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Application of beam mechanics to sensing the cure development of wood-phenolic joints by dynamic mechanical analysis

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Abstract

Modeling and optimizing of wood-based composite manufacture is playing a larger role in the design of processes and manufacturing equipment. In these models, internal temperature and moisture conditions are predicted with an aim towards predicting when polymeric cure is sufficient to avoid delamination. However, most cure kinetics models are focused on predicting the chemical state of the resin rather than the resulting mechanical properties. The objective of this research is to examine the feasibility of obtaining kinetic cure data using dynamic mechanical analysis (DMA). Dynamic three-point bending tests were conducted on a sandwich specimen of two wood adherends bonded with an adhesive layer. The specimen was cured using various isothermal and linear heating regimes. In addition, two commercial PF resins of different molecular weights distributions (labeled as PF-high and -low, respectively) were evaluated under different experimental conditions influencing moisture loss. Theoretically, the E' ratio, defined as, $R = E'_{\max}/E'_{\min}$ should be good parameter to evaluate bond development because it eliminates the variation in adherend modulus. However, this parameter was found to be sensitive to variables such as resin loading and changes in the adherend modulus due to moisture loss and thermal softening. The shear modulus and flexural storage modulus of the adhesive were calculated by an analytical solution. The values were in general agreement with the results obtained by parallel-plate rheometry. Overall, the sandwich beam was deemed to be simple in both sample preparation and measurement procedure for obtaining PF resin cure transitions and modulus development.
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Keywords: Dynamical mechanical analysis (DMA); Phenol formaldehyde resins; Shear modulus; Storage modulus

1. Introduction

The curing of thermoset resins is most typically characterized using differential scanning calorimetry (DSC) where the measurement of the energy release rate provides information for modeling the reaction kinetics. In contrast, dynamic mechanical analysis (DMA) offers a quantitative view of the adhesion mechanics from which the glass transition, gelation, and vitrification points may be inferred [1]. Thermosetting resins used as adhesives are usually in a fluid state at ambient temperatures. Different approaches have been used to obtain the solid specimens suitable for DMA. Resin samples may often be cured beyond the gel point where material can be machined to a sample suitable for DMA testing. Then the cure development and characteristic transitions of the partially cured materials can be measured [1]. In the region below the gel point, the dynamic shear modulus may be measured with a torsional rheometer [2]. Experimental data describing the change in the viscoelastic properties during curing and application of constitutive models based on linear viscoelasticity can be found in the literature [2,3]. In addition, a fairly comprehensive overview of the state of the art in modeling curing resins is given by Halley and Mackay [4]. More recently, Lion and Hofer developed a general physically based approach of finite thermo-viscoelasticity to represent the curing behavior of adhesives [5].

Phenolic resins are produced industrially by the reaction of phenol with formaldehyde in the presence of a catalyst. They are grouped into two general classes, novolacs and resoles, based upon the molar ratios of reactants as well as the type of catalyst used. These two types of resins differ significantly in terms of both properties and applications. Resoles are the major type of resin used in the wood-based composite industry. Commercial

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versions of these PF resins typically contain around 50% water and are formulated to be used as adhesives for bonding wood. The curing process of PF resin involves two processes: water evaporation and crosslinking of hydroxymethylated phenols, which present a difficulty for defining the gel point. Consequently, the gel point of phenol–formaldehyde resins is not well characterized in the literature and is a subject of further investigation [6]. In addition, cured resols are highly crosslinked and very brittle so that their glass transition cannot be determined with traditional thermal analysis techniques. Finally their bulk properties differ from those in a wood joint. One source of these differences is the fact that the low molecular weight fractions of the PF resin can be absorbed by the wood polymers forming intimate associations, which alter the viscoelastic performance of both the resin and the wood polymers [7]. Due to difficulties to characterize the relationship between gelation, glass transition and degree of cure, the approaches proposed by O'Brien et al. [2], Simon et al. [3], and Halley and Mackay [4] are problematic for investigating resols. Therefore, to fully characterize the PF resin cure from the fluid to solid states necessitates the use of a support. Both an impregnated, multifilament glass braid [8] and a glass cloth [9,10] have been investigated. A glass cloth impregnated with the PF resol was used to evaluate the effects of pre-treatment and *in situ* cure conditions on cure development [10]. These supports are inert to the PF resins [10] and successfully provided information regarding the cure development for the neat resins. However, it is well established that for PF resins, cure kinetics are influenced by the presence of wood [6,11,12]. In addition, the adhesive/glass cloth interface is very different from the interphase formed between PF and wood [13]. Therefore, it is important to characterize PF cure *in situ* when seeking a realistic view of adhesive bond development. Towards this end, other researchers have impregnated poplar strips [7] and sandwich specimens, composed of two wood strips separated by an adhesive layer [14,15] to study the PF cure development. A sandwich structure was favored in that the compliant adhesive layer was subjected to the maximum shear force within the specimen and thus enhancing any phase transitions [16]. More importantly, the sandwich geometry more closely resembles the practical application of the adhesives when compared to impregnated specimens. As compared with a fiber glass support, wood is a hygroscopic and viscoelastic material that can display significant variation in storage modulus (E') resulting from moisture loss and thermal softening during the DMA scans that may reach 200 °C. This condition presents a challenge to interpret the resulting DMA spectra [10].

The difference in the storage modulus ($\Delta E'$) before and after cure has been used as a criterion to evaluate the effects of resin synthesis parameters [15], bio-scavengers [17], and catalysts [18] on the rigidity of PF/wood strip sandwich joints. He and Yan [19] realized that $\Delta E'$ was affected by the wood substrate. They recommended that $\Delta E'$ should be normalized by minimum E', i.e., a parameter containing the ratio of maximum storage modulus to the minimum storage modulus. Onic et al. [18] recommended using the difference between maximum E' and that at 200 °C ($E'_{max} - E'_{200}$) for evaluating the softening and degradation of wood-adhesive joints.

It is also worthwhile to mention that the DMA signal may be dominated by the substrate, rather the resin layer depending on the ratio of the adherend (h) to adhesive (t) thicknesses. When h/t is high, the sensitivity of the beam stiffness to the presence of adhesive layer is low. Therefore, some researchers [20] have recommended a thick adhesive layer to enhance the behavior of the resin when polymer properties, not interphase behavior, are of interest. The characteristic properties associated with pure polymers may not be observed with a sandwich structure. It is important to remember that the DMA thermogram should only be interpreted as the behavior of the total joint rather than that of the polymeric resin alone [18].

Considerable interest exists in measuring the *in situ* shear properties of an adhesive when it is used in a bonded joint. Such measurements allow one to assess the state of the adhesive as a function of time and temperature. For example, during hot-pressing of wood-based composites, the wood-adhesive system experiences a thermodynamic and viscoelastic process of consolidation. The pressing time should be minimized to reduce energy use and production time while avoiding defects such as delamination during press opening. The *in situ* shear or flexural modulus of adhesive during cure is one of basic material parameters needed to construct a useful hot-pressing model. Adams and Weinstein [21] provided an analytical expression to calculate the shear modulus of the adhesive in a sandwich beam. In this solution, the adherends were assumed to be thin enough that the induced axial stress can be approximated as constant along the cross-section. Moussiaux et al. [22] provided another analytical solution to deduce the shear modulus for similar geometry. This analysis assumed that the adhesive is constrained to a thin layer at the core of a thick, bonded structure. He et al. [23] confirmed Adams and Weinstein's solution using a finite element analysis and concluded that it provided a better estimate of shear modulus than the more simplistic Moussiaux's solution. The analytical results produced significantly different values of shear modulus compared to those obtained from rheometry of neat resins evaluated in the glassy region. However, the results were in good agreements in rubbery region [23]. Miyagi et al. [24] found that the behavior of sandwich beam was linear viscoelastic. Consequently, application of the Weinstein solution to the storage modulus might be possible.

2. Objectives

Understanding cure kinetics and property development in wood/adhesive systems is important for evaluating adhesive performance, formulating new resins, and optimizing process parameters. DMA is a commonly used analytical technique for evaluating cure development of polymer systems but has not been standardized in wood adhesion research. Therefore, the objectives of this research are to:

- Explore improved techniques for directly evaluating wood-adhesive systems.
- Investigate the potential to use an analytical expression of sandwich specimens to estimate the *in situ* shear modulus development of the adhesive layer during a curing process.

3. Experimental

3.1. PF resins

Two PF resole resins, tailored as adhesives for oriented strand boards, were obtained from Georgia-Pacific Company and then frozen for storage at −20 °C until use. The low molecular weight resin (PF-low) had a weight-average molecular weight (M_w) of 621 g/mol and a polydispersity (M_w/M_n) of 1.41. The high molecular weight resin (PF-high) displayed an $M_w = 6576$ g/mol and $M_w/M_n = 1.72$. The resin solid contents were 54.5 and 45.0% for PF-low and PF-high, respectively. In addition, elemental analysis showed the presence of 3.9 and 3.7 wt% nitrogen for PF-low and PF-high, respectively, indicating the presence of urea in both systems.

3.2. Specimen preparations

Planed basswood strips (Midwest Products, Inc.) were obtained commercially. The nominal dimensions of the strips were 50 mm × 12 mm × 1 mm. The wood was oven-dried at 103 °C and stored in a desiccator over anhydrous calcium sulfate until use. Sandwich-type specimens (Fig. 1) were produced using a layer of PF resin between two wood strips. Care was taken to match the grain, thickness, and weight of the adherend pairs within the specimen to maintain a balanced composite design. The bonding surfaces were lightly hand sanded along the grain with 220-grit sandpaper and cleaned with a paper towel immediately prior to resin application. The resin was uniformly applied to the prepared surface of both wood strips using a small airbrush (BADGER Model 350). The samples were weighed before and after resin application. The amount of resin solid applied to each surface was set at ca. 50 g/m^2, which equates to ca. 12% of dried wood mass, and ca.12% moisture content of wood. Several sources of variability exist in the behavior of the resin in the wood joint. Although researchers have noted the importance of consistent resin applications [25], variability in the wood structure will also have a strong influence on the structure of the resin film as controlled by the liquid absorption into the substrate.

Maintaining a consistent resin content was deemed important to repeated cure analysis. He and Yan [19] demonstrated that the degree of resin loading can influence the cure development. They concluded that this influence occurred primarily through water absorption and evaporation during the DMA test. Therefore, other measures to maintain moisture content during the tests were investigated. These include (1) short open and closed assembly times in producing the specimens and (2) foil wrapping of the specimens for the DMA analysis.

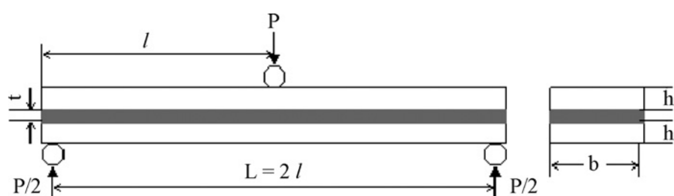

Fig. 1. The three-point bending sandwich beam, with the gray adhesive layer between two wood adherends.

3.3. DMA and rheology

DMA measurements were conducted on the sandwich specimens in three-point bending mode using either a Tritec 2000 instrument (Triton Technology) (span 25 mm) or a Rheometric RSA II DMA (span 48 mm). The frequency was fixed at 1 Hz. Strain sweep tests were conducted to establish the linear viscoelastic ranges at the working temperatures. An amplitude of the oscillation displacement of 0.03 mm was chosen for Tritec DMA and a strain of 10^{-4} for RSA II DMA. DMA was performed isothermally at 90, 100, 110, 115, 120, and 130 °C. In each test, the DMA oven was preheated to the isothermal temperature, and then the specimen was quickly installed and held at that temperature until both modulus and damping approached a constant value signifying the completion of detectable cure. The specimen was then cooled down to room temperature, and a rescan was conducted at 2 °C/min. In addition, ramp experiments were performed at heating rates of 2, 3, 4, and 5 °C/min from room temperature to 250 °C. Low heating rates were selected to minimize the effect of thermal lag.

Rheological experiments of the uncured resins were conducted on a Rheometric RDA III rheometer using the 25 mm parallel plates. A strain of 1% and linear heating rate of 3 °C/min from 25 to 200 °C were used.

4. Results and discussion

4.1. In situ shear modulus development of adhesives

An idealized sandwich specimen geometry for the three-point bending test is shown in Fig. 1. Under the forced oscillation test used by most DMA instruments, the load (P) and mid-span deflection (Δ) of the beam are out of phase by some angle δ. The storage component of the sandwich beam stiffness is given as $C' = P'/\Delta$ where $P' = P \cos \delta$. The beam stiffness can be related to the material properties and geometric variables of the adherends and adhesive using an analytical solution analog to the static mechanic solution as following [21]. In this solution, we consider the dynamic stiffness properties (K) for (1) the assembled components where shear transfer across the interface is zero and (2) the total laminate where shear transfer is complete, respectively:

$$K = E'_a I_a + 2E'_f I_f, \qquad K_T = E'_a I_a + 2E'_f I_{fa}$$

These beam stiffness equations consider the storage modulus (E') and moment of inertia values (I) of both the adhesive and adherend as represented by subscripts a and f, respectively. For the separate components, the I for the adhesive and adherend layers can be computed as $I_a = bt^3/12$ and $I_f = bh^3/12$, respectively. Likewise, the stiffness of total bonded assembly may be computed using the fictitious variable: $I_{fa} = bh^3/12 + bh(t+h)^2/4$. Applying Adams and Weinstein's sandwich beam solutions to the dynamic case at hand, the experimentally determined values for C' may be related to the shear storage modulus of the

adhesive (G'_a) through the following three equations:

$$C' = \frac{P'}{\Delta} = \frac{6K_T}{l^3(1+M)} \quad (1)$$

$$M = \frac{3(K_T - K)}{l^3 K \gamma^2}\left(l - \frac{\tanh \gamma l}{\gamma}\right) \quad (2)$$

$$\gamma^2 = G'_a\left(\frac{2K + (t+h)^2 E'_f bh}{K E'_f ht}\right) \quad (3)$$

where γ and M represents variables used to combine terms and simplify the expression without specific physical meaning. The units for γ are the reciprocal of length while M is dimensionless. Further, M will be bound by $0 \le M \le 3$ depending on the shear modulus of the adhesive layer as will be discussed later. Note that these equations assume that the adhesive layer is isotropic when relating the adhesive E and G using $E'_a = 2(1+\nu_a)G'_a$, where ν_a represents the Poisson's ratio of adhesive.

Eqs. (1) through (3) provide a means to compute the G'_a from the experimentally determined C'. Modern DMA instruments such as the Tritec 2000 and Rheometric RSA II allow storage stiffness C' to be directly output as an option. The change in C' during curing process is shown in Fig. 2 for a typical test at a linear heating rate. In addition, a number of material properties must be assumed. In our case, a constant adhesive Poisson's ratio of $\nu_a = 0.35$ and wood flexural storage modulus $E_f = 9000$ MPa at 12% MC [26] were used. For any specific specimen, the geometric variables (L, b, h, and t) are measured. With these known variables, K and K_T can then be computed. Finally, G'_a was solved using a reverse interpolation process implemented to avoid iterations. First, an assumed vector of $\bar{G}'_a$ was created (e.g., $\bar{G}'_a = [1, 100, 200, \ldots, 10^8]$ Pa). Then, the corresponding vectors $\bar{\gamma}$, $\bar{M}$, and $\bar{C}'$ were computed by sequential substitution into Eqs. (2), (3), and (1), thereby, producing a one to one mapping between values of G'_a and C'. Finally, the corresponding G'_a value for each measured C' from a scan was determined using the interpolation function within Matlab and the previously established $\bar{G}'_a$ and $\bar{C}'$ vectors. The calculated G'_a values for a representative specimen are also shown in Fig. 2. Note that

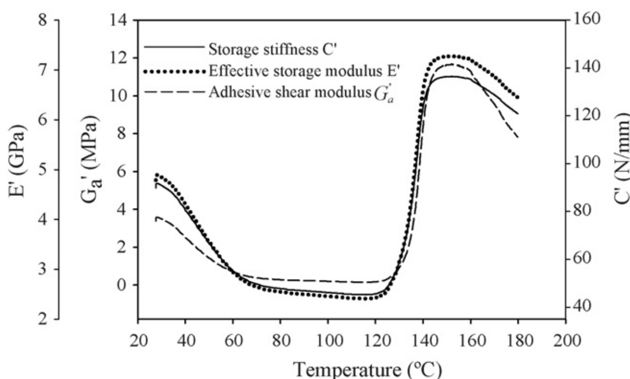

Fig. 2. A typical of DMA output. Effective storage modulus (E') and storage stiffness (C') changes with temperature during curing at 3 °C/min for a foil-wrapped PF-high bonded wood joint. Shear modulus of the adhesive layer (G'_a) was calculated with an analytical solution from C'.

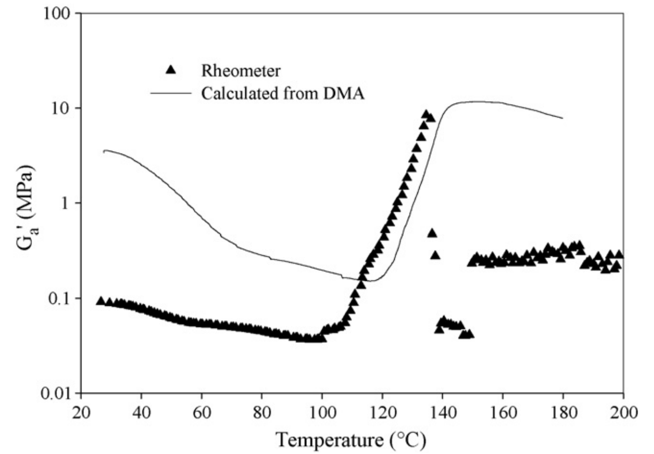

Fig. 3. Comparison of shear storage modulus (G'_a) calculated from DMA and experimental data from a rheometer at 3 °C/min.

G'_a follows the same trend as C' but has a slight difference in the slope at the beginning and final stages.

The calculated value for G'_a for this specific test changes from 0.01 to 11 MPa during the curing process for a foil-wrapped wood joint bonded with PF-high resin. This range is in general agreement with experimental data collected with a parallel-plate rheometer using the same linear heating rate, however differences exist (Fig. 3). Before the onset of the curing process, both techniques determined that G'_a decreased with temperature. However, the decrease in G'_a determined with DMA was much more pronounced than that determined using the rheometer. Recall that the beam solutions assume that the adherend modulus is constant throughout the test. The softening that occurs in the wood substrate is, therefore, combined with the resin softening. In contrast, the rheometer showed difficulty in determining a consistent value for G'_a for temperatures following vitrification. The latter difficulty is consistent with observations by others [27]. Both Laza et al. [28], and Peng and Riedl [29] also reported a similar range of G'_a for a PF resin using parallel-plate rheology. In addition, Dean et al. [30] have shown that the G'_a changes from 10^{-6} to 1 MPa for epoxy resins during curing at 150 °C (lager than its fully cured T_g). These reported values are of the same order with the calculated storage shear modulus of PF resin here and lend credibility to the results.

It was noted that the tool/machine system compliance in rheometry after vitrification leads to an effective modulus that can be significantly lower than expected, complicating the interpretation of some results in the literature [31]. If this was the case, the shear storage modulus was underestimated due to the negligible contribution of the adhesive layer to the beam stiffness in the glassy state.

Fig. 4 depicts a comparison of the G'_a development calculated from wood joints bonded with PF-low and PF-high resin and cured at an isothermal temperature of 120 °C. The G'_a of the PF-low resin developed more slowly and reached a higher value than that of the PF-high bonded wood joint. The bulk shear modulus of the fully cured PF resin was reported to be 209.9 MPa at room temperature [32], which is an order of magnitude higher than that calculated here by DMA. The discrepancy might be explained by

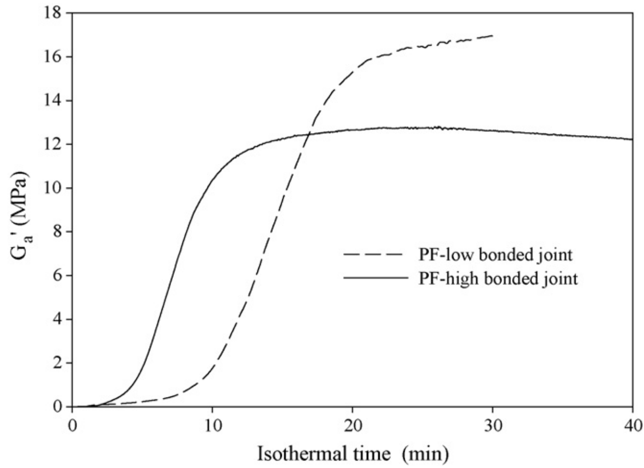

Fig. 4. Comparison of calculated G_a' for PF-low and PF-high bonded wood joints at isothermal temperature 120 °C.

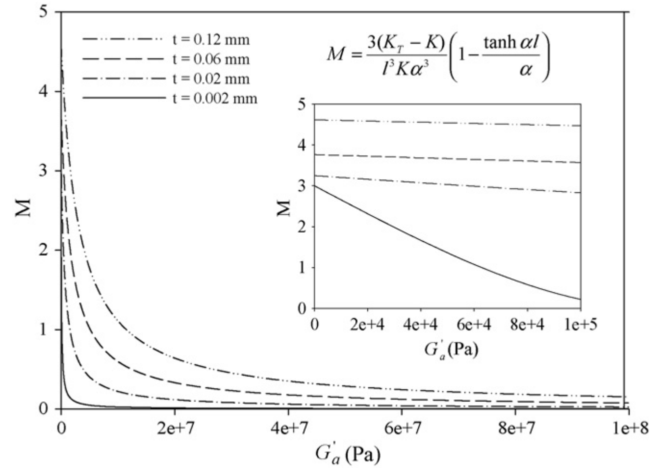

Fig. 5. The effects of thickness of the adhesive layer on the item M.

the fact that the DMA measures the *in situ* shear modulus under the effects of the elevated temperature and somewhere near or in the rubbery state. Residual stress due to shrinkage during curing or imperfection of the interphase between the adhesive and wood may also contribute to this reduction [33]. Using torsion tests on fully cured epoxy resins, Dean et al. [30] found that the shear modulus decreased from 1800 to 5 MPa while passing through the glass to rubber transition. He et al. [23] found that the shear modulus calculated with the Adams and Weinstein's Eq. (1) was in agreement with the bulk shear modulus obtained using torsion when the resin is in the rubbery state. However, the negligible contribution of the adhesive layer to the beam stiffness in the glassy state (i.e., dC'/dG_a' is very small) places doubt on the calculation [23].

4.2. Theoretical limits of the ratio $R = E'_{max}/E'_{min}$ of PF bonded joints

The accuracy of shear modulus calculation depends on the accuracy of estimating material properties and the sensitivity of the analysis to geometric variables. For instance, the wood modulus is affected by changes in moisture content and temperature during thermal scanning. In addition, the Poisson ratio of the PF resin is expected to change during the curing process where it experiences the sol, gelation, and vitrification stages. Finally, there are uncertainties in measuring the adhesive because the layer undergoes severe physical and morphological changes. Hence, the calculated shear modulus as mentioned above is merely an estimate of the interfacial shear modulus in the specimen.

During the curing process, the shear modulus of the adhesive layer changes from a minimum to a maximum as it passes from a sol to vitrified state. Let us investigate the two extreme cases of the resin in the lowest and highest shear modulus states. When the resin softens to a minimum viscosity before curing, the sandwich beam behaves as three individual beams bending about their own neutral axes, i.e., G_a' approaches zero. In this case, the variable M in Eq. (1) approaches 3 if the thickness of the adhesive layer is small (Fig. 5). This state of minimum shear modulus is referenced with the subscript 0. Hence, Eq. (1) can be simplified as follows:

$$C_0' = \frac{6(E_{a0}' I_a + 2E_{f0}' I_{fa})}{4l^3} \tag{4}$$

In contrast, when the shear modulus of the fully cured resin becomes large comparable to that of the adherend, then M approaches zero (Fig. 5) and the shear deformation of the bonded layer becomes negligible. The point of minimum shear deformation is referenced with a subscript ∞. In this case, Eq. (1) can be simplified as follows:

$$C_\infty' = \frac{6(E_{a\infty}' I_a + 2E_{f\infty}' I_{fa})}{l^3} \tag{5}$$

Now, when h/t is high and $E_f' I_f \gg E_a' I_a$, then $I_{fa} \approx bh^3/4$, i.e., assuming that the adhesive layer is in a state of pure shear and the contribution of adhesive bending to the total beam stiffness is negligible. Hence, Eqs. (4) and (5) become:

$$E_{f0}' \frac{P_0' L^3}{48\Delta_0\, 2bh^3/12} = \frac{P_0' L^3}{48\Delta_0 2I_f} \tag{6}$$

$$E_{f\infty}' = \frac{P_\infty' L^3}{48\Delta_\infty\, 8bh^3/12} = \frac{P_\infty' L^3}{48\Delta_\infty 8I_f} \tag{7}$$

Note that Eq. (6) indicates that when the adhesive shear modulus is very low and the h/t is large, the sandwich beam can be treated as two separate homogenous beams bending about their own axes. Consequently, the total flexural rigidity of sandwich beam can be reasonably approximated by the sum of flexural rigidities for the two adherends. Note also that Eq. (7) indicates that when the adhesive modulus is comparable to that of the adherend, the total flexural rigidity of the beam converges to the pure bending rigidity of the beam treating assembly as a homogeneous beam, since the shear deformation of the bonded layer becomes negligible.

For metals and other composites whose modulus is not significantly influenced by moisture and temperature, $E_{f0}' = E_{f\infty}'$. That is saying that the flexural storage modulus should not

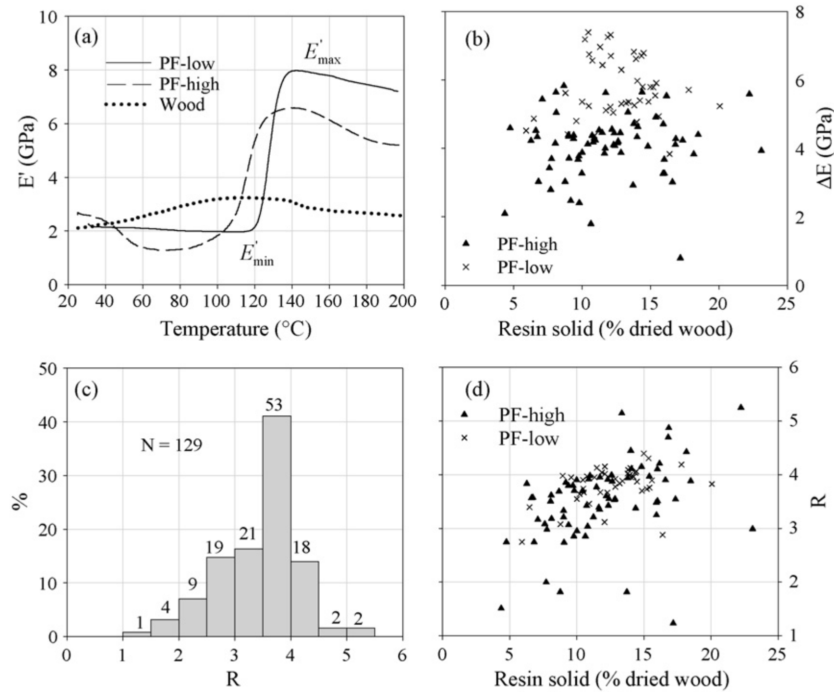

Fig. 6. Summary of effective storage modulus (E') development: (a) Typical E' development for PF-low and PF-high bonded wood joints and double pieces of wood at MC of 12%, (b) $\Delta E' = E'_{max} - E'_{min}$ vs. resin loads, (c) the histogram of $R = E'_{max}/E'_{min}$, and (d) R vs. resin loads.

change during the curing process. However, DMA uses the simple beam theory treating the three-layer sandwich structure as a solid homogeneous beam without including the contribution of the shear deformation in the adhesive. The result is an effective or nominal flexural modulus E'_0 when the shear modulus of the adhesive is in minimum:

$$E'_0 = \frac{P_0 L^3}{48\Delta_0\, 8bh^3/12} \tag{8}$$

Comparing Eqs. (7) and (8) we can deduce that the calculated effective shear modulus of the sandwich beam when the resin is at its lowest shear modulus is one fourth of its cured state ($E'_0 = E'_{f0}/4 = E'_{f\infty}/4$). This finding leads to the theoretical conclusion that the ratio of the uncured to cured modulus of the sandwich system ($R = E'_{t=0}/E'_{t=\infty}$) would be the most effective parameter to monitor for cure because this variable would eliminate variability in the adherend properties. However, this assumption is only valid if the storage modulus of the adherends does not change during curing process.

4.3. DMA derived parameters for evaluating wood-adhesive systems

In Fig. 6a, two-example cure scans depicting the ideal case where $R \approx 4$ are shown for both a PF-high and -low resin systems. For cases where the bond formation is deficient, R should vary in the following manner: $1 < R < 4$. To test this hypothesis, a histogram of experimentally determined R-values ($n = 129$) from all specimens is shown in Fig. 6c. Recall that all specimens were cured under distinct conditions and therefore are expected to lead to bonds of different quality. For these specimens 83% fell into the expected range where $1 < R < 4$, whereas the remaining 17% displayed $R > 4$.

We speculate that in some cases values for R may be elevated because the assumption that adherend properties invariant throughout the test is violated. To investigate this hypothesis, the DMA scan for two wood laminates (MC = 12%) is shown in Fig. 6a. Note that the modulus increased for temperatures less than 120 °C and then decreased somewhat for higher temperatures. This behavior likely originates from initial moisture loss followed by thermal softening. Whatever the exact mechanism, it is clear that the adherend stiffness changes during the test and that it results in a higher value at completion. Assuming that the wood completely dries during the test, the ratio of the modulus in the dry and wet states could reach ca. 1.5 [26]. Following this reasoning, R could now be considered to range accordingly: $1 < R < 4(1.5)$ or $1 < R < 6$. Note that this range is consistent with the histogram presented in Fig. 6c. In the previous paragraph, we showed that the R ratio should approach a theoretical value of four if the bond quality was perfect. Fig. 6d indicates that most R-values are indeed four or lower as expected from evaluating 129 samples that were cured under distinct conditions to lead different bond qualities. The average R-value and coefficient of variation for PF-high is 3.5 and 21%, and 3.8 and 9% for PF-low. These values indicate that PF-low leads to greater bond quality than PF-high. The difference of maximum and minimum modulus (ΔE) also demonstrated this point (Fig. 6b). However, there are some R-values beyond four. It is important to remember that the measured value of R reflects not only the change in resin modulus but also the wood adherend. Therefore, any conclusions made using this experimentally determined value should be tempered for this uncertainty.

5. Conclusion

The experiment involved measuring the bending stiffness of the sandwich beam using DMA under linear and isothermal heating regimes, and combining an analytical solution to determine the *in situ* shear modulus of the adhesive. The *in situ* shear modulus of the PF resins changed from 0.01 to around 16 MPa during the curing process and was typical of the rubber range for polymers. The measured value was in general agreement with results independently produced by parallel-plate rheometry. In practice, the DMA test was much easier to execute than the rheology test for PF resols since water vaporization induced a large shrinkage and non-uniform curing under the parallel plate, especially in the later stage of the curing process. Although the combined use of a sandwich specimen and an analytical solution to measure shear modulus development during curing of an adhesive layer is simple for both sample preparation and measurement procedure, the sensitivity of the technique is unknown. Further research should be conducted to explore the effects of experimental variables on the calculation of shear modulus.

During a DMA test of a wood-PF sandwich beam, the effective modulus E' was calculated by the instrument under the assumption of a homogeneous beam throughout the curing process. Therefore the ratio of the maximum to minimum E' (R) approaches a value of 4 in two extreme cases when the shear modulus is negligible before curing and is comparable to the adherends after curing. Experimentally, a large portion of measured values for R was near 4. The fact that the modulus of wood adherend increased from moisture lost during the test accounted for the large values of R in excess of 4. Despite this uncertainty, the ratio, R, can be used as a parameter for the direct evaluation of wood-adhesive system performance. Further, R showed some dependency on resin loading indicating that a consistent sample preparation is important for evaluating cure performance with DMA.

References

[1] R.B. Prime, Thermosets, in: E.A. Turi (Ed.), Thermal Characterization of Polymeric Materials, Academic Press, New York, 1997, pp. 435–569.

[2] D.J. O'Brien, P.T. Mather, S.R. White, Viscoelastic properties of an epoxy resin during cure, J. Compos. Mater. 35 (10) (2001) 883–904.

[3] S.L. Simon, G.B. McKenna, O. Sindt, Modeling the evolution of the dynamic mechanical properties of a commercial epoxy during cure after gelation, J. Appl. Polym. Sci. 76 (2000) 495–508.

[4] P.J. Halley, M.E. Mackay, Chemorheology of thermosets—an overview, Polym. Eng. Sci. 36 (5) (1996) 593–609.

[5] A. Lion, P. Hofer, On the phenomenological representation of curing phenomena in continuum mechanics, Arch. Mech. 59 (1) (2007) 59–85.

[6] J. Wang, Cure kinetics of wood phenol–formaldehyde system, PhD Dissertation, Washington State University, Pullman, WA, 2007, 212 pp.

[7] M.-P.G. Laborie, L. Salmen, C.E. Frazier, A morphological study of the wood/phenol–formaldehyde adhesive interphase, J. Adhes. Sci. Technol. 20 (8) (2006) 729–741.

[8] P.R. Steiner, S.R. Warren, Rheology of wood-adhesive cure by torsional braid analysis, Holzforschung 35 (6) (1981) 273–278.

[9] M.G. Kim, W.L.-S. Nieh, R.M. Meacham, Study on the curing of phenol–formaldehyde resol resins by dynamic mechanical analysis, Ind. Eng. Chem. Res. 30 (4) (1991) 798–803.

[10] R.A. Follensbee, J.A. Koutsky, A.W. Christiansen, G.E. Myers, R.L. Geimer, Development of dynamic mechanical methods to characterize the cure state of phenolic resole resins, J. Appl. Polym. Sci. 47 (8) (1993) 1481–1496.

[11] S.-Z. Chow, A kinetic study of the polymerization of phenol–formaldehyde resin in the presence of cellulosic materials, Wood Sci. 1 (4) (1969) 215–221.

[12] A. Pizzi, B. Mtsweni, W. Parsons, Wood-induced catalytic activation of PF adhesives. Auto-polymerization vs. PF/wood covalent bonding, J. Appl. Polym. Sci. 52 (13) (1994) 1847–1856.

[13] R.O. Ebewele, Differential scanning calorimetry and dynamic mechanical analysis of amine-modified urea–formaldehyde adhesives, J. Appl. Polym. Sci. 58 (10) (1995) 1689–1700.

[14] R. Garcia, A. Pizzi, Crosslinked and entanglement networks in thermomechanical analysis of polycondensation resins, J. Appl. Polym. Sci. 70 (6) (1998) 1111–1119.

[15] G. He, N. Yan, Influence of the synthesis conditions on the curing behavior of phenol–urea–formaldehyde resol resins, J. Appl. Polym. Sci. 95 (6) (2005) 1368–1375.

[16] V. Carlier, M. Sclavons, R. Legras, Supported dynamic mechanical thermal analysis: an easy, powerful and very sensitive technique to assess thermal properties of polymer, coating and even nanocoating, Polymer 42 (12) (2001) 5327–5335.

[17] S. Kim, H.-J. Kim, H.-S. Kim, H.H. Lee, Effect of bio-scavengers on the curing behavior and bonding properties of melamine–formaldehyde resins, Macromol. Mater. Eng. 291 (9) (2006) 1027–1034.

[18] L. Onic, V. Bucur, M.P. Ansell, A. Pizzi, X. Deglise, A. Merlin, Dynamic thermomechanical analysis as a control technique for thermoset bonding of wood joints, Int. J. Adhes. Adhes. 18 (2) (1998) 89–94.

[19] G. He, N. Yan, Effect of wood species and molecular weight of phenolic resins on curing behavior and bonding development, Holzforschung 59 (6) (2005) 635–640.

[20] H.W. Starkweather Jr., M.R. Giri, Use of a dynamic mechanical analyzer to study supported polymers, J. Appl. Polym. Sci. 27 (4) (1982) 1243–1248.

[21] R.D. Adams, A.S. Weinstein, Flexural stiffness of sandwich beams, J. Eng. Mater. Technol. 97 (3) (1975) 264–270.

[22] E. Moussiaux, H.F. Brinson, A.H. Cardon, Bending of a bonded beam as a test method for adhesive properties, in: A.H. Cardon, G. Verchery (Eds.), Mechanical Behavior of Adhesive Joints., Pluralis, Paris, 1987, pp. 3–25.

[23] J. He, M.Y.M. Chiang, D.L. Hunston, Assessment of sandwich beam in three-point bending for measuring adhesive shear modulus, J. Eng. Mater. Technol. 123 (7) (2001) 322–328.

[24] Z. Miyagi, S. Zaghi, D. Hunston, H. Brinson, The sandwich bending specimen for characterizing adhesive properties, in: Proceedings of the 22nd Annual Meeting of the Adhesion Society, 1999, pp. 119–121.

[25] G.D. Smith, A laboratory technique for coating strands with resin droplets of controlled size and spacing, Forest Prod. J. 53 (7/8) (2003) 70–76.

[26] Wood Handbook, Wood as an engineering material. General Technical Report 113, U.S. Department of Agriculture, Forest Service, Forest Products Laboratory, Madison, WI, 1999, 463 pp.

[27] K.P. Menard, Dynamic Mechanical Analysis: A Practical Introduction to Techniques and Applications, Published by CRC Press, 1999 (Chapter 6).

[28] J.M. Laza, J.L. Vilas, M. Rodriguez, M.T. Garay, F. Mijangos, L.M. Leon, Analysis of the crosslinking process of a phenolic resin by thermal scanning rheometry, J. Appl. Polym. Sci. 83 (2002) 57–65.

[29] W. Peng, B. Riedl, The chemorheology of phenol–formaldehyde thermoset resin and mixtures of the resin with lignin fillers, Polymer 35 (6) (1994) 1280–1286.

[30] D. Dean, R. Walker, M. Theodore, E. Hampton, E. Nyairo, Chemorheology and properties of epoxy/layered silicate nanocomposites, Polymer 46 (9) (2005) 3014–3021.

[31] K. Schroter, S.A. Hutcheson, X. Shi, A. Mandanici, G.B. McKenna, Dynamic shear modulus of glycerol: corrections due to instrument compliance, J. Chem. Phys. 125 (2006) 214507-214507-4.

[32] J.N. Lee, Q. Wu, Continuum modeling of engineering constants of oriented strandboard, Wood Fiber Sci. 35 (1) (2003) 24–40.

[33] B. Spigel, S. Roy, Comparison of the adhesive shear modulus in bulk and bonded states, J. Adhesion 47 (1994) 151–163.