Kinetic analysis of phenol–formaldehyde bonded wood joints with dynamical mechanical analysis

Jinwu Wang[a], Marie-Pierre G. Laborie[b,*], Michael P. Wolcott[b]

[a] Weyerhaeuser Company, WTC 2B2, PO Box 9777, Federal Way, WA 98063, USA
[b] Civil and Environmental Engineering, Washington State University, Pullman, WA 99164-1806, USA

ARTICLE INFO

ABSTRACT

Cure development of phenol–formaldehyde (PF) resins has been extensively modeled based on chemical advancement. However, it is *in situ* mechanical development of wood–adhesive systems that is most relevant with process optimization such as hot-pressing of wood-based panels. The objective of this research is to examine the feasibility of applying common model-fitting kinetic analyses to describe cure development based on storage modulus development recorded with dynamic mechanical analysis (DMA). Dynamic three-point bending tests were conducted on a sandwich specimens composed of two wood adherends bonded with an adhesive layer. Two commercial PF resins of different molecular weights distributions (labeled as PF-high and PF-low, respectively) were used as adhesives. In addition, PF-high bonded wood joints were also wrapped by aluminum foil to investigate the effect of moisture loss. The specimen curing process was monitored using various isothermal and linear heating regimes. The results showed that the PF-low joints cured more slowly than the PF-high joints. The foil-wrapped PF-high joints displayed slower curing process than the unwrapped joints and rendered two peaks in the tan δ curves. These peaks were attributed to gelation and vitrification, respectively. Overall, model-fitting kinetic analyses were effective to describe the mechanical development of wood–adhesive systems.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Cure development of phenol–formaldehyde resins has been extensively modeled based on chemical advancement in their neat state or in wood–resin blends [1,2]. These investigations most commonly utilize differential scanning calorimetry (DSC) to monitor the chemical advancement and are important for understanding PF resin formulations and wood–resin interactions. However, it is *in situ* mechanical development of wood–adhesive systems that is most relevant with process optimization such as hot-pressing of wood-based panels. Wang et al. [3] demonstrated that a wood–adhesive sandwich beam evaluated in dynamic three-point bending provided a basis to probe the *in situ* shear and flexural modulus development during curing process.

Whether gelation and vitrification occur during curing process depends on the curing regime and glass transition temperature (T_g) of the fully cured materials [4–6]. In base-catalyzed phenol–formaldehyde resins (resoles), the high cross-link density of the fully cured resins prohibits a straightforward detection of

its T_g. There is in the literature one report of T_g measurement in neat resoles [7]. In this work the authors demonstrated that resoles cured isothermally at temperatures up to 140 °C achieved vitrification since their final T_g reached the cure temperature. This suggests that T_{ginf} of resoles is higher than 140 °C. Other report proposed that the T_{ginf} of phenolics can reach 250 °C [8]. Studying the cure of epoxy resins with torsional braids, Enns and Gillham [9] found two peaks in the tan δ curve. The first peak was defined as gelation point and the second as vitrification. Similarly, some researchers have detected two peaks in the tan δ curve of resoles [10,11] enabling the construction of partial time–temperature–transformation cure diagrams for the PF–wood bonded joint and PF impregnated strips, respectively. Other researchers have only detected a single tan δ peak [12–14]. Most this peak has been interpreted as vitrification [12–14]. When only one peak is present, some researchers interpret the onset of increase in E' [13] or the onset of the tan(δ) rise as gelation [14]. All together this literature supports that vitrification occurs during a heating scan up to 150–200 °C.

Understanding cure kinetics and strength 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

* Corresponding author. Tel.: +1 509 3358722.
E-mail address: mlaborie@wsu.edu (M.-P.G. Laborie).

been standardized in wood adhesion research. To date, all cure kinetic analyses are exclusively used for modeling DSC data [1,2]. Model-free kinetic analysis involves evaluating a dependence of the effective activation energy on conversion or temperature and using this dependence for making kinetic predictions and for exploring the mechanisms of thermally stimulated processes [15]. For commercial PF resins, model-free kinetics has recently demonstrated excellent modeling and prediction abilities for both degree of cure and reaction rate during dynamic and isothermal cure with DSC data [2]. This algorithm should also be capable to model the mechanical degree of cure in a similar way with the chemical cure. However, model-free kinetics involves complex computations that may not be easily implemented in a comprehensive hot-pressing model of wood composites. Indeed, hot-pressing models require solving simultaneously two governing partial differential equations, one on heat transfer and one on mass transfer. As a result, an explicit cure kinetic model can be more easily incorporated into the solving process [16]. In contrast, model-fitting methods assume a definite reaction model facilitating simple computations with kinetic parameters such as activation energy, reaction order and pre-exponential factor. As such, they remain of interest when an approximate prediction of cure development is needed if the use of kinetics to decipher cure mechanism is not a major goal, and will be easily incorporated into a hot-pressing model. In this perspective, the objectives of this research are to investigate the effectiveness of DMA in characterizing the gelation and vitrification events for PF resins and evaluate model-fitting kinetics for DMA data with a view to developing a predictive mathematical tool rather than gaining insight on cure reaction mechanism.

2. Experimental

2.1. PF resins

Two PF resole resins, tailored as adhesives for oriented strand boards, were obtained from Georgia-Pacific Company, frozen and stored at $-20\,^{\circ}$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.

2.2. Specimen preparations

Planed basswood strips (Midwest Products, Inc.) with nominal dimensions of 50 mm × 12 mm × 1 mm were oven-dried at 103 °C for 24 h and stored in a desiccator over anhydrous calcium sulfate until use. Sandwich-type DMA specimens were produced from a layer of PF resin between two pieces of wood strips. Care was taken to match the grain, thickness, and weight of the two wood strips 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 amount of resin solid applied to each surface
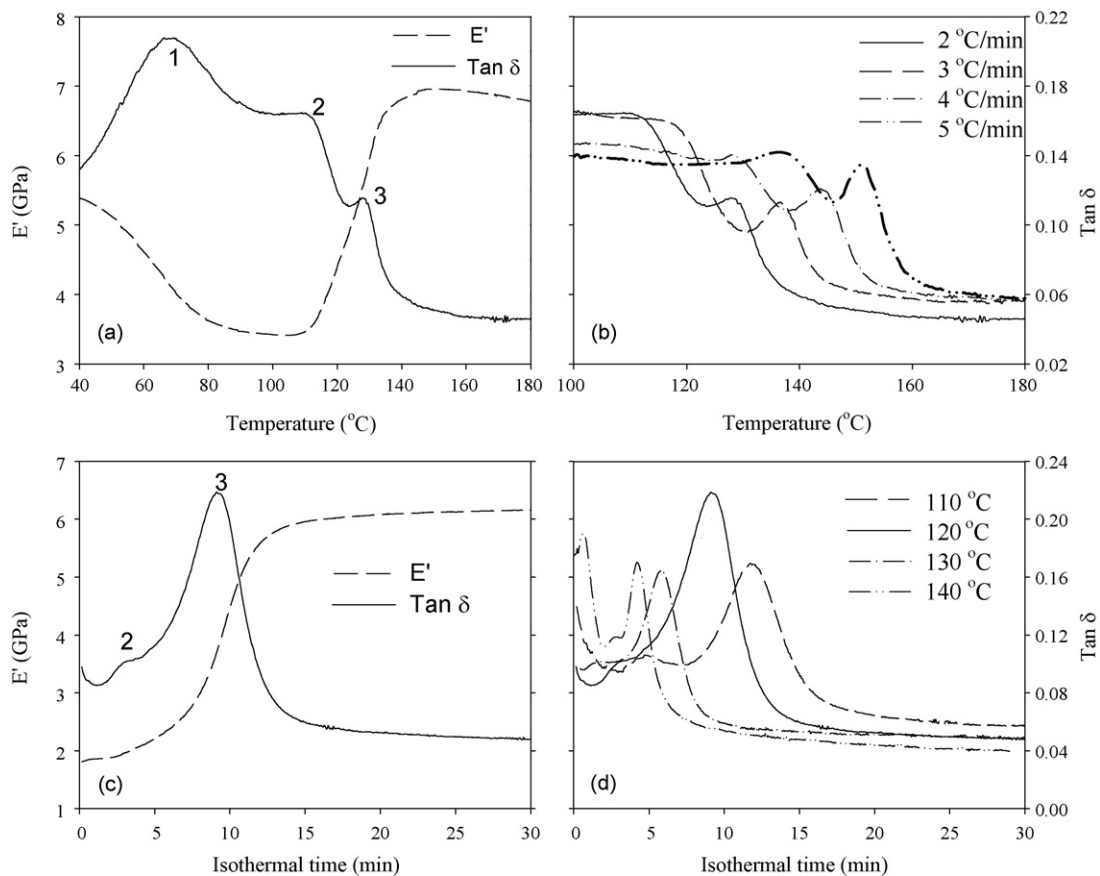

Fig. 1. The DMA cure profiles of the aluminum foil-wrapped PF-high bonded wood joints: (a) storage modulus development (E') and three peaks in tan δ showing glass transition temperature of the uncured and dehydrated PF resin or plasticized wood polymers (Peak 1), gelation (Peak 2), and vitrification (Peak 3) events at 2 °C/min; (b) gelation and vitrification temperature dependence on heating rates; (c) modulus development and gelation (small shoulder 2) and vitrification (Peak 3) in tan δ curve at 120 °C; (d) tan δ at different isothermal temperatures.

was set at ca. 50 g/m^2, which equates to ca. 12% of dried wood mass.

Maintaining a consistent resin content was deemed important for obtaining reproducible repeated cure analysis. He and Yan [13] 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.

2.3. DMA

DMA measurements were conducted on the sandwich specimens in three-point bending mode (span 25 mm) using a Tritec 2000 instrument (Triton Technology). Scans were conducted using a fixed frequency of 1 Hz under various isothermal conditions from 70 to 180 °C and thermal ramps from 2 to 5 °C/min. Low heating rates were selected to make sure that the effect of thermal lag was minimal. When conducting isothermal tests, the DMA oven was preheated to the predetermined isothermal temperature, upon which time the specimen was quickly installed. After the scan began, the oven was maintained at the cure temperature until both the E' and tan δ approached a constant value signifying the completion of detectable cure. The specimen was then cooled to room temperature, and re-scanned at 2 °C/min. Strain sweep tests were conducted to establish the linear viscoelastic ranges at each working temperature. Typical strain settings ranged from 1 to 2×10^{-4}.

3. Results and discussion

3.1. Effect of wood adhesive joint preparation on DMA thermograms

The representative changes for E' and tan δ with temperature is represented in Fig. 1a for a typical aluminum foil-wrapped PF-high bonded wood joint cured at 2 °C/min. Three distinct zones were observed from E' curve: thermal softening of uncured wood–resin system, resin curing, and thermal softening of cured wood–resin system. Upon application of the liquid PF resin to the dry wood surface, water is absorbed by the wood causing the adhesive layer to become semi-solid at room temperature. In this state, the adhesive can transfer partial shear forces between two pieces of wood. With increasing temperature, the resin–wood system gradually softens and the E' decreases reaching a minimum E' plateau. This event appears on tan δ curve as the first peak centered at ca. 50–70 °C (Fig. 1a). It may be ascribed to the glass transition temperature of the uncured PF resin [17] or to wood lignin that is known to soften in this temperature range when plasticized [18]. After this point, the E' reaches a minimum plateau corresponding to a competitive relationship between the resin softening and curing during the heating process. With the subsequent increase in E', the resin cure began to outpace the softening. For convenience, the onset of storage modulus rise (E'_{min}) is defined here as the onset of the mechanical cure ($\beta = 0$). Shortly after E'_{min}, a second peak is evident in tan δ (Fig. 1a). Although a subject of controversy, this second peak is taken to be the gelation point, where the cross-links progressed to form an infinite molecular weight network [9]. When only a single peak is evident in the tan δ curve, gelation was similarly defined by temperature corresponding to the onset of increase in E' since two points almost occurred at same temperatures.

Finally, the third peak in the tan δ curve was defined as the vitrification point, i.e. the attainment of a glass state where the glass transition temperature of the forming polymer reached the oven cure temperature as proposed in previous work [9,12,14]. This peak also describes the transition temperature of the mechanical properties of network where maximum rate of the mechanical curing development occurred. The attained maximum, E'_{max}, may represent progressive degradation of wood substrate or differential expansion between resin and wood and ever-increasing cross-linked resin [19].

Typical plots of the E' and tan δ of the foil-wrapped PF-bonded wood joints as a function of the time during isothermal cure were presented in Fig. 1c and d. The E' curve displayed a sigmoidal shape while the tan δ exhibited two peaks followed by a decrease toward an asymptotic limit. The first shoulder (Peak 2) is ascribed to gelation and Peak 3 is again present and ascribed to vitrification. As expected, gelation and vitrification points move to lower cure time as the cure temperature is increased (Fig. 1d). At 120 °C, it required around 20 min to complete the cure for foil-wrapped PF-high bonded joints. This state was confirmed by re-scanning the cured sample where no secondary curing was detected.

However, the gelation point detected in the isothermal cure regime appears only as a small shoulder (Fig. 1c) and cannot be reproducibly quantified in some samples. It was assumed that the sudden temperature increase from room temperature might account for this problem because gelation could occur while the instrument established equilibrium. Therefore, the isothermal temperatures were limited to below 180 °C. When temperature was higher than that, raw data was not clean. Thus, caution should be exercised when extrapolating beyond the experimental conditions.

Next we evaluate the cure development for PF-bonded joints when foil-wrapping was not used and therefore moisture evaporated during the DMA scan, Typical tan δ traces for PF-low bonded wood joints are shown in Fig. 2. Without the aluminum foil-wrap, only one tan δ peak is recorded and it is ascribed to the vitrification. For unwrapped samples, the gelation peak was not evident both under linear heating and isothermal regimes. It was assumed that rapid moisture loss in the unwrapped samples was responsible for unrecorded gelation peaks.

3.2. Mechanical cure development

Using DMA, the degree of mechanical cure (β) can be defined [20] as

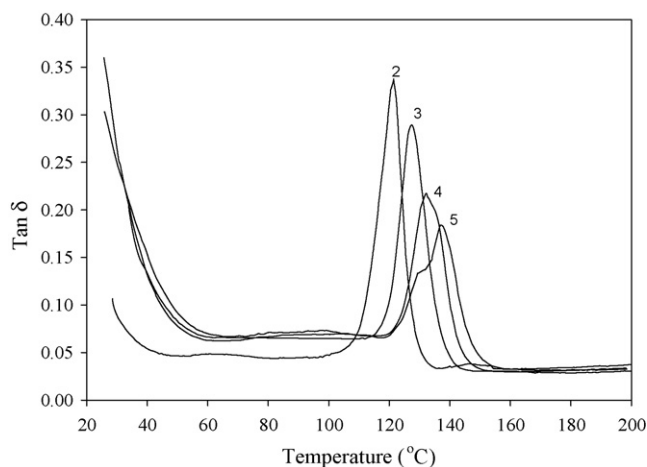$$\beta = \frac{E'(t) - E'_{min}}{E'_{max} - E'_{min}} \tag{1}$$

Fig. 2. DMA tan δ traces for PF-low bonded wood joints (without foil-wrapping) at different heating rates designated on the curves (°C/min). Only vitrification has been recorded at all heating rates.

Table 1
Characteristic temperature (°C) at different heating rates and corresponding mechanical degree of cure for the aluminum foil-wrapped PF-high bonded wood joints.

Heating rate (°C/min)	2	3	4	5
Gelation temperature (°C)	112	120	129	138
β at the gelation	0.04	0.04	0.03	0.04
Vitrification temperature (°C)	129	137	147	151
β at the vitrification	0.58	0.60	0.62	0.64

Table 2
Vitrification time (min) at different isothermal cure temperatures and corresponding mechanical degree of cure for the aluminum foil-wrapped PF-high bonded wood joints.

Isothermal cure temperature (°C)	90	100	110	120	130
Time at the vitrification (min)	30.3	16.0	11.0	9.6	5.8
β at the vitrification	0.34	0.50	0.52	0.55	0.58

where $E'(t)$ is the storage modulus at time t. According to this definition, mechanical degree of cure at gelation and vitrification points is shown in the Tables 1 and 2.

Gelation and vitrification temperatures at different ramp rates and under isothermal cure regimes are also summarized in the tables for the aluminum foil-wrapped PF-high bonded wood joints. The gelation point defined by second peak on tan δ curve (Fig. 1a) was very close to the onset of mechanical cure as evidenced by small value for β. Vitrification occurred at higher mechanical degrees of cure with increasing cure temperatures. Such a result was reasonable since at high temperature, the resin needed to reach a high degree of cure to achieve a glass transition to exceed the cure temperature.

Note also that the β for gelation is constant regardless of the heating rate which supports the assignment of the underlying peak to gelation since it is expected to be an isoconversional event. In contrast for vitrification β varies with cure temperature, an observation that is again in line with the non-isoconversional nature of vitrification.

The effects of foil-wrapping on the mechanical cure development of PF-high bonded wood joints cured under linear heating and isothermal regimes are shown in Figs. 3 and 4, respectively. Assuming that the primary influence of the foil-wrap is to limit moisture loss in the specimen, the cure development appears to be determined by at least two processes: moisture loss and resin cross-linking. Therefore, it is the superposition of these two processes that dictate mechanical cure development, especially during early stages for unwrapped samples. Under linear heating regimes,
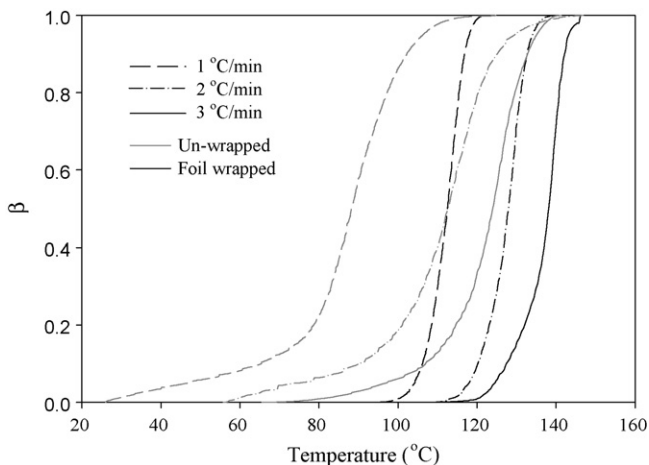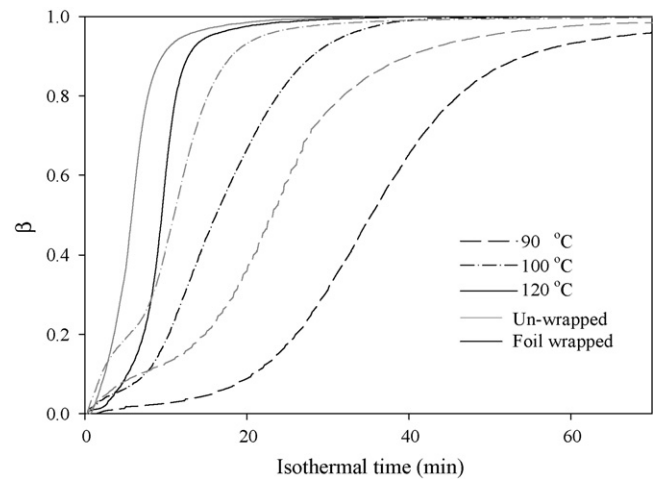

Fig. 4. The effects of foil-wrapping on the mechanical cure development under isothermal regime for the PF-high bonded wood joints.

the foil-wrapping delays the beginning of cure as well as the peak temperature. The long initial tail in the storage modulus curves of unwrapped PF-high bonded samples likely results from both moisture loss and resin curing. It is assumed that the abrupt inflection represents a shift to a process dominated by resin curing. Under isothermal temperature, moisture loss promoted a fast initial mechanical cure as compared with foil-wrapped PF-high bonded joints. However, these specimens experienced a plateau in the rising E' which was likely associated with the shifting mechanisms.

In Fig. 5, it is shown that under the linear heating regime the unwrapped PF-high bonded wood joints begin curing at a lower temperature than PF-low bonded joints. These specimens were also observed to cure faster at the same isothermal temperature. It seems that the effect of moisture loss on cure development of PF-high bonded joints is larger than that on PF-low bonded joints. However, we note that the interaction between water and the PF-high resin is weaker than that between water and PF-low since PF-high is more advanced and has less hydroxyl groups available. Thus the moisture in the PF-high bonded adhesive layer is less restricted and evaporated at lower temperature and faster than in the PF-low bonded adhesive layer. This potential moisture influence simply adds to the demonstrated increased cure rate of the PF-high resin when compared to the PF-low [2]. Despite the difference in initial cure rate between the PF-high and PF-low bonded joints, they
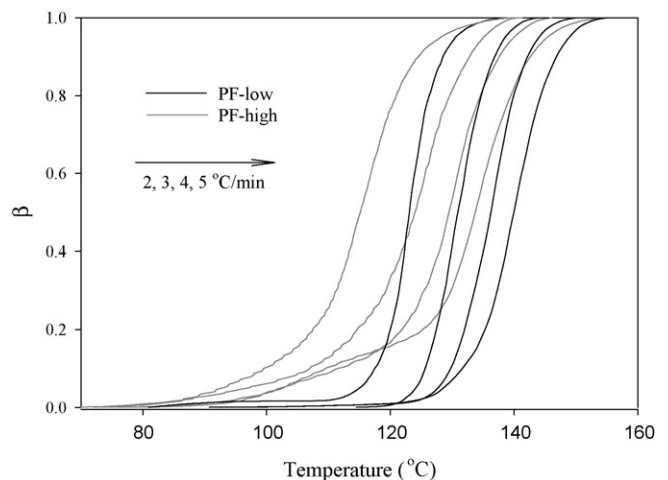

Fig. 3. The effects of foil-wrapping on the mechanical cure development at linear heating rate for the PF-high bonded wood joints.

Fig. 5. Comparison of the mechanical cure development at linear heating rate between the PF-high and PF-low bonded wood joints.
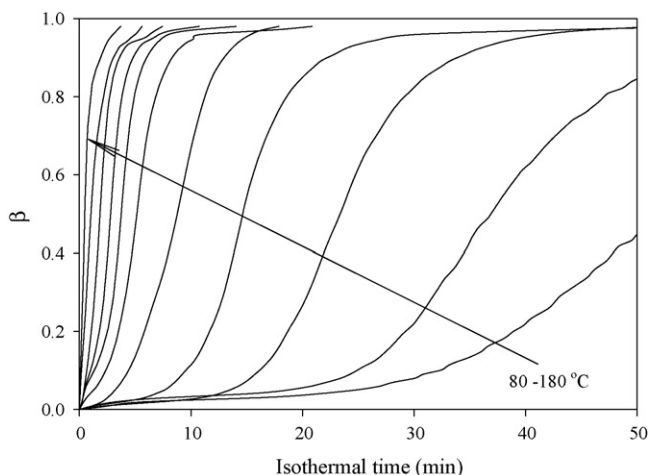
Fig. 6. An example of cure development under isothermal temperatures for unwrapped PF-low bonded wood joints.

Table 3
Summary of parameters for Prout–Tompkins model under different heating regimes.

	Parameters under isothermal	Parameters under linear heating rate (ϕ)
	$\beta = \frac{1}{1+\exp(k(t-t_0))}$ $k = A\exp(-E/R(T+273))$	$\beta = \frac{1}{1+\exp(T_0 - T/k_T)}$
PF-low	$\ln(t_0) = -0.0447T + 19.812$ (min) $E = 53.3$ (kJ/mol) $\ln(A) = 11.68$ (1/s)	$T_0 = 5.59\varphi + 113.01$ $k_T = 2.73$ (0.23)
PF-high	$\ln(t_0) = -0.0366T + 16.182$ (min) $E = 49.6$ (kJ/mol) $\ln(A) = 10.59$ (1/s)	$T_0 = 6.24\varphi + 104.21$ $k_T = 5.64$ (0.27)
PF-high, foil-wrapped	$\ln(t_0) = -0.0409T + 18.392$ (min) $E = 49.8$ (kJ/mol) $\ln(A) = 8.85$ (1/s)	$T_0 = 11.93\varphi + 101.76$ $k_T = 3.00$ (0.19)

All regression $R^2 > 0.96$; T: temperature in °C; φ: heating rate in °C/min; number in parentheses is standard deviation.

appear to reach full mechanical cure at same temperature under linear heating regime. This observation is also consistent with the results characterized by DSC [2]. In summary, PF-low bonded wood joints cured more slowly than PF-high bonded joints, while foil-wrapped samples of PF-high bonded joints reduced the cure rate to the similar extent comparable to that of PF-low bonded joints.

3.3. Model-fitting kinetics

It was observed that the E' development under an isothermal cure regime followed a sigmoidal shape as illustrated in Fig. 6 for a PF-low bonded wood joint. The Prout–Tompkins (Eq. (2)) was used to fit the curve at each curing regime [21]

$$\frac{d\beta}{dt} = k\beta(1 - \beta) \tag{2}$$

where $d\beta/dt$ is rate of mechanical cure; k is rate constant.

The advantage of the Prout–Tompkins is that it can obtain explicit equations for the degree of cure at specific cure times (Eq. (3)). Therefore, Eq. (3) can be used to directly fit the experimental data under isothermal cure regimes.

$$\beta = \frac{1}{1 + \exp(k(t - t_0))} \tag{3}$$

In addition, Eq. (3) can be rewritten into Eq. (4) for describing mechanical cure development under a linear heating regime.

$$\beta = \frac{1}{1 + \exp\left(T_0 - T/k_T\right)} \tag{4}$$

where T is temperature in °C; T_0 and k_T are two fitting constants. The variables required to conduct an isothermal kinetic analyses include β and t under isothermal conditions, and β and T under a linear heating regime. These data are then tested for fitting accuracy to the model. A non-linear regression with Levenberg–Marquardt algorithm [22] was used to extract constants using the explicit equation forms found in Eqs. (3) and (4). For each individual temperature program, the model fits the data very well with $R^2 > 0.96$.

The constants of the Prout–Tompkins model for the PF-low, PF-high, and foil-wrapped PF-high bonded wood joints are summarized in Table 3 for both the isothermal and linear heating regimes. The Prout–Tompkins constants t_0 and T_0 change with time and temperature. With these models and extracted parameters, the mechanical cure development can be readily described for both the isothermal and linear heating rate regimes and can be incorpo-

rated into other kinds of models where resin curing as a constitutive part.

4. Conclusion

The transition temperatures of the curing process and cure development could be assigned to storage modulus changes or to tan δ. The reproducibility among samples for recording curing process was good although the variations of sample preparations affected the glass transition temperature of uncured wood–adhesive systems. Vitrification was probed in all samples, while gelation point was only detected for foil-wrapped wood joints under linear heating regime. It is assumed that moisture loss in unwrapped joints muffled the gelation points. DMA mechanical cure development showed that the PF-low bonded wood joints cured slower than PF-high bonded wood joints. Foil-wrapping retarded moisture loss and delayed mechanical degree of cure for PF-high bonded wood joints.

Model-fitting kinetics of Prout–Tompkins was selected to model mechanical cure development since the E' development followed a sigmoid. The model is capable to describing cure development.

References

[1] G. He, B. Riedl, Wood Sci. Technol. 38 (2004) 69–81.
[2] J. Wang, M.-P.G. Laborie, M.P. Wolcott, Thermochim. Acta 439 (2005) 68–73.
[3] J. Wang, M.-P.G. Laborie, M.P. Wolcott, Thermochim. Acta 465 (2007) 18–24.
[4] K. Hofman, W.G. Glasser, Thermochim. Acta 166 (1990) 169–184.
[5] X. Ramis, A. Cadenato, J.M. Morancho, J.N. Salla, Polymer (2003) 2067–2079.
[6] G. Wisanrakkit, J.K. Gillham, J.B. Enns, J. Appl. Polym. Sci. 41 (1990) 1895–1912.
[7] R.G. Schmidt, C.E. Fraizier, Int. J. Adhes. Adhes. 18 (1998) 139–146.
[8] T.N. Morrison, Practical Guidelines for the Efficient Postbaking of Molded Phenolics By Plastics Engineering Co. Thermosets 2004, the Soc. Plastics Engineers Itasca, Illinois.
[9] J.B. Enns, J.K. Gillham, J. Appl. Polym. Sci. 28 (1983) 2567–2591.
[10] R. Garcia, A. Pizzi, J. Appl. Polym. Sci 70 (1998) 1111–1119.
[11] M.-P.G. Laborie, Ph.D. Thesis, Virginia Tech, VA, 2002.
[12] M.G. Kim, W.L.-S. Nieh, R.M. Meacham, Ind. Eng. Chem. Res. 30 (1991) 798–803.
[13] G. He, N. Yan, Holzforschung 59 (2005) 635–640.
[14] G. He, B. Riedl, J. Polym. Sci. B: Polym. Phys. 41 (2003) 1929–1938.
[15] S. Vyazovkin, N. Sbirrazzuoli, Macromol. Rapid Commun. 27 (2006) 1515–1532.
[16] B.G. Zombori, F.A. Kamke, L.T. Watson, Wood Fiber Sci. 35 (2003) 2–23.
[17] B.-D. Park, X.-M. Wang, Thermochim. Acta 433 (2005) 88–92.
[18] S.S. Kelley, T.G. Rials, W.G. Glasser, J. Mater. Sci. 22 (1987) 617–624.
[19] L. Onic, V. Bucur, M.P. Ansell, A. Pizzi, X. Deglise, A. Merlin, Int. J. Adhes. Adhes. 18 (1998) 89–94.
[20] G. Vazquez, F. Lopez-Suevos, J. Gonzalez-Alvarez, G. Antorrena, J. Therm. Anal. Calorim. 82 (2005) 143–149.
[21] M.E. Brown, Thermochim. Acta 300 (1997) 93–106.
[22] P.E. Gill, W. Murray, SIAM J. Numer. Anal. 15 (1979) 977–992.