J Wood Sci (2013) 59:262–268
DOI 10.1007/s10086-013-1329-3

NOTE

Dynamic wettability and curing characteristics of liquefied bark-modified phenol formaldehyde resin (BPF) on rice straw surfaces

Ming-Yu Wen · Jun-You Shi · Hee-Jun Park

Received: 12 May 2012 / Accepted: 28 January 2013 / Published online: 5 March 2013
© The Japan Wood Research Society 2013

Abstract Larch bark was liquefied in the presence of phenol and the obtained liquefied resultant was reacted with formaldehyde to prepare the liquefied bark-modified phenol formaldehyde resin (BPF) in an attempt to apply for preparing straw boards. The dynamic wettability of the BPF resin was evaluated on the surfaces of rice straw; either on the alkali solution treated or untreated rice straw surfaces. A new wetting model was employed to quantify the resins' penetration performances using the spreading–penetration parameters (K value) as a constant to characterize penetration rate. The bigger the K value was, the stronger the penetration and spreading capacity was. Moreover, the curing kinetics of the BPF resin was also investigated with dynamic differential scanning calorimetry. The results showed that the K value of BPF resin was the highest, followed by those of BPF mixed with polymethylene diphenyl diisocyanate PMDI resin and conventional phenol formaldehyde (PF) resin, indicating that the BPF resin had the best wettability. The activation energy of BPF was close to that reported for wood/phenol/formaldehyde resins, but was higher than that of PF resin. The curing reaction was almost complete at 40 % conversion.

M.-Y. Wen · H.-J. Park (✉)
Department of Housing Environmental Design, Research Institute of Human Ecology, College of Human Ecology, Chonbuk National University, 567 Baekje-daero, Deokjin-gu, Jeonju-si, Jeollabuk-do 561-756, Korea
e-mail: jlwenmingyu@hotmail.com

J.-Y. Shi
Key Laboratory of Jilin Province of Forestry and Ecological Environment, Wood Science and Technology Department, Forestry College, Beihua University, Jilin 132013, China

Keywords Liquefied bark-modified phenol formaldehyde resin (BPF) · Straw · Wettability · Curing kinetics

Introduction

Phenol formaldehyde resin (PF) is one of the most widely used wood adhesives. The constant rise in oil prices and decreasing fuel energy led to the development of replacement materials from natural resources in the wood adhesive industry. Many efforts have been devoted to the phenolation of wood waste in the presence of various catalysts and application of phenolated wood to adhesives [1–5]. Some researchers have studied the modification of PF using biomass materials such as lignocellulosics. Wood bark is an excellent renewable resource for replacing phenolic compounds. Tannin, which is concentrated in the inner layer of the bark, has been utilized in the adhesive industry in Africa, South America, and Oceania [6]. Also, lignin in the wood has been studied as a substitute for phenol in the synthesis of PF resin since its structure is similar to that of phenol. Moreover, lignin is the most susceptible wood component to the liquefaction reaction [7, 8].

Wood bark, as a major source of forest residue, constitutes a considerable volume of a tree, normally ranging from 9 to 24 % depending on the species and diameter. It has a great deal of lignocellulosic potential because it contains various natural polymers, such as lignin, cellulose, condensed tannin, and resin acid. The increasingly scarcity of wood resources enables us to consider all possible methods of utilizing bark residue as raw material. Many studies have investigated bark utilization [9, 10]. Alma and Yoshioka [11] studied the phenolation of bark

from several species in the presence of sulfuric acid, and then used this liquefaction method to prepare novolak resin-type molding materials. Pan [12] liquefied Chinese tallow tree sawdust using phenol as a solvent under different conditions and synthesized a novolak-type liquefied wood/phenol/formaldehyde (LWPF) resin, then used this resin to prepare a bio-composite. It was found that the liquefied wood could partially substitute for phenol in composite synthesis applications and the resultant bio-composites exhibited desirable physical and mechanical properties. Furthermore, it was found by dynamic DSC analysis that the activation energies of the LWPF resin were higher than that of conventional PF resin.

The chemical components of rice straw are similar to those of wood including cellulose, hemi-cellulose, lignin, and extractives. Whereas, there is high silicon and wax content concentrated on the exterior surface of rice straw, forming the bonding barrel. Adhesive wettability is the ability of an adhesive to make contact with a surface. Most previous studies focused on the wettability of wood by determining the instantaneous or equilibrium contact angles at the solid/adhesive interface [13–15] using the Young equation. However, the wetting process includes the formation of a contact angle at the solid/adhesive interface, the spreading of adhesive on the solid surface, and adhesive penetration into the porous solid substrate. Therefore, it is essential to measure the contact angle change as a function of time to evaluate substrate wettability. Shi and Gardner [16] developed a new wetting model to quantify the spreading and penetration ability using the spreading–penetration parameters (K value) to represent how fast the liquid spreads and penetrates into the porous substrate. Then, the model was applied to compare the adhesive wettability between two resins, along and cross grain, as well as that of the sapwood and heartwood of Southern pine and Douglas fir. Liu [17] also applied the wetting model to evaluate the wettability of different resins on untreated and treated wheat straw surfaces.

In this paper, larch bark was liquefied in the presence of phenol and the obtained liquefied resultant was reacted with formaldehyde to prepare the liquefied bark-modified phenol formaldehyde resin (BPF) for preparing straw boards. The objectives of this study were first to investigate the dynamic wettability of BPF resin on rice straw surfaces (untreated and treated, exterior and interior), compared to that of BPF resin mixed with PMDI and the conventional PF. Second, the cure kinetic of BPF resin is investigated with dynamic DSC using the Kissinger equation with an object to get curing reaction characteristic and provide a theoretical basis for using BPF to prepare rice straw-based panels.

Materials and methods

Materials

Larch bark was purchased from Yakeshi Forestry Bureau; holocellulose, cellulose, lignin and tannin content was determined as 41.9, 24.9, 19.5 and 6.0 %, respectively, for inner larch bark, and 40.8, 23.0, 38.6 and 16.0 % for outer larch bark (Yuan JL, unpublished data). The larch bark was oven-dried at 80 °C, passed through an 80-mesh sieve, and then dried in an oven at 105 °C and kept in desiccators at room temperature before use. Liquid industry-grade phenol (90 % concentration) was used as liquefaction reagent. Sulfuric acid was used as catalyst. PMDI (5091#) was purchased from Huntsman Co., Ltd, Shanghai. Conventional phenol formaldehyde resin was used as comparison, with the molar ratio of 2.1/1 and 0.29/1 for formaldehyde/phenol and sodium hydroxide/phenol, respectively. All the other chemicals were reagent-grade.

Larch bark liquefaction and synthesis of liquefied bark modified phenol formaldehyde resin

Larch bark powder, phenol (phenol/bark = 3/1 w/w) and sulfuric acid (5 % w/w phenol) were mixed thoroughly in a four-branch flask equipped with a stirrer, thermometer, reflux condenser and dropping funnel. The flask was immersed in an oil bath preheated at 150 °C. After 60 min liquefaction, the flask was immersed in cold water to yield liquefied larch bark. A small amount of the reactant was diluted by acetone, and then the diluted resultant was separated to residue and dissolved resin through vacuum-filter. The residue was dried at 105 °C to a constant weight. The residue rate of larch bark was calculated by the following equation:

$$\text{Residue content } R\ (\%) = (W_r - W_o) \times 100$$

where W_r is the oven-dried weight of larch bark residue (g) and W_o is the original weight of bark meals.

After obtaining the liquefied larch bark product (residue 8 %, combined phenol 25.2 %), 300 g liquefied larch bark, 419 g formaldehyde (36 % aqueous solution) and 191 g sodium hydroxide aqueous (40 % concentration) were prepared for BPF resin. First, liquefied larch bark, two-thirds of formaldehyde and one-third of sodium hydroxide aqueous were charged into flask and temperature gradually increased to 85 °C. This temperature was maintained for 25 min. Then, one-third of the remnant formaldehyde was loaded into the reactant and two-thirds of sodium hydroxide aqueous was gradually dropped into the reactant, also additional water was added. The reaction was continued at the temperature of 75–80 °C to the desired viscosity, and then the resulting resin was cooled to 40 °C. The gel time

and free formaldehyde was determined as 315 s and 1.89 %.

In this study, it is in attempt to use the BPF to prepare straw board. And PMDI presented excellent adhesion for straw materials, therefore it is considered to apply appropriate PMDI when using BPF in order to get better bonding strength. Based on resin spreading when preparing straw board, 16 and 0.5 % for BPF and PDMI based on the dry straw (the mass ratio of BPF to PMDI is 32/1) were mixed together. The major specifications of resins are shown in Table 1.

Rice straw treatment

The rice straw was obtained from outside Jilin City. A 0.5 % (wt) diluted alkali (NaOH) solution was sprayed on the straw surface at a solution to straw mass ratio of 1:1, at which the straw particle could be wetted adequately. The straw was conditioned for 8 h to saturate the surface then oven-dried to a moisture content of 4 %.

Contact angle measurement

Resin type: BPF, BPF–PMDI, PF.

Dimension of straw specimen: 2 mm × 5 mm.

Drop volume: 5 μl.

Drop location: the exterior and interior surfaces of untreated and treated rice straw surfaces along the grain direction.

The contact angles were measured using a JC2000, and the images were captured and saved every 2 s. Four drops were observed for each recorded drop datum, and five replicates were performed for each sample. The K values were obtained using the wetting model equation [16]:

$$\theta = \frac{\theta_i \cdot \theta_e}{\theta_i + (\theta_e - \theta_i)\exp\left[K\left(\frac{\theta_e}{\theta_e - \theta_i}\right)t\right]} \quad (1)$$

where θ_i is initial contact angle, and θ_e is equilibrium contact angle.

Differential scanning calorimetry (DSC) analysis

A Perkin Elmer DSC7 was used for DSC analysis. About 10–15 mg of BPF, BPF–PMDI, and PF resin were put into an aluminum sample pan and sealed. Dynamic scan was conducted with heating rates of 2.5, 5, 10, and 15 °C/min in a scanning temperature range from 20 to 200 °C. The Kissinger equation was employed to calculate the activation energy of the adhesives.

$$-\ln\frac{\beta}{T_p^2} = \frac{E}{R}\cdot\frac{1}{T_p} - \ln\left(\frac{RA}{E}\right) \quad (2)$$

where β is the heating rate (K/s), T_P is the peak temperature (K) at a given heating rate, A is the pre-exponent factor, R is the gas constant, and E is the activation energy. The plot of $\ln\beta/T^2$ versus $1/T$ is a straight line, in which β is the heating rate and T is the temperature at the conversion of α. The activation energy at the conversion of α can be obtained from the slope of the line.

Results and discussion

Wettability of adhesives on straw surfaces

Morphologically, as lignocellulose material, straw is more complicated than wood. Straw contains other elements, including the actual fibers, parenchymal cells, vessel element and epidermal cells, which contain a high amount of ash and silica [18]. The epidermal cells are the outmost surface cells, covered by a thin wax layer. Since the wax layer consisted of lipophilic substance such as fatty acid aliphatic alcohol, it could be examined indirectly by measuring the content of benzene–alcohol extractives and an extractive content of 2.98 % was reported [19]. In our previous study, the exterior surfaces of the treated and untreated straw were scanned by means of FTIR and the figures were shown in Fig. 1. It was found that the adsorption peak were changed board in the region of 3400 cm^{-1} which was assigned to the stretching of –OH group easily being found in cellulose, lignin and aliphatic fraction of waxes. It meant

Table 1 Specifications of resins used in the experiments

Specification	Resins used in the experiments			
	BPF resin	PMDI	BPF–PMDI mixture[a]	PF
Color	Dark red to black	Dark brown	Dark red to black	Pale red-brown to maroon
Nonvolatile content (%)	50	100	53	48
pH value	11.56	7.86	11.61	11.45
Viscosity (mPa s)/20 °C	430	315	685	325

[a] The mass ratio of BPF to PMDI is 32:1 (the glue spreading of BPF is 16 and PMDI is 0.5 % based on the absolute dried rice straw)

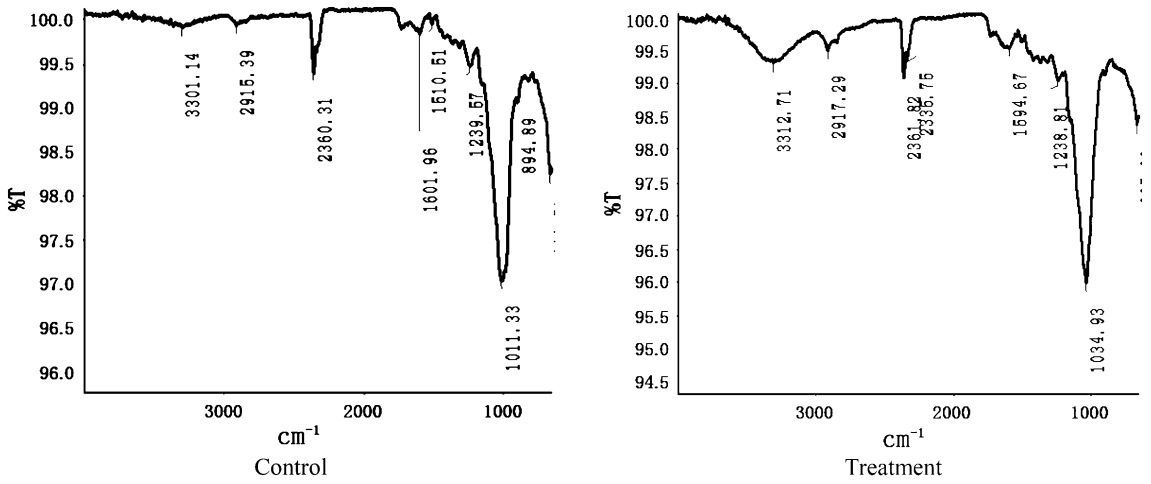


Fig. 1 FTIR spectrum of straw exterior surface without and with treatment

that the –OH group was more exposed resulting from the diluted alkali partially destroying the wax layer. A strong adsorption peak at 1035 cm^{-1} was assigned to the C–O stretching in cellulose, hemicelluloses and lignin; in the region of 1300–1000 cm^{-1}, assigned to Si–O and O–Si–O stretching [19]; the peak at 1238 cm^{-1} was weak, indicating that the silicon layer could be partially removed. It implied that the diluted alkali treatment method was effective in partially decomposing cellulose and lignin and removing and destroying wax layer and silicon substance.

Table 2 and Fig. 2 show the contact angle changes as a function of time for different surfaces of rice straw. BPF resin exhibited better wettability on all surfaces, regardless of whether the rice straw was treated or untreated. The *K* value of BPF resin was two to three times greater than that of others, which was consistent with the fact that BPF resin also had a greater percent decrease in the contact angle from the initial measurement to equilibrium (15.2–25.0 %) compared to BPF–PMDI (8.3–13.4 %) and PF (5.5–8.2 %). It is reported that the PMDI had a lower surface tension (41.2 MJ/m^2) than other resins, and according to the Young equation, a higher solid surface tension or lower liquid surface tension will result in a lower contact angle. Therefore, it seems reasonable that when BPF resin was mixed with PMDI, the adhesive would exhibit better wetting performance than BPF resin alone. However, unexpectedly, the *K* value of the BPF resin was significantly higher than that of BPF–PMDI. The explanation for this behavior likely involves factors related to the reaction between BPF and PMDI when they were mixed. Therefore, in view of employing PMDI to enhance bonding strength of straw bond, it is recommended that PMDI is spread first and then the BPF resin rather than spreading the resin by mixing both together.

In the larch bark liquefaction, using strong acid as catalyst can promote degradation of wood lignocellulose and reduce its molecular weight, thus facilitating bark liquefaction and introducing phenol into the side chain portion of the lignin and degrading the polysaccharide during phenolysis. Consequently, the process enhanced the reactivity of bark toward formaldehyde [9]. Therefore, due to the higher reactivity, milder resinification condition was employed to prepare BPF with desire properties. The relatively lower viscosity could be one of the reasons responsible for the better wettability.

Furthermore, the *K* values of the interior surfaces were slightly higher than those of the exterior surfaces. Meanwhile, for all the resins, the *K* values of the surfaces treated with alkali solution were higher than those of untreated surfaces. As stated above, this is attributed to the chemical changes on the surface of straw, especially the exterior surface. The existence of wax and silica layer results in a low surface polarity, and a subsequently low compatibility between the resin and straw. Thus, good resin penetration and diffusion cannot be expected. After the straw was treated with diluted alkali, the cutin on the exterior surface was decomposed exposing the hydroxyls on the surface of lignin, cellulose, and hemicellulose, which could make the straw more hydrophilic. In addition, as observed in previous study by SEM [20], the untreated straw showed smooth and dense exterior surface. However, alkali treatment turned the smooth surface into a coarse surface and removing and destroying the cuticle composed of cutin and waxes to some extent; this is called chemical etching. The coarse appearance and exposed inner structure is favorable for resin anchoring; consequently, the wettability of the treated straw was improved.

Table 2 Contact angles of rice straw on different surfaces with different adhesives

Resin	Surface sample	Contact angle			K value ($\times 10^{-2}$) (1/s)
		θ_i	θ_e	Percent decrease (%)	
BPF	T-E	70.0	54.4	22.3	1.154
	T-I	62.0	48.8	25.0	1.368
	UT-E	76.6	63.5	14.1	1.084
	UT-I	71.0	60.2	15.2	1.121
BPF–PMDI	T-E	75.8	67.5	10.9	0.493
	T-I	72.5	62.8	13.4	0.666
	UT-E	81.9	75.1	8.3	0.347
	UT-I	75.6	66.4	12.2	0.453
PF	T-E	78.0	73.7	5.5	0.372
	T-I	75.6	69.4	8.2	0.389
	UT-E	83.5	80.1	4.1	0.197
	UT-I	84.7	78.3	7.6	0.344

T-E treated exterior surface, *T-I* treated interior surface, *UT-E* untreated exterior surface, *UT-I* untreated interior surface

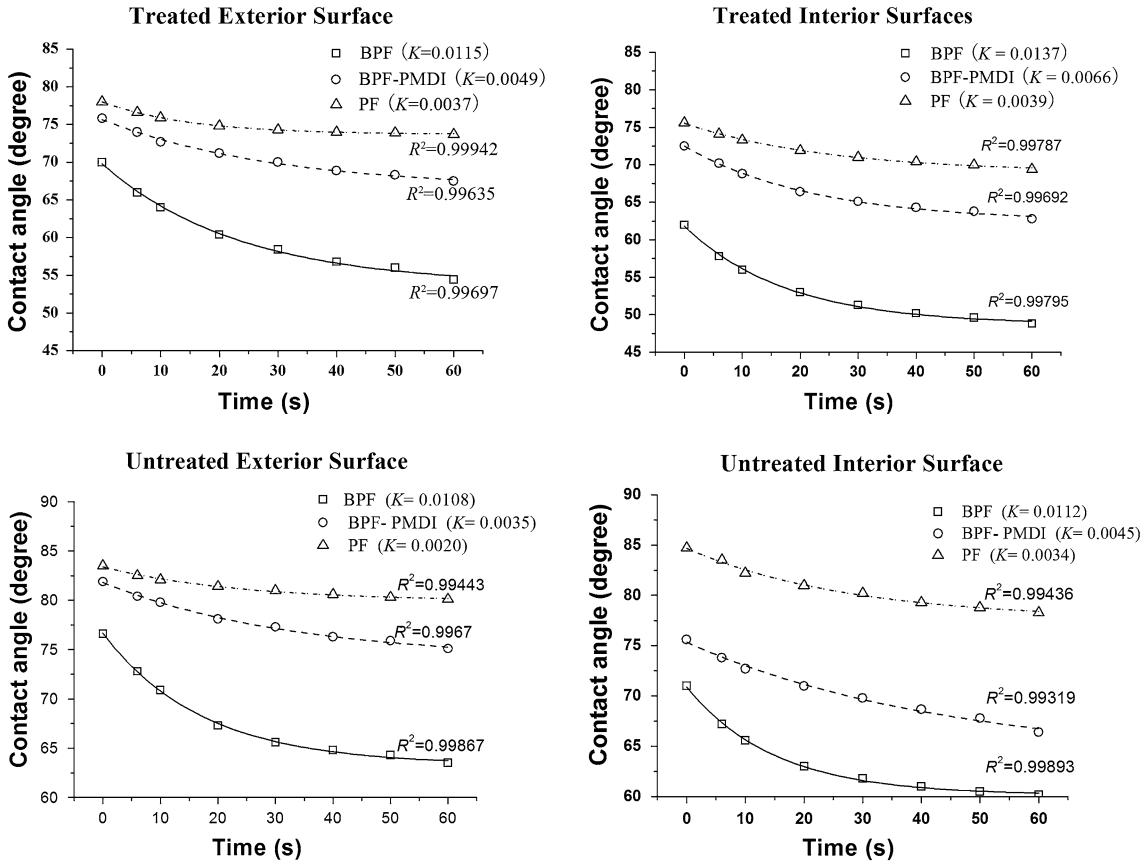


Fig. 2 Contact angle change as a function of time

Dynamic DSC analysis

The curing reactions of PF resin are typically exothermic. The Kissinger method adopts the activation energy at the peak point of DSC curves as the activation energy of the curing reactions. The activation energy can be calculated by linear regression from Eq. (2).On the basis of this method, the activation of BPF resin was 94.75 kJ/mol. The value was higher than that of a typical PF (60–70 kJ/mol) resin reported by other researchers; however, it was similar

to that of LPF and LWPFs (96.55 and 97.54 kJ/mol). On the one hand, it is considered that due to the liquefied residues with lower reactivity incorporated into the BPF resin the diffusion and further condensation was hindered [21, 22]. On the other hand, the liquefied lignin fragments combined with phenol forming steric hindrance during the condensation, in comparison with phenol in conventional phenol resins. Moreover, the lower gel time and higher solid content of BPF indicates highest crosslinking and the network formation and lower molecular mobility. Thus, all of these functioned together resulted in the higher activation energy. Dynamic curves of BPF resin at different heating rates are shown in Fig. 3, and the results are listed in Table 3.

As listed in Table 3, the cure reaction of BPF resin started at approximately 90–121 °C, and the exothermic peak appeared around 119–143 °C. In this peak region, the methylene linkage between phenolic ring for chain extension and cross-linking was formed, together with methyl–phenol, benzaldehyde, and other structures. The heat flow varied from 124 to 145 J g^{-1}. In an early study by Lee [9], the curing parameters at a heating rate of 10 k/min of resol-liquefied bark (Chinese fir and Taiwan acacia) formaldehyde resins with 3:1 and 3.5:1 phenol:bark ratios were as follows: an onset temperature ranging from 94 to 111 °C, a peak temperature ranging from 146 to 147 °C, the heat flow between 66 and 77 J g^{-1}. As it is known, the reaction of PF resin is a complex process [22]. The curing reaction of phenol-liquefied larch bark and formaldehyde becomes more complicated. The formaldehyde not only reacts with the unreacted phenol remaining after liquefied bark, but also with the liquefied larch bark components, which has higher molecular weight and lower mobility. It is assumed that small amount of large molecular weight liquefied lignin ingredients in BPF resin and more stable resinification reactant resulted in the slightly higher onset temperature and more heat release.

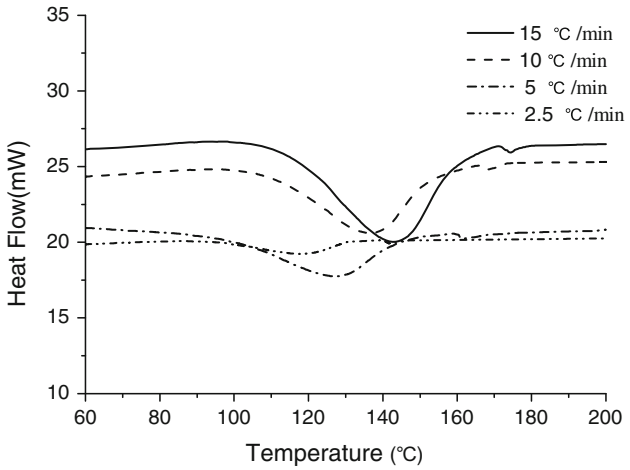


Fig. 3 DSC curves at different heating rates

Table 3 Curing parameters at different heating rates

Heating rate (°C/min)	Onset temperature (°C)	Peak temperature (°C)	Terminal temperature (°C)	Heat flow (J g^{-1})
2.5	89.7	118.9	168.0	124.2
5	97.3	128.8	171.7	132.6
10	114.9	137.0	180.0	138.3
15	121.2	143.0	190.0	144.7

The relationship between activation energy and conversion during the curing process was assessed using the Kissinger method, in which the activation energy at each conversion point was calculated. The activation energy curve as a function of the degree of conversion is shown in Fig. 4. The activation energy curve of a typical PF resin includes two stages, a kinetic regime and a diffusion regime. In Fig. 4 the curve initially increases, indicating parallel addition and condensation reactions occur, although the extent of addition reaction was small. The curve then decreases, yielding a convex shape that suggests a change from the kinetic to diffusion stage after the reaction system underwent cure reaction including gelation, vitrification, transition, and cross-linking. The curve changes at 40 % conversion for highly condensed resin, which indicates that the curing reaction reached a relatively stable state in the first stage. This was because the higher molecular weights of liquefied bark components and bark residues in the resin increased the steric impediments [22]. The DSC curves confirmed this result. A small shoulder was observed following the main peak indicating some of the curing reaction occurred under higher temperature.

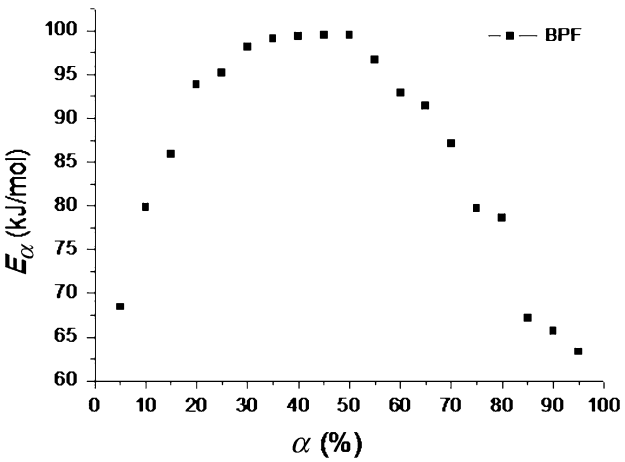


Fig. 4 Activation energy curve as a function of conversion degree

Conclusion

Larch bark was liquefied in the presence of phenol and the obtained liquefied resultant was reacted with formaldehyde to prepare the liquefied BPF for preparing straw boards. This BPF exhibited better wettability, highest K value and lowest equilibrium contact angle on all surfaces regardless of whether the rice straw was treated or untreated. The K values of the interior surfaces were slightly higher than those of the exterior surfaces. The activation energy of synthesized BPF resin based on a dynamic assessment method is 94.75 kJ/mol, which is similar to that of other liquefied lignocellulose phenol resins but higher than that of typical PF resin. Curing reaction temperature is relative lower. The reaction reached complete curing at 40 % conversion, indicating the curing reaction occurred relatively mildly.

References

1. Alma MH, Yoshioka M, Yao YG (1995) Preparation of oxalic acid-catalyzed resinified phenolated wood and its characterization. Mokuzai Gakkaishi 41:1122–1131
2. Alma MH, Yoshioka M, Yao YG (1995) Some characterizations of hydrochloric acid catalyzed phenolated wood-based materials. Mokuzai Gakkaishi 41:741–748
3. Alma MH, Yoshioka M, Yao YG (1996) Preparation and characterization of the phenolated wood using hydrochloric (HCl) as a catalyst. Wood Sci Technol 30:39–47
4. Alma MH, Maldas D, Shiraishi N (2002) Resinification of NaOH-catalyzed phenolated wood–phenol mixture with formalin for making molding materials. Adhes Sci Technol 16:1141–1151
5. Pu S, Shiraishi N (1993) Liquefaction of wood without a catalyst I—time course of wood liquefaction with phenols and effects of wood/phenol ratios. Mokuzai Gakkaishi 39:446–452
6. Pizzi A, Valenezuela C (1994) Low formaldehyde emission, fast pressing, pine and pecan tannin adhesives for exterior particleboard. Holz als Roh-und Werkstoff 52:311–315
7. Pan H, Shupe FT, Hse CY (2009) Characterization of novolac type liquefied wood/phenol/formaldehyde (LWPF) resin. Eur J Wood Wood Prod 67:427–437
8. Pan H, Shupe FT, Hse CY (2007) Characterization of liquefied wood residues from different liquefaction conditions. J Appl Polym Sci 105:3739–3746
9. Lee WJ, Liu CT (2003) Preparation of liquefied lark-based resol resin and its application to particle board. J Polym Sci 87: 1837–1841
10. Lee WJ, Liu CT (2001) Manufacture of phenol–formaldehyde wood adhesive using liquefied bark of *Cunninghamia lanceolata*. For Prod Ind 20:217–226
11. Alma MH, Yoshioka M (1998) Preparation of sulfuric acid-catalyzed phenolated wood resin. Wood Sci Technol 32:297–308
12. Pan H, Shupe FT, Hse CY (2008) Synthesis and cure kinetics of liquefied wood/phenol formaldehyde resins. J Appl Polym Sci 108:1837–1844
13. Collett BM (1972) A review of surface and interfacial adhesion in wood science and related field. Wood Sci Technol 6:1–42
14. Hse CY (1972) Wettability of southern pine veneer by phenol formaldehyde wood adhesives. For Prod 22:51–56
15. Sun XF, Sun RC (2002) Comparative study of acetylation of rice straw fiber with or without catalysis. Wood Fiber Sci 34:306–317
16. Shi SQ, Gardner DJ (2001) Dynamic adhesive wettability of wood. Wood Fiber Sci 33:58–68
17. Liu ZM, Wang FH, Wang XM (2004) Surface structure and dynamic adhesive wettability of wheat straw. Wood Fiber Sci 36(2):239–249
18. Han GP, Umemura K, Zhang M, Honda T, Kawai S (2001) Development of high-performance UF-bonded reed and wheat straw medium-density fiberboard. J Wood Sci 47:350–355
19. Shen JH, Liu ZM, Li J, Niu J (2011) Wettability changes of wheat straw treated with chemical sand enzymes. J For Res 22(1): 107–110
20. Shi JY, Wen MY (2009) The manufacturing of rice straw particle board with modified phenol–formaldehyde resin. China For Prod Ind 36(2):38–40
21. Pan H, Shupe FT, Hse CY (2008) Synthesis and cure kinetics of liquefied wood/phenol/formaldehyde resin. J Appl Polym Sci 108:1837–1844
22. He GB, Riedl B (2002) Model-free kinetics: curing behavior of phenol formaldehyde resins by differential scanning calorimetry. J Appl Polym Sci 87:433–440