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Reactivity of Larch and Valonia Tannins in Synthesis of Tannin-Formaldehyde Resins

Jiongjiong Li,[#] Cheng Li,[#] Wen Wang, Wei Zhang,* and Jianzhang Li *

Tannin-formaldehyde resins (TFR) were prepared by copolycondensation of tannins (larch tannin or valonia tannin) and formaldehyde. The performances of TFR and the free formaldehyde residue in the system during the course of reaction were tested. Chemical and structural changes of TFR during the reaction process were detected by Fourier transform infrared spectroscopy (FTIR) and ^{13}C nuclear magnetic resonance spectroscopy (^{13}C NMR). The results indicated that larch tannin-formaldehyde (LTF) resins demonstrated higher viscosity, higher solids content, shorter gel time, and lower free formaldehyde content than valonia tannin-formaldehyde (VTF) resins. The FTIR and ^{13}C NMR tests demonstrated that larch tannin had higher reactivity than valonia tannin with formaldehyde, which was confirmed by the results of the free formaldehyde content measurement and the characteristics of TFR.

INTRODUCTION

Tannins can be extracted from the root, bark, fruits, and leaves of several plants and are economical and environmentally friendly. Generally, tannins can be classified as condensed or hydrolysable tannins (Nakano *et al.* 2000; Schofield *et al.* 2001). Condensed tannins have been identified as oligomers with varying degrees of polymerization, formed by condensation and polymerization reactions of flavonoid repeating units (Nicollin *et al.* 2013; Radebe *et al.* 2013). Hydrolysable tannins are classified into gallotannins and ellagitannins according to their differing structural characters (Khanbabaee and van Ree 2001). Tannins have been extensively studied and are widely used in a number of industries, such as in synthesizing wood adhesives, manufacturing inks, manufacturing corrosion inhibitors for steel, and producing leather (Bisanda *et al.* 2003; Seeram *et al.* 2005; Özacar *et al.* 2006). In recent years, with the increasing cost and shortage of petrochemicals, many researchers are increasingly interested in plant-based polymeric resins, especially tannin-based resins (Zhao *et al.* 2013a; Basso *et al.* 2014).

Tannins are polyphenols, which have multiple adjacent polyhydroxy-phenyl groups in their chemical structures. Many studies have found that tannins are a suitable phenol substitute in resin and adhesive preparation (Zhao *et al.* 1994; Moubarik *et al.* 2009; Bertaud *et al.* 2012; Ucar *et al.* 2013). Condensed tannins composed of tannin-based resins extracted from the bark of wattle (Zhao *et al.* 1994; Vázquez *et al.* 2003; Stefani *et al.* 2008; Valenzuela *et al.* 2012), larch (Zhang *et al.* 2014), pine (Sealy-Fisher and Pizzi 1992; Zhao *et al.* 2013b), and quebracho (Moubarik *et al.* 2009) have been investigated and show

properties that qualify them as suitable phenol substitutes. Previous studies have shown that hydrolysable tannins, such as valonia tannin and gallotannins, are also effective in wood adhesive formulation (Garro-Galvez *et al.* 1996; Özacar *et al.* 2006; Can *et al.* 2013). Investigations have revealed that condensed tannins, when compared with phenols, have higher reactivity with formaldehyde (Joseph *et al.* 1996; Bisanda *et al.* 2003; Özacar *et al.* 2006). Hydrolysable tannins possess greater reactivity toward formaldehyde, compared with phenols, while not being as reactive as phloroglucinol (Garro-Galvez and Riedl 1997; Özacar *et al.* 2006). Other studies of tannin-based resins have mostly focused on lowering formaldehyde emissions (Pizzi *et al.* 1995; Kim 2009). However, previous research has minimally distinguished which kind of tannins had higher reactivity toward formaldehyde in the synthesis of TFR.

Larch (*Larix gmelinii*) tannin is a condensed tannin. The flavonoid units in larch tannin are linked to each other at C4–C8 or C4–C6 (Tondi *et al.* 2009) (Fig. 1). Valonia tannin (Fig. 2) is a hydrolysable tannin and can be easily converted to gallic acid (Fig. 3) and other phenolic acids when dissolved in water. When studying the reactions of valonia tannin with formaldehyde, gallic acid produced from valonia tannin has been most frequently used as the representative polyphenolic polymer (Garro-Galvez *et al.* 1996; Haslam 1996).
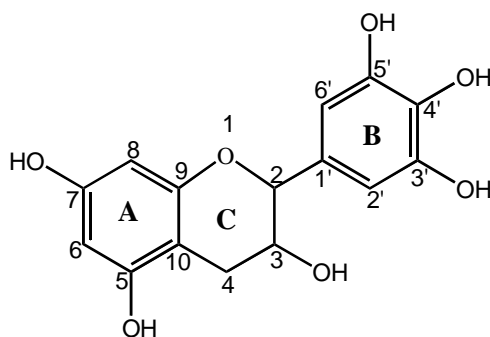

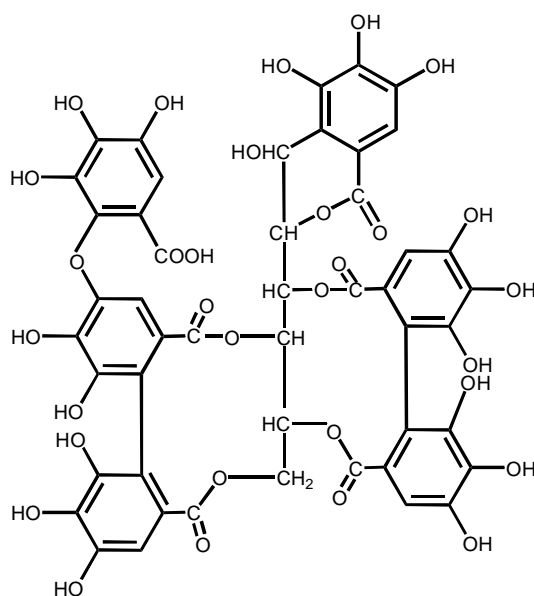**Fig. 1.** The flavonoid unit in larch tannin

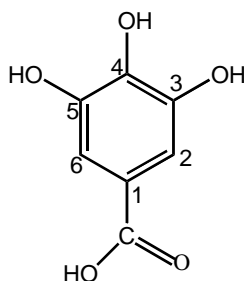**Fig. 2.** Typical structure of valonia tannin

Fig. 3. Structure of gallic acid

This study aimed to investigate the reactivity of condensed and hydrolysable tannins toward formaldehyde, which can provide theoretical guidance for the formulations of tannin-formaldehyde resins (TFR) and tannin-phenol-formaldehyde resins. Larch and valonia tannins were used to synthesize TFR. The performances, free formaldehyde residue, and structural molecular changes of the TFR were determined.

EXPERIMENTAL

Materials

Analytical grade (AR) formaldehyde (37 wt%) was purchased from Xilong Co. Ltd. (China). Two types of commercial tannin extracts, larch and valonia tannin, were purchased from Tian'guan Biotech Co., Henan, China. Sodium metabisulfite and sodium hydroxide (AR) were obtained from Beijing Chemical Works, Beijing, China.

Methods

Tannin composition analysis and determination

The moisture content of tannin was determined by drying samples at 105 °C to constant weight in accordance with JIS Standard P8002 (1996). The content of tannin in raw tannin material was determined with corresponding GB/T15686 (2008). With ultraviolet-visible spectrophotometer at 280 nm wavelength, the tannin content of raw powder was determined utilizing standard curve.

Synthesis of TFR

First, 94 g of (larch or valonia) tannin and 115 g of distilled water were placed into a 500-mL four-neck bottle and mixed by stirring. Then, 31 g of sodium hydroxide solution (50 wt%) and 6 g of sodium metabisulfite were added, and the mixture was stirred for 30 min at ambient temperature, followed by the addition of 162 g of formaldehyde solution. After this, the mixture was heated to 80 °C and kept at that temperature for a set period of time. Each specimen (30 mL) was removed from the reaction media at 0, 1, 2, 3, 10, 20, 30, and 60 min during the reaction process.

Property measurements of TFR

The viscosity and solids content of TFR were determined in accordance with ASTM D 1084 (1997) and BS EN 827 (1995), respectively. The gel time of TFR was obtained according to Chinese National Standard GB/T 14074 (2006). Approximately 5 g of TFR was placed into a 16 mm × 160 mm test tube and maintained in a 130 °C oil bath,

and a thin wire spring was used to manually mix the sample until gelation occurred. The viscosity, solids content, and gel time were recorded with three replicates tested for each sample, respectively. The free formaldehyde content of the reaction solutions was determined by the hydroxylamine hydrochloride method in accordance with Chinese National Standard GB/T 14074 (2006). An equimolar acid was obtained from the reaction of free formaldehyde and hydroxylamine hydrochloride solution. Subsequently, the mixed solution was titrated with sodium hydroxide solution and the dosage of sodium hydroxide solution was determined to measure free formaldehyde content. Three replicates were tested for each sample.

FTIR analysis

Samples removed from the reaction media at various times were freeze-dried by placing them in a vacuum freeze-drier for 48 h, followed by filtering through a 200-mesh screen. FTIR analysis of freeze-dried residues was conducted using a Nicolet 6700 spectrophotometer (Thermo Scientific, USA) at resolution of 2 cm^{-1}. The spectra were obtained between 4000 and 600 cm^{-1} using KBr powder.

Solid state ^{13}C NMR spectroscopy analysis

The solid state CP-MAS (cross-polarization/magic-angle-spinning) ^{13}C NMR spectra of the freeze-dried residues were recorded on a Bruker 400 spectrometer (Bruker, Switzerland) at a frequency of 100 MHz and at a contact time of 5 ms. Chemical shifts were calculated relative to tetramethylsilane (TMS). The rotor was spun at 4 kHz on a double-bearing 4-mm Bruker probe (Bruker, Switzerland). All spectra were acquired with a relaxation delay of 1.5 s.

RESULTS AND DISCUSSION

Properties of TFR

Tannin extracts were used in the polymerization experiments without further purification, and the tannin content of the two tannin extracts are shown in Table 1. The moisture contents of the two tannin extracts were 9.5% and 10.2%, respectively. The tannin content of larch tannin was slightly higher than that of valonia tannin. A small amount of insoluble content and non-tannin content, mostly consisting of sugars, existed in the two tannin extracts.

Table 2 shows the characteristics of TFR. The solid content of the larch tannin-formaldehyde (LTF) resins was higher than that of the valonia tannin-formaldehyde (VTF) resins, indicating that there were more residual monomers in the VTF resins than in the LTF resins. This phenomenon may be attributed to a higher amount of formaldehyde that had reacted with the larch tannin, during the copolycondensation process, than with the valonia tannin.

The viscosity of the VTF resins at 25 °C was lower than that of the LTF resins because of the higher molecular weight of LTF resins (Gao *et al.* 2007). The above results indicate that the polymerization degree of LTF resins was higher than that of VTF resins. The gel time of the VTF resins was longer than that of the LTF resins; this phenomenon can be attributed to the higher reactivity of LTF resins than VTF resins.
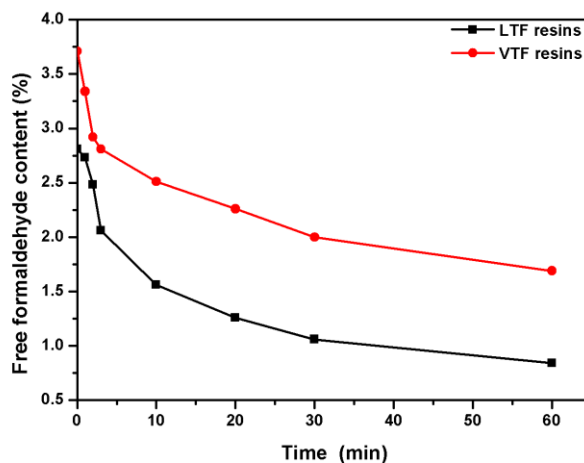
Table 1. Analysis of Tannin Extract Content

Tannin extract material	Moisture (%)	Total extract (%)	Solubles (%)	Insolubles (%)	Non-tannin (%)	Tannin (%)
Larch tannin	9.5	90.5	87.5	3.0	27.4	60.1
Valonia tannin	10.2	89.8	87.6	2.2	29.6	58.0

Table 2. Characteristics of LTF and VTF Resins

Parameters	LTF resins	VTF resins
Viscosity (mPa s)	35.0 ± 5.0	12.0 ± 5.0
Solid content (%)	37.5 ± 0.2	33.7 ± 0.2
Gel time (min)	17.2 ± 0.5	26.1 ± 0.5

Free Formaldehyde Content Analysis

The free formaldehyde contents of the reaction media after various reaction times are shown in Fig. 4. For the curve of LTF resins, there was a sharp decline in the free formaldehyde content when the reaction time increased from 0 min to 3 min, indicating the ongoing reaction of formaldehyde and larch tannin. The rate of free formaldehyde loss slowed down from 3 min to 30 min. When the reaction time increased above 30 min, the curve gradually flattened, which indicated the polycondensation reaction slowed down.

Fig. 4. Free formaldehyde content of the reaction media

Some obvious differences can be observed between the free formaldehyde content of LTF and VTF resins. The free formaldehyde content of the VTF resins was 3.7% at 0 min, which was higher than that of the LTF resins (2.8%). These percentages indicated that more formaldehyde had reacted with larch tannin, than with valonia tannin, at low temperatures (< 80 °C). At 60 min, the free formaldehyde content of LTF and VTF resins were 0.8% and 1.7%, respectively. When the reaction time increased from 2 min to 10 min, the falling rate of the free formaldehyde content in the LTF resins was higher than that in the VTF resins. However, the decreasing rate of free formaldehyde content in these two resins were similar from 10 min to 60 min. These results were consistent with the results

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of viscosity, solids content, and gel time, indicating that larch tannin had higher reactivity toward formaldehyde than valonia tannin, probably because of the structural differences between the two tannins. The higher reactivity of larch tannin toward formaldehyde may be attributed to larch tannin's resorcinolic nuclei or phloroglucinolic A-ring in the repeating flavonoid units, as described in previous studies (Sowunmi _et al._ 2000). The lower reactivity of the gallic acid produced from the valonia tannin may be due to the steric hindrance caused by hydroxyl aromatic groups, as previous research has indicated (Garro-Galvez _et al._ 1996).

FTIR Studies

Figure 5 shows the FTIR spectra of larch tannin and LTF resins after reaction times of 0, 10, and 60 min. The broad peak observed in the region from 3550 to 3100 cm^{-1} is attributable to –OH bridging groups. The small peaks near 2920 cm^{-1}, in the spectrum of larch tannin, are due to aromatic C–H stretching vibrations in the benzene rings (Silverstein and Webster 1998; Kim and Kim 2003). The elongations of the aromatic –C=C– bonds gave absorption bands in the range from 1616 to 1447 cm^{-1}, and the deformation vibrations of the C–C bonds in the phenolic groups gave absorption bands in the range 1500 to 1400 cm^{-1} (Özacar _et al._ 2006). The single peak at 1521 cm^{-1} indicates that procyanidin was predominant in the extracted larch tannin, and the high intensity band at 1616 cm^{-1} indicates that the extracted larch tannin had a high number of C4–C8 interflavonoid linkages (Kim and Kim 2003; Oo _et al._ 2008). Bonds at 1280 and 1150 cm^{-1} were produced by aromatic C–O stretching, and others at 1063 cm^{-1} correspond to aliphatic C–O stretching.
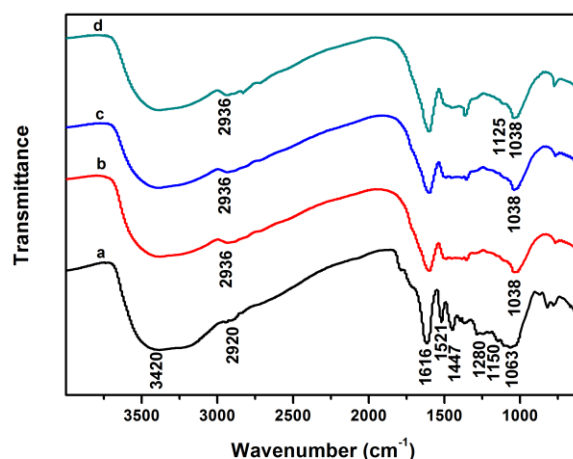

Fig. 5. FTIR spectra of larch tannin and LTF resins: (a) larch tannin, (b) (c) (d) LTF resins after reaction times of 0, 10, and 60 min, respectively

The spectra of the LTF resins were compared with that of the larch tannin. Bonds in the region of 2824 to 2940 cm^{-1}, produced by the methylene (–CH_2–) bridges of LTF resins (Garro-Galvez _et al._ 1996; Özacar _et al._ 2006), showed a gradual increase as a function of reaction time. This increase indicates that larch tannin gradually reacted with formaldehyde, forming the –CH_2– bridges. The intensity of C–O bonds at 1063 cm^{-1} increased, which may be attributed to the formation of dimethylene ether (–CH_2–O–CH_2–) linkages. Small peaks at 1125 cm^{-1} in the spectra of LTF resins can be observed. These

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peaks were caused by the asymmetrical –CH_2–O–CH_2– stretching (Silverstein and Webster 1998). The peaks at 1038 cm^{-1} were related to –CH_2OH bridges, formed in the methylolation reaction. Bonds in the region of 820 to 775 cm^{-1} resulted from the deformation vibrations of the C–H bonds in the benzene rings (Özacar *et al.* 2006).

The FTIR spectra of valonia tannin and VTF resins after reaction times of 0, 10, and 60 min are shown in Fig. 6. The wide bonds in the range of 3550 to 3100 cm^{-1} are associated with the –OH stretching of the phenolic and methylol group of valonia tannin. Peaks near 2923 cm^{-1}, both in the spectrum of valonia tannin and the spectra of VTF resins, can be assigned to aromatic C–H stretching vibrations (Silverstein and Webster 1998; Kim and Kim 2003). The peak of ketone (1732 cm^{-1}) was found in the spectrum of valonia tannin. The peaks at 1610 and 1445 cm^{-1} belong to –C=C– bonds in the aromatic nucleus. The peaks at 1325 and 1038 cm^{-1} in the spectrum of valonia tannin indicate phenol groups (Garro-Galvez *et al.* 1996; Holopainen *et al.* 1998; Lin *et al.* 2011). The deformation of the carboxylic acid O–H group can be observed at 1177 cm^{-1} (Can *et al.* 2013).

Compared with the FTIR spectrum of valonia tannin, the spectra of VTF resins underwent some changes. The peaks between 3550 and 3100 cm^{-1} gradually became broader with increasing reaction time, which may be caused by the existence of intense hydrogen bonds in the VTF resins. The peak intensity at 1445 cm^{-1} reduced and shifted to 1452 cm^{-1}, creating a weak peak, which was caused by the formation of –CH_2– bridges (Kim and Kim 2003; Poljanšek and Krajnc 2005). The formation of –CH_2–O–CH_2– bridges appeared in the region between 1150 and 1085 cm^{-1} in the spectra of VTF resins. The –CH_2–O–CH_2– bridges were formed by the reaction of –CH_2OH groups, which can be observed at 1018 and 1020 cm^{-1}. The peaks at 1732 and 1610 cm^{-1}, associated with C=O and –C=C– bonds, gradually combined and broadened. This change may be due to environmental changes to the C=O groups of the VTF resins, as the vibration of C=O groups was affected by the formation of –CH_2– bridges in the ortho position of valonia tannin in the polycondensation process (Silverstein and Webster 1998; Özacar *et al.* 2006).
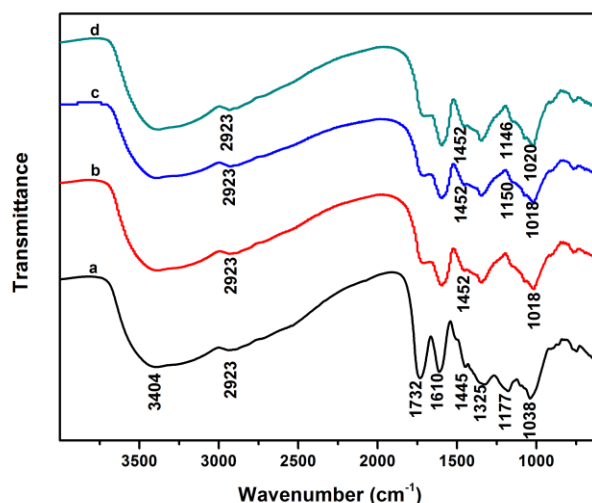

Fig. 6. FTIR spectra of valonia tannin and VTF resins: (a) valonia tannin, (b) (c) (d) VTF resins after reaction times of 0, 10, and 60 min, respectively

The results of the FTIR analysis of LTF and VTF resins indicate that both larch tannin and valonia tannin can react with formaldehyde in the formation of wood adhesive as a substitute for phenol. The intensity of peaks related to –CH_2OH groups were weaker

in the FTIR spectra of the VTF resins than that of the LTF resins. This outcome indicates that larch tannin had higher reactivity toward formaldehyde than valonia tannin, which was consistent with the results of free formaldehyde content analysis and the characteristics of TFR. This result can also be confirmed by the weaker intensity of peaks associated with –CH_2– bridges in the FTIR spectra of VTF resins than in those of LTF resins.

^{13}C NMR Studies

The solid state ^{13}C NMR spectra of larch tannin and LTF resins after reaction times of 2 and 60 min are shown in Fig. 7. From the spectrum of larch tannin, the peak at 176 ppm indicates the presence of gallic acid residues linked in C3 to the heterocycle ring of a flavonoid structure. The peak at 155 ppm belongs to the C5, C7 carrying –OH groups (Davis *et al.* 1996; Wawer *et al.* 2006; Oo *et al.* 2008). The band at 144 ppm corresponds to C3' and C4', and C1' and C5' can be observed at 130 and 116 ppm, respectively. The 105 ppm peak belongs to the interflavonoid bonds C4–C8 and C4–C6. Peaks were absent between 95 and 96 ppm, both indicating that C4–C8 was the predominant interflavonoid linkage, in agreement with the results of FTIR analysis. The peak at 97.9 ppm belongs to unreacted C6, C8, and C10 (Wawer *et al.* 2006; Oo *et al.* 2009; Navarrete *et al.* 2010). Resonance at 71 ppm corresponds to C3, and the band at 37 ppm relates to C4 involved in the interflavonoid band. The peak at 29 ppm indicates the free C4 sites of the flavonoid (Lorenz and Preston 2002; Wawer *et al.* 2006; Basso *et al.* 2014).
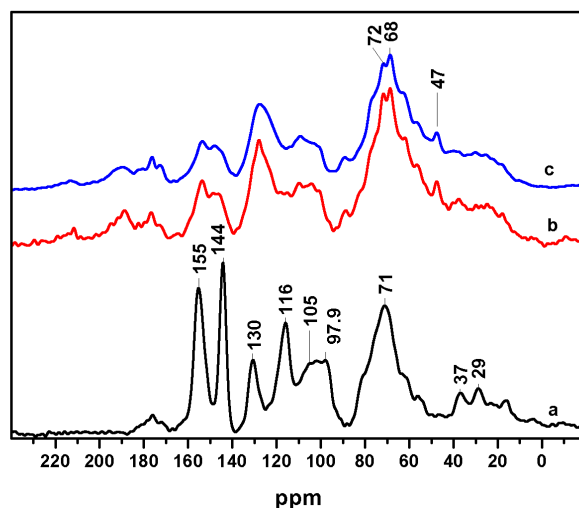

Fig. 7. ^{13}C NMR spectra of larch tannin and LTF resins: (a) larch tannin, (b) LTF resins after the reaction time of 2 min, (c) LTF resins after the reaction time of 60 min

The ^{13}C NMR spectra of the LTF resins were compared with those of the larch tannin. The peak at 68 ppm belongs to –CH_2OH groups, and the peak at 47 ppm corresponds to –CH_2– groups linked to aromatic rings. The formation of –CH_2–O–CH_2– bridges can be observed at 72 ppm. These results indicate that free sites of the flavonoid units reacted with formaldehyde, and –CH_2OH bridges, –CH_2–O–CH_2– bridges, and –CH_2– groups co-existed in the reaction solutions. The peak at 97.9 ppm, which corresponds to unreacted C6 and C8, disappeared in the spectra of the LTF resins. This result probably indicated that the signal of these carbons was displaced by the reactions occurring at this position. The peak at 153 ppm corresponds to the C5, C7, and C9 of the flavonoid, and the

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band at 146 ppm corresponds to the C3', C4', and C5' of the flavonoid B–ring (Tondi *et al.* 2009). The bond intensity of the peaks belonging to aromatic carbons decreased, compared with the spectrum of the larch tannin. This difference may be caused by the reactions of hydroxymethyl groups, resulting in the formation of methylene bridges.

Figure 8 shows the solid state ^{13}C NMR spectra of the valonia tannin and the VTF resins after reaction times of 2 and 60 min. For the spectrum of valonia tannin, the peaks at 171 and 173 ppm are related to C=O bands of the gallic acid, and the peak at 144 ppm belongs to C3 and C5 of gallic acid. The band at 136 ppm belongs to C4, and the 124 ppm band belongs to C1. C2 and C6 of the gallic acid can be clearly observed at 108 ppm. The peak at 72 ppm is due to the C–O–C bridges of valonia tannin (Hsu *et al.* 2007; Muddathir *et al.* 2013; Kang *et al.* 2014).

The solid state ^{13}C NMR spectra of the VTF resins were compared with that of the valonia tannin, and some differences were observed. The absence of the 108 ppm peak indicates that the free C2 and C6 sites reacted with formaldehyde, and this result can be further confirmed by the appearance of the 68 ppm peak belonging to –CH$_2$OH groups. The increasing intensity of the peak at 72 ppm may be caused by the formation of –CH$_2$–O–CH$_2$– bridges (Trosa and Pizzi 1998). The peak at 129.4 ppm relates to the ortho sites of gallic acid linked with –CH$_2$– bridges, indicating the formation of –CH$_2$– groups. This result can be confirmed by the emergence of the peak at 38 ppm, which corresponds to –CH$_2$– bridges.

The results of the solid state ^{13}C NMR spectra of LTF and VTF resins indicate that both larch tannin and valonia tannin can react with formaldehyde as a substitute for phenol, which has been discussed above. The peak intensity at 68 ppm in the NMR spectrum of the LTF resins was stronger than that of the VTF resins, and the intensity of peaks related to –CH$_2$– groups was weaker in the NMR spectra of VTF resins than in those of LTF resins. These results indicated that larch tannin had a higher reactivity toward formaldehyde than valonia tannin, which agreed with the FTIR data, the characteristics of TFR, and the results of free formaldehyde content analysis.
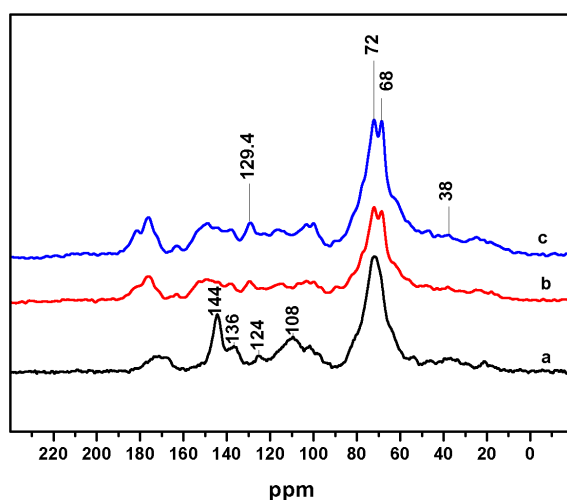

Fig. 8. The ^{13}C NMR spectra of valonia tannin and VTF resins: (a) valonia tannin, (b) VTF resins after the reaction time of 2 min, (c) VTF resins after the reaction time of 60 min

CONCLUSIONS

1. Larch-tannin-formaldehyde (LTF) resins had higher viscosity, higher solids content, and shorter gel time than valonia-tannin-formaldehyde (VTF) resins.

2. Free formaldehyde content analysis indicated that the free formaldehyde content of LTF resins was lower than that of VTF resins, and more formaldehyde reacted with larch tannin than with valonia tannin at low temperatures (< 80 °C).

3. FTIR analysis revealed that larch tannin had higher reactivity toward formaldehyde than valonia tannin. Both larch tannin and valonia tannin can react with formaldehyde as a substitute for phenol in the formation of wood adhesives, which can be confirmed by the free formaldehyde content and ^{13}C NMR data of the reaction media.

ACKNOWLEDGMENTS

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