of MUF whose crosslink density may be high compared with that of epoxy, which is another thermoset polymer. The ductile polymers PP, PUR, and PVAc are capable of absorbing more than twice the work of MUF. Assuming that the ratio between W_e and W_p is an indicator for brittleness, MUF with a ratio of 1.04 is most brittle, whereas PVAc with a ratio of 0.28 is very ductile. On average, W_e/W_p was 0.73. The capability of a polymer to absorb deformation energy may be interpreted as an indicator of fracture toughness, which increases with increasing deformation energy.

Finally, the elastic moduli determined by nanoindentation in the bond line were compared with elastic moduli determined by tensile tests using a macromechanical extensometer (Fig. 7) described in the first part of this study.[10] Again a highly significant correlation, but also a significant offset was observed.
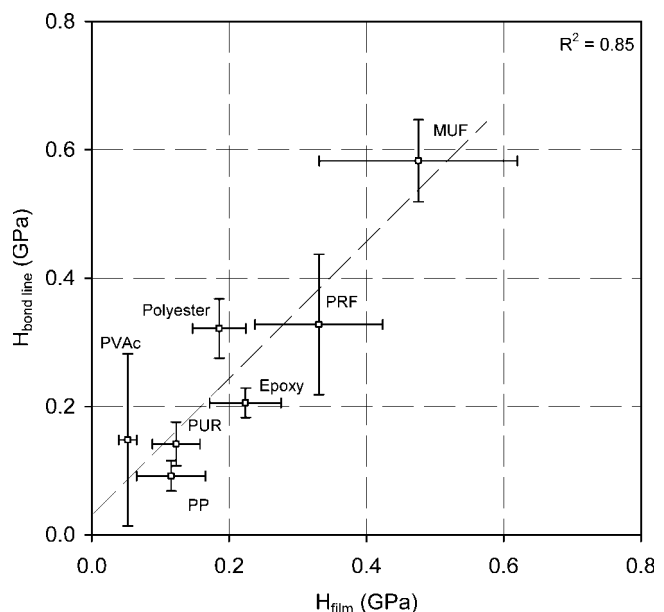

Figure 4 Comparison of the hardness from nanoindentation of pure polymer films and polymers in adhesive bond lines (error bars correspond to standard deviation).
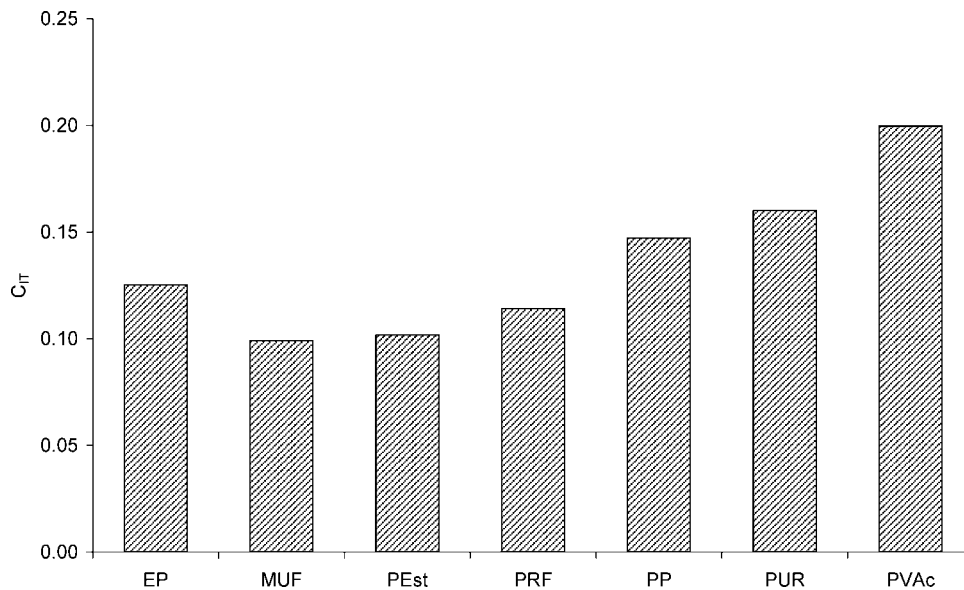
Figure 5 Indentation creep C_{IT} from nanoindentation of polymers in adhesive bond lines (measured for a peak load of 800 µN, application of load within 3 s and holding time of 20 s).

Throughout all measurements, the elastic modulus of the studied polymers was overestimated by nanoindentation. Also Zheng et al.[19] and Van Landingham et al.[12] found significantly increased elastic moduli determined by depth sensing indentation compared with those determined by uniaxial tests. They concluded that the difference was caused by different stress conditions, size effects, and the chosen unloading rates, which are contributing to viscoelastic effects. The overestimation observed in the case of the tested PUR was very high ($> 400\%$). This difference is, however, easily explained by the porosity of PUR in macro-sized specimens. Also in the ad-

hesive bond line, a porosity of about 25% was observed. However, measurements by nanoindentation were taken only in solid PUR, which explains the considerably higher modulus.

CONCLUSION

It was shown in the present study that the tested polymers perform essentially alike in the shape of pure films and in an adhesive bond line with spruce wood. A notable exception from this observation is PVAc, which shows very high variability in the bond
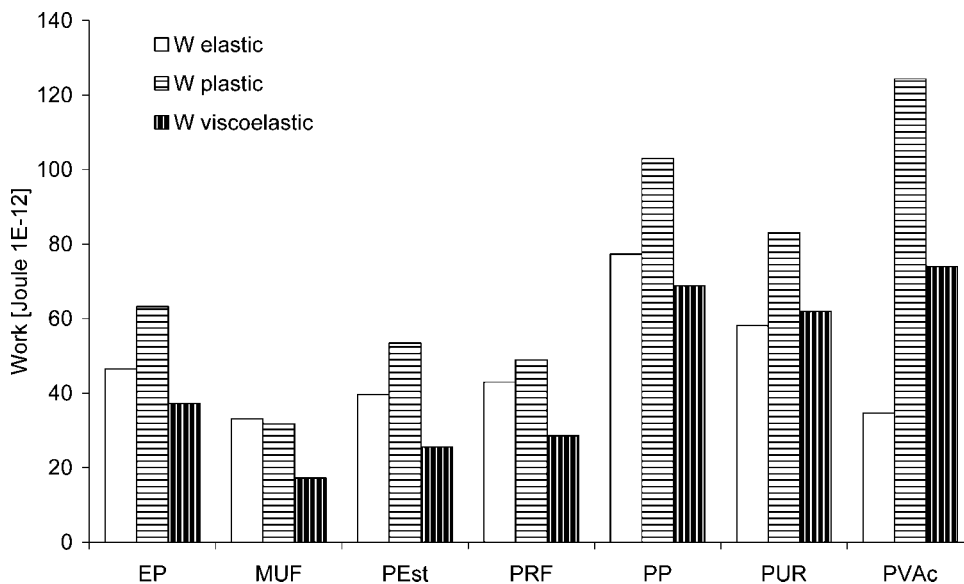

Figure 6 Components of the work of indentation for seven polymers in the bond line.
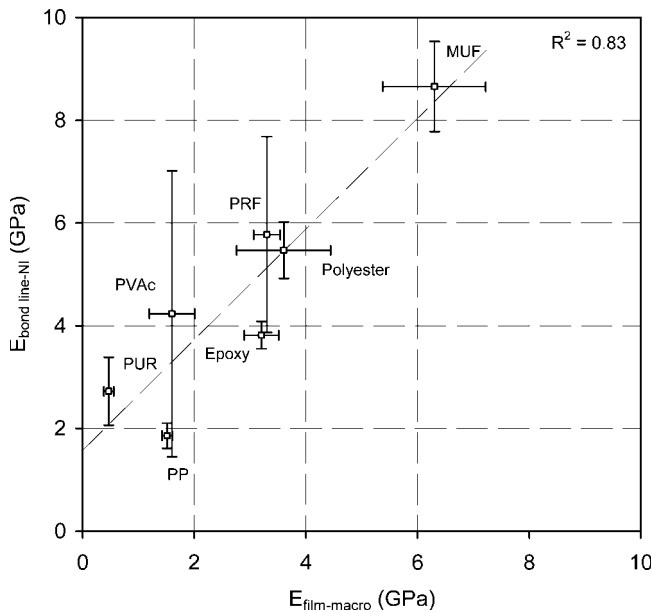
Figure 7 Comparison of the elastic modulus from nano-indentation and the elastic modulus from uniaxial tensile tests (error bars correspond to standard deviation).

line. A highly significant correlation exists between the elastic modulus measured by tensile tests and by nanoindentation. In general, the elastic modulus measured by nanoindentation is higher than the elastic modulus measured by tensile tests. Having established important mechanical properties of pure polymers in this study, similar studies will be performed on the wood/fiber–polymer interface in future, to enable a better understanding of the mechanics of adhesive bonds in wood, wood composites, and natural fiber-reinforced composites.

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