

## EFFECT OF CMC FORMIC ACID SOLUTION ON BONDING PERFORMANCE OF MUF FOR INTERIOR GRADE GLULAM

JUN ZHOU,<sup>\*</sup> KONG YUE,<sup>\*</sup> WEIDONG LU,<sup>\*</sup> MENGJU LI,<sup>\*</sup> ZHANGJING CHEN,<sup>\*\*\*\*</sup>  
XIUCAI CHENG,<sup>\*\*</sup> WEIQING LIU,<sup>\*</sup> CHONG JIA<sup>\*\*\*</sup> and LIJUAN TANG<sup>\*</sup>

<sup>\*</sup>*College of Civil Engineering, Nanjing Tech University, Nanjing, China*

<sup>\*\*</sup>*Nanjing Institute of Product Quality Inspection, Nanjing, China*

<sup>\*\*\*</sup>*College of Wood Science and Technology, Nanjing Forestry University, Nanjing, China*

<sup>\*\*\*\*</sup>*Department of Sustainable Biomaterials, Virginia Tech University, Blacksburg, USA*

✉ *Corresponding author: Kong Yue, yuekong@njtech.edu.cn*

*Received April 26, 2016*

This work aimed at determining the effect of adding a carboxymethyl cellulose (CMC) formic acid solution to melamine urea formaldehyde (MUF) on the bonding performance of the adhesive. The bonding performance, chemical structure and curing behavior of MUF adhesives with CMC (1%, 1.5% and 2.0% w/w) formic acid solutions were evaluated by the compressive shear test, Fourier transform infrared spectroscopy (FTIR) and differential scanning calorimetry (DSC). Considering practical timber construction projects, the effect of higher wood moisture content on the bonding strength of the adhesive was investigated. The compressive shear strength of MUF adhesives was nearly twice higher than required by BS EN 386 standard. The bonding strengths of the specimens at 18% moisture content (MC) were 7.18%, 4.8% and 4.95% lower than those at 12% MC with the addition of 1%, 1.5% and 2.0% (w/w) CMC contents, respectively. The bonding strengths of 12% and 18% MC blocks glued by the MUF adhesive containing 2% CMC reached 10.60 and 10.08 MPa, respectively.

**Keywords:** MUF, carboxymethyl cellulose, moisture content, bonding performance

### INTRODUCTION

Glued laminated timber (glulam) has been widely used worldwide due to its great performance and member sizes without much restriction. There are various adhesives used in the production of glulam on the market. Melamine-urea-formaldehyde (MUF) adhesive, the most common amino plastic adhesive used in constructing wooden structures, has gained wide acceptance over the years in some European countries, as they have many advantages over other adhesives, including moderate curing rate, long pot-life, low cost, colorlessness, elastic modulus closer to transverse wood properties and good thermal stability.<sup>1-4</sup> The participation of melamine can make the urea-formaldehyde (UF) adhesive form a network structure, which reduces and protects hydrophilic groups.<sup>5</sup> MUF adhesives are thermosetting adhesives, with higher moisture resistance than that of UF adhesives.

As an important renewable natural resource, cellulose has been widely used in various industries.<sup>6,7</sup> Carboxymethyl cellulose (CMC), a modified cellulose, has been also used in the field of adhesives.<sup>8</sup> A. Pizzi *et al.*<sup>9,10</sup> used a formic acid solution based CMC as an addition agent in the mean of an experimental fast-setting process. CMC not only enhanced the cross-linking degree of the adhesive, but also reduced the existence of free formaldehyde.<sup>11</sup> Moreover, water-soluble carboxymethyl cellulose can be used to improve the interfacial characteristics.<sup>12</sup>

The viscosity of MUF adhesives is low and it affects the curing rate. MUF adhesives usually use acid as curing agent, but excessive acidity in bond lines can result in hydrolysis of the bonding interface, leading to poor water resistance. The addition of a formic acid solution based on CMC to a MUF adhesive has been reported to still ensure

higher wet bonding strength at the bond lines (24 h soak and 2 h boil) for glulam.<sup>9</sup>

In the last ten years, glulam has become gradually accepted in China due to its many advantages. However, currently, the Chinese timber construction industry chain is still in the need of timely and adequate supply of structural dimensional lumber. At present, in China, most of the lumber intended for glulam is imported from North America and Europe. In order to reduce the weight and improve the corrosion resistance of dimensional lumber,<sup>13</sup> the moisture content (MC) of wood materials is generally controlled to be around 18% MC. With regard to glulam, the MC specified in standards is between 9 and 15.

The MC is a major factor affecting the formation of interfacial adhesion.<sup>14</sup> Bonding performance is also seriously affected by MC.<sup>15,16</sup> Researchers found that both bonding strength and wood failure percentage of wet wood laminates met standard requirements after the samples were dried to low wood MC.<sup>17,18</sup> Green wood promoted the penetration of adhesives,<sup>19,20</sup> and exhibited poor bonding.<sup>21</sup> In the curing process, reducing the penetration of the adhesive and a rapid increase in molecular weight were found to be key to gluing green wood materials.<sup>22</sup> At present, in some Chinese glulam-processing plants, imported dimensional lumber with 18% MC is sometimes directly glued, and the effect of 18% MC of wood materials on bonding strength is often ignored.

Because of their viscosity and curing rate, MUF adhesives are not suitable for existing equipment and materials of glulam-processing plants in China, especially when the temperature is low, and no fully automated equipment is available. This work was conducted to investigate the effects of adding

different CMC formic acid solutions to MUF on the bonding performance of the adhesive and to determine the feasibility of using CMC addition agent in gluing timber with high wood MC.

## EXPERIMENTAL

### Wood material

Douglas fir specimens were imported from Canada and used as test samples. The wood densities of Douglas fir at 12% and 18% MC were 481 and 501 kg/m<sup>3</sup>, respectively. Clear wood was selected. The wood was sampled tangentially, and the pieces with average annual ring widths of 2.1 to 3.0 mm were used as test specimens.

### MUF adhesive preparation

MUF adhesive was prepared in the laboratory according to a MUF adhesive formulation.<sup>23</sup> An amount of 332 g of 37% formaldehyde solution was added to a reactor and the solution was heated to 65 °C. The pH value of the reaction solution was controlled to be 10. An amount of 91 g of urea was then added to the reaction solution, which was then heated to 90-92 °C under continuous mechanical stirring for 30 minutes. 20 g of melamine, 1.86 g of dimethylformamide and 3.88 g of diethylene glycol were added and the reaction solution was again stirred for 30 minutes at 90-92 °C. The pH value of the reaction solution was controlled to be 6.5, and then the reaction solution was stirred for another 30 minutes at 90-92 °C. The pH value of the reaction solution was decreased to 6, and the reaction solution was continuously stirred at 90-92 °C until its water soluble ratio reached 200%. Then, 23 g of urea was added, and the reaction solution was stirred again at 90-92 °C until its water soluble ratio reached 150%. Finally, the reaction solution was cooled to 35 °C. The technical characteristics of the obtained MUF adhesive were measured and presented in Table 1.

Table 1  
Technical data of MUF adhesive

Adhesive	Color	Solid content (%)	pH value (25 °C)	Viscosity (23 °C, mPa·s)	Spread per surface* (g/m <sup>2</sup> )
MUF	Milky	50.0	5.5	30	100

\* Applied on two sides of a laminate

Table 2  
Formulation of the addition agent

CMC amount (%)	CMC (part by weight)	Water (part by weight)	Formic acid (part by weight)
0.5	1	170	27
1.0	1	70	27
1.5	1	40	27
2.0	1	20	27

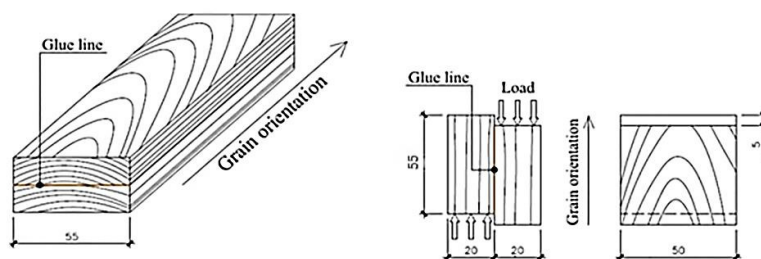


Figure 1: Schematic representation of the test specimen and compressive shear test setup

The preparation of the addition agent was done by the following procedure: 1 part by mass of CMC was dissolved well in a certain amount of water by stirring and then set aside for one day. Subsequently, 27 parts of formic acid solution were added. Due to the poor compatibility of CMC with aqueous materials, the solution was stirred thoroughly during the preparation process. The percentage of CMC was controlled by adding different amounts of water (Table 2).

### Specimen preparation

Specimens were cut from heartwood with the dimensions of  $550 \times 55 \times 25$  mm, and divided into two groups. They were conditioned to MC of 12% and 18% at room temperature for more than 7 days until constant weight was reached. Then,  $100 \text{ g/m}^2$  of the MUF adhesive was applied to one of the bonding surfaces of the specimens, while the formic acid solution with a certain amount of CMC (1%, 1.5%, 2% w/w) was spread on the another face. The specimens were assembled, clamped and kept in the clamp for 24 h. The pressure applied was  $1.0 \text{ N/mm}^2$ , all at  $25^\circ \text{C}$ .

Flat sawn specimens were bonded to each other according to BS EN 392. In order to facilitate the fabrication of the specimens and shear testing, the block-shear specimens respected the configuration specified in ASTM D-905, which is similar to that of BS EN 392. The excess parts were trimmed, and the test specimens were thus obtained (Fig. 1).

### Characterization methods

#### Tests for bonding strength

The bonding strength test was carried out in a universal test machine (MTS System Co., Ltd., China) with a 30KN load cell, and the bonding strength of the specimens was assessed and computed according to the procedure of BS EN 392 standard. The loading speed was set to  $5 \text{ mm} \cdot \text{min}^{-1}$ . Eight specimens were tested for each group. Solid wood was labeled as the control group, while the specimens with 1.0%, 1.5% and 2.0% CMC formic solutions were denoted as M1.0, M1.5 and M2.0, respectively.

Bonding strength was calculated by Eq. 1:

$$\tau = \frac{P_{\max}}{A} \quad (1)$$

where  $\tau$  is the maximum compressive shear strength ( $\text{N} \cdot \text{mm}^{-2}$ ),  $A$  is the actual bonding area of specimens ( $\text{mm}^2$ ), and  $P_{\max}$  is the peak load (N). The wood failure percentage of each test specimen was also measured to the nearest 5%.

### FTIR analysis

The cured MUF adhesives mixed with different proportions of CMC formic solution by weight were subjected to FTIR analysis on a PerkinElmer FTIR spectrometer (UK). This work concentrated on the range of  $450\text{--}2000 \text{ cm}^{-1}$  against an air background. Pure MUF and different CMC formic acid solutions were mixed in equal parts. Cured MUF adhesive mixtures were used to obtain test samples. Pure MUF adhesive cured at  $100^\circ \text{C}$  for an hour was labeled as the control group, while cured MUF adhesives containing 1.0%, 1.5% and 2.0% CMC formic solutions were noted as M1.0, M1.5 and M2.0, respectively.

### DSC measurement

The parameters of curing kinetics for MUF adhesives were characterized with a NETZSCH DSC200F3 (Germany). Due to the expansibility of the adhesives during curing, the amount of each sample was about 10mg. Scanning was done in the temperature range from  $20^\circ \text{C}$  to  $200^\circ \text{C}$ , at heating rates of 10, 15, 20 and  $25 \text{ K} \cdot \text{min}^{-1}$ , under a nitrogen atmosphere (flow rate of  $30 \text{ mL} \cdot \text{min}^{-1}$ ). The results were analyzed by NETZSCH DSC software.

Kissinger's differential method (Eq. 2) was used to analyze the characteristics of the MUF adhesives.<sup>24</sup> Using the Kissinger differential equation relating  $\ln(\beta/T_p^2)$  and  $1/T_p$ , we can determine the relativity index, similar to the activation energy ( $E_a$ ):

$$\frac{d[\ln(\beta/T_p^2)]}{d(1/T_p)} = -\frac{E_a}{R} \quad (2)$$

where  $\beta$  is the heating rate ( $\text{K} \cdot \text{min}^{-1}$ ),  $T_p$  is the peak temperature (K),  $E_a$  is the activation energy ( $\text{KJ} \cdot \text{mol}^{-1}$ ), and  $R$  is the ideal gas constant ( $\text{KJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ ).

## RESULTS AND DISCUSSION

### Physicochemical characteristics

As may be noted in Figure 2, the viscosity of the addition agent exhibited an exponential growth, as the amount of CMC increased. The viscosity did not increase rapidly until the CMC content of 1.5%. When the amount of CMC reached 2%, the viscosity of the addition agent rose to 12500 mPa·s. When the amount of CMC was 2.5%, the addition agent was very hard to dissolve. Since the solution could be hardly stirred and applied in the production of glulam, it can be concluded that the amount of CMC should not exceed 2%. Thus, CMC amounts of 1%, 1.5% and 2% were selected for further investigation. Due to the acidity of formic acid, the pH value decreased almost linearly as the water content decreased.

### Compressive shear strength

The compressive shear strengths of solid wood and those of the samples glued with MUF with

different CMC amounts are presented in Figure 3. The shear strength assessed after 24 h curing was used to judge a good bonding performance for a fast-set adhesive.<sup>25</sup> It was nearly twice as high as that of the BS EN 386 standard, and wood failure percentage is 100%.

The results were obviously different from the values recorded for glued wet wood in previous research.<sup>16</sup> At 12% MC, there was no obvious change in shear strength, which illustrated that the CMC content had little effect on shear strength. The shear strengths of solid wood were of 9.95 and 9.26 MPa at 12% and 18%, respectively, decreasing with increasing wood MC. The shear strengths of the samples glued with MUF adhesives were slightly higher than those of solid wood at 12% and 18%, respectively (Fig. 3), which indicated that, at 12%-18% MC, the shear strength of the MUF adhesive can be mainly attributed to wood strength rather than to adhesive bonding.

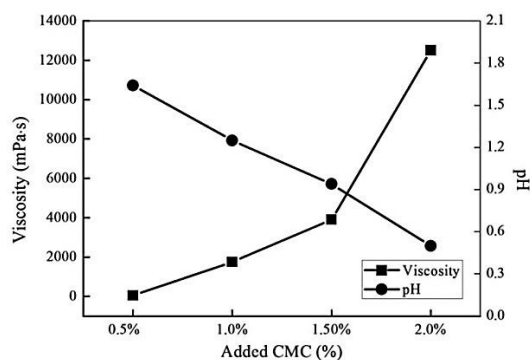


Figure 2: Physicochemical characteristics of solutions with added CMC

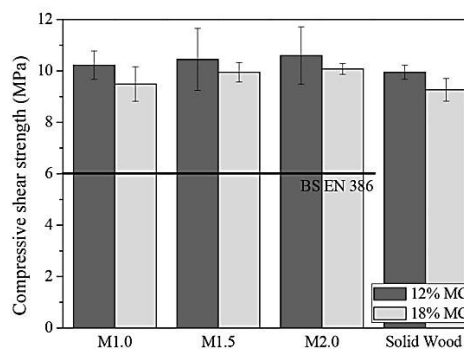


Figure 3: Compressive shear strength of MUF with CMC amount at 12% and 18% moisture content

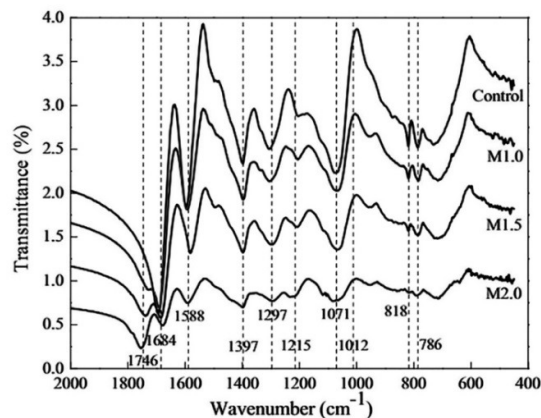


Figure 4: FTIR spectra of cured MUF adhesives

The bonding strengths of the sample blocks at 18% MC were 7.18%, 4.8% and 4.95% lower than those at 12% MC with 1%, 1.5% and 2.0% (w/w) CMC contents, respectively, which illustrated that the MC of wood in the range of 12%-18% just had a limited impact on the bonding performance. The increasing CMC content can mitigate the influence of wood MC. Within the tested range, the bonding strength of the blocks at 12% and 18% MC glued by the MUF adhesive with 2% CMC was the highest, and reached 10.60 and 10.08 MPa, respectively.

### FTIR analysis

The FTIR spectra of cured MUF with different concentrations of the CMC formic solution are presented in Figure 4. The bonding performance of the adhesive system is mainly determined by the chemical structure of the adhesive after curing. FTIR was performed to confirm the effect of CMC formic acid solution on the chemical structure of the MUF adhesive. The absorption peaks of C=O at  $1746\text{ cm}^{-1}$  increased remarkably due to the presence of CMC. It was observed that the peaks at around  $1684\text{ cm}^{-1}$  and  $1588\text{ cm}^{-1}$  for all the samples were related to the stretching vibration of the C=O and the deformation vibration of the C-N and N-H,<sup>27</sup> which possibly resulted from the formation of the amide bond. The peak at  $1397\text{ cm}^{-1}$  was associated with C-H bending vibration, and the peaks at 1295

$\text{cm}^{-1}$  and  $1215\text{ cm}^{-1}$  were attributed to asymmetric stretching vibration of the ether linkage. The peak at  $1071\text{ cm}^{-1}$  was attributed to the stretching vibration of the C-O, which mainly resulted from the hydroxymethyl groups. The peak at  $818\text{ cm}^{-1}$  was associated with the absorption peak of melamine out-of-plane vibration. It was also observed that the peak at around  $786\text{ cm}^{-1}$  corresponded to the absorption peak of C-N deformation vibration in the amide group.

As shown in Figure 4, with the increase of the CMC content and acidity in the CMC formic acid solution, the amount of hydroxymethyl groups decreased dramatically after MUF adhesive curing. The characteristic absorption peak intensity at  $818\text{ cm}^{-1}$  also gradually reduced, which indicated that the curing of the MUF adhesive mainly occurred between the hydroxymethyl groups, hydroxymethyl and reactive hydrogen.<sup>28</sup> The reaction between the hydroxymethyl groups mainly generated dimethylene ether linkages. The intensity of the absorption peaks at  $1684$  and  $1588\text{ cm}^{-1}$  decreased gradually with the increase of the CMC content and acidity, which illustrated that amide contents decreased in cured MUF adhesive systems. Compared with the pure MUF adhesive, the intensity at  $1295$  and  $1215\text{ cm}^{-1}$  had a slight change, which indicated a higher amount of dimethylene ether linkages pyrolysis during the curing process.

Table 3  
Parameters of curing kinetics of MUF adhesives

Added CMC(%)	$B(\text{K} \cdot \text{min}^{-1})$	$T_p(\text{K})$	$1/T_p \times 10^3 (\text{K}^{-1})$	$-\ln(\beta/T_p^2)$
0	10	385.03	2.597	9.604
	15	387.05	2.584	9.209
	20	390.89	2.558	8.941
	25	393.76	2.540	8.733
1	10	388.21	2.576	9.621
	15	392.83	2.546	9.239
	20	396.50	2.522	8.970
	25	399.40	2.504	8.761
1.5	10	388.01	2.577	9.619
	15	392.70	2.546	9.238
	20	398.07	2.512	8.978
	25	400.37	2.498	8.765
2	10	388.51	2.574	9.622
	15	394.36	2.536	9.246
	20	397.53	2.516	8.975
	25	404.08	2.475	8.784

Table 4  
Values of the activation energy ( $E_a$ ) of MUF adhesives

Adhesive types	$E_a$ (KJ·mol <sup>-1</sup> )
Control	118.6
M1.0	99.0
M1.5	85.7
M2.0	71.8

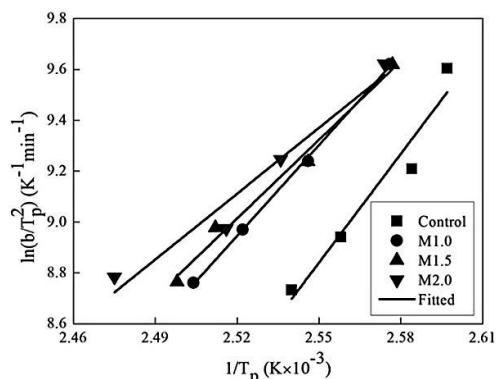


Figure 5: Kissinger's fitted curves of four MUF adhesives

The absorption peak at 1746 cm<sup>-1</sup> enhanced with increasing CMC content in the addition agent. The CMC addition agent affected the chemical structure and group content in the cured MUF adhesive system. A higher amount of CMC not only promoted the reaction, but also contributed to a higher curing degree of the MUF adhesive. The cured system still retained a certain amount of active groups, for example, of reactive hydrogen and hydroxymethyl groups. Their existence was the reason of poor water resistance. However, the shear test results discussed above indicated that wood MC of 18% had limited influence on bonding performance.

#### DSC analysis

The parameters of MUF adhesive curing kinetics, according Eq. 2, are shown in Table 3. As can be seen in Figure 5, the relationship between the natural logarithm of  $\beta/T_p^2$  and the reciprocal of  $T_p$  was linear with the correlation coefficient ( $R^2$ ) of the control, M1, M2 and M3 of 0.94, 0.99, 0.99 and 0.96, respectively. The parameter  $E_a$  of the adhesive systems can be obtained from the slope of each regressed line in Figure 5. The values of  $E_a$  for all the adhesives tested in this work are presented in Table 4.

Significant differences can be noted among the adhesives. The addition agent can reduce the energy

required during MUF adhesive curing. Thus, the curing of the control group needed more energy, and it cannot cure quickly at room temperature. On the other hand, higher acidity and the presence of CMC in the addition agent resulted in speeding up the curing process. It was evident that the 2% CMC formic acid solution contributed to faster MUF curing at room temperature.

#### CONCLUSION

a) The compressive shear strengths of Douglas fir wood samples glued with MUF/CMC at 12% MC ranged from 10.22 MPa to 10.60 MPa, and were 70.33-76.67% higher than the specified value in the BS EN 386 standard at 100% wood failure percentage. The curing of MUF was speeded up by the presence of the CMC formic solution, while the bonding strength of sample M2.0 reached the highest value of 10.60MPa.

b) The bonding strengths of the sample blocks at 18% MC were 7.14%, 4.78% and 4.91% lower than those at 12% MC in the presence of 1.0%, 1.5% and 2.0% (w/w) CMC addition agent, respectively. The bonding strength of M2.0 was higher than that of the other samples with 18% MC, and reached 10.08 MPa. When comparing the compressive shear strengths, at 18% MC, the wood samples glued with MUF/CMC showed slightly reduced, but acceptable strength values, compared to those at

12% MC.

c) Hydroxymethyl was the radical group involved in the curing reaction of the MUF adhesive. A higher curing degree and lower activation energy of the MUF adhesive were determined with the addition of the 2% CMC formic acid solution.

**ACKNOWLEDGEMENT:** The authors wish to acknowledge funding from the National Forestry Public Sector Research and Development project (No. 201304504), the Science-Technology project of Jiangsu Bureau of Quality and Technical Supervision (No.KJ155425) and the Natural Science Foundation of the Jiangsu Higher Education Institutions of China (No. 14KJB220001).

## REFERENCES

- <sup>1</sup> F. Stöckel, J. Konnerth, W. Kantner, J. Moser and W. Gindl, *Holzforschung*, **64**, 337 (2010).
- <sup>2</sup> F. Stoeckel, J. Konnerth and W. G. Altmutter, *Int. J. Adhes. Adhes.*, **45**, 32 (2013).
- <sup>3</sup> S. Clauß, M. Joscak and P. Niemz, *Eur. J. Wood Prod.*, **69**, 101 (2011).
- <sup>4</sup> H. Lei and C. E. Frazier, *Int. J. Adhes. Adhes.*, **62**, 40 (2015).
- <sup>5</sup> X. G. Bao and P. Huang, *Adhesion*, **4**, 23 (1991).
- <sup>6</sup> J. J. Li, Z. Q. Song, D. G. Li and S. B. Shang, *Chem. Ind. For. Prod. Sci.*, **5**, 15 (2015).
- <sup>7</sup> X. Y. Guo, Z. W. Jiang and G. J. Ma, *J. Harbin Eng. Univ.*, **2**, 147 (2015).
- <sup>8</sup> Z. B. Qiao, J. Y. Gu, Y. F. Zou, H. Y. Tan and Y. H. Zhang, *Bioresources*, **9**, 6117 (2014).
- <sup>9</sup> M. Properzi, A. Pizziani and L. Uzielli, *HolzRohWerkst.*, **59**, 413 (2001).
- <sup>10</sup> A. Sauget, A. Pizzi, A. Guillot, S. Godart, R. Apolit *et al.*, *Eur. J. Wood Prod.*, **72**, 697 (2013).
- <sup>11</sup> Z. H. Huang, X. Yu, W. Li and S. X. Liu, *J. For. Res.*, **26**, 253 (2015).
- <sup>12</sup> Y. Cao, H. L. Li and X. Xu, *Acta Polym. Sinica*, **1**, 3 (2001).
- <sup>13</sup> L. Meyer and C. Brischke, *Int. Biodeter. Biodegrad.*, **103**, 23 (2015).
- <sup>14</sup> M. Properzi, A. Pizzi and L. Uzielli, *HolzRohWerkst.*, **61**, 77 (2003).
- <sup>15</sup> J. Custódio, J. Custódio and H. Cruz, *Int. J. Adhes. Adhes.*, **29**, 173 (2009).
- <sup>16</sup> O. Kläusler, S. Clauß, L. Lübke, J. Trachsel and P. Niemz, *Int. J. Adhes. Adhes.*, **44**, 57 (2013).
- <sup>17</sup> B. Na, A. Pizzi and X. N. Lu, *Eur. J. Wood Prod.*, **63**, 473 (2005).
- <sup>18</sup> B. Na, X. N. Lu and A. Pizzi, *Wood Res.*, **59**, 265 (2014).
- <sup>19</sup> D. E. Brady and F. A. Kamke, *Forest Prod. J.*, **38**, 63 (1988).
- <sup>20</sup> W. T. Nearn, *Wood Sci.*, **6**, 285 (1974).
- <sup>21</sup> W. K. Murphey and W. T. Nearn, *Forest Prod. J.*, **6**, 194 (1956).
- <sup>22</sup> B. Na, X. N. Lu and A. Pizzi, *Chin. Wood Ind.*, **23**, 31 (2009).
- <sup>23</sup> K. Yue, Z. R. Fang, W. Q. Liu, W. D. Lu and W. K. Zhang, CN patent 201310710649.8., 2014.
- <sup>24</sup> H. E. Kissinger, *Anal. Chem.*, **29**, 1702 (1957).
- <sup>25</sup> B. S. Pierre, R. Beauregard, M. Mohammad and C. Bustos, *Forest Prod. J.*, **55**, 9 (2005).
- <sup>26</sup> A. Kandelbauer, A. Despres, A. Pizziani and I. Taudes, *J. Appl. Polym. Sci.*, **106**, 2192 (2007).
- <sup>27</sup> J. Q. Xie, F. M. Feng, W. Hu, H. J. Mao and H. Yan, *J. Funct. Mater.*, **39**, 293 (2008).
- <sup>28</sup> H. Wang, G. B. Du and J. K. Liang, *J. Northwest Forest Univ.*, **2**, 166 (2013).