Synthesis and Characterization of Sucrose-Melamine-Formaldehyde Adhesives

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The objective of this project was to use sucrose as a partial substitute for melamine in the synthesis of sucrose–melamine-formaldehyde (SMF) resin. The SMF was synthesized in a base condition. The wet bonding strength, shelf life, and formaldehyde emission of the SMF resin were determined. Fourier transform infrared spectroscopy (FT-IR) and mass spectroscopy (MS) were employed to analyze the chemical structure of the SMF resin. The shelf life of SMF resin increased as the sucrose content increased. Also as the sucrose content increased, the wet bonding strength decreased and the formaldehyde emissions decreased. The FT-IR and MS spectra revealed the structures of sucrose, melamine, and formaldehyde in the SMF, and chemical reactions of SMF resins occurred between the three primary hydroxyl groups of sucrose and methylolmelamine. Based on the results of this study, a sucrose to melamine mole ratio of 0.4:1 was determined to be the optimal ratio for the SMF resin.

Keywords: Sucrose-melamine-formaldehyde (SMF) Adhesive; Synthesis; Characterization

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INTRODUCTION

Melamine-formaldehyde (MF) resins are synthesized from formaldehyde and melamine through a condensation reaction (Park *et al.* 2009). Melamine-formaldehyde resins have been used in paper laminates because of their high bonding strength, good boiling-water resistance, and low curing temperature (Gu 1999; Roberts and Evans 2005). However, because of their short shelf-life and high cost of melamine, the applications of MF resins have been limited (Hansmann *et al.* 2006). Therefore, there is a demand for the modification of MF resins for use in the wood industry.

MF resin has been used to modify other adhesives for performance enhancement and cost reduction. Ma *et al.* (2013) conducted a fire resistance study to evaluate melamine-modified urea-formaldehyde resin using intumescent fire-retardant ammonium polyphosphate. Cakić *et al.* (2012) studied the properties of coatings based on alkyd resin improved *via* blending with epoxy resins and melamine resins. Their results showed that samples with 30 wt% melamine resin had a higher hardness of baked enamels then that with 20 wt%. The resin system with an alkyd/melamine ratio of 70:30 and 30 wt% epoxy resin had the lowest apparent activation energy of 141.5 kJ/mol. Liu and Zhu (2014) investigated the formaldehyde and volatile organic compound (VOC) emissions from wood-based panels coated with nanomaterial-modified melamine impregnate. Tseng *et* *al*. (2015) studied the CO_2 adsorption capabilities at atmospheric pressure on activated carbons prepared from melamine-modified phenol-formaldehyde resins.

Recently, there has been an increasing demand for renewable resources as bioproducts to replace petroleum-based products (Onishchenko and Reva 2013). As a result, MF resin modified by tannin and carbohydrates has shown potential to be used as wood adhesive (Holmberg 1982; Gindl and Jeronimidis 2004; He *et al.* 2009; Kohlmayr *et al.* 2012; Costa *et al.* 2013; Gangi *et al.* 2013).

Sucrose is renewable, biodegradable, and abundant, with low cost. It is rich in hydroxyl groups, which can react with amino or formaldehyde groups (Costa *et al.* 2013). Technically, sucrose can be a good modifier for MF resin to reduce the condensation time because the hydroxyl group of sucrose can form covalent bonds with MF resin (Gindl and Jeronimidis 2004; Chen *et al.* 2007; He *et al*. 2009; Song *et al.* 2010).

The objective of this paper is to investigate the synthesis of sucrose-modified MF (SMF) resin and to evaluate the performance of the SMF resin as affected by the sucrose content.

EXPERIMENTAL

Materials

Chemicals

Sucrose, melamine, and formaldehyde were obtained from Sinopharm Chemical Reagent Co., Ltd, Shanghai, China. Borax (analytical reagent) was obtained from Xingdong Chemical Co., Ltd, Yingkou, China. Sodium hydroxide (analytical reagent) was obtained from Tianjin Kemiou Chemical Reagent Co., Ltd, Tianjin, China. Starch (food grade) was purchased from Wuming Guiquan Starch Chemical Plant, Nanning, China.

Wood

Eucalyptus veneers with a moisture content of 8% to 12% were obtained from Guangxi Zhenshuo Wood Co., Ltd, Nanning, China.

Testing equipment

The equipment used for the resin synthesis and specimen preparation/ characterization included a digital cantilever electric mixer (GZ120-S, Baoli Scientific Research Apparatuses Co., Ltd, Jiangyin, China), heating magnetic stirrer (ZNCL-G/190*90 mL, Shanghai Yike Co., Ltd, Shanghai, China), NDJ-9 rotational viscometer (Shanghai Changji Geological Instrument Co., Ltd, Shanghai, China), hot press (XLB100-D, Zhejiang Shuangli Groups Co., Ltd, Huzhou, China), electric blast oven (101A-2B, Shanghai Jinghong Laboratory Instrument Co., Ltd, Shanghai, China), microcomputer-controlled electronic universal testing machine (CMT5504, Shenzhen Sans Material Test Instrument Co., Ltd, Shenzhen, China), electronic balance (JM-B20002, Chaozhe Hengqi Instrument Co., Ltd, Zhuji, China), electronic balance (FA224, Shanghai Shunyu Hengping Scientific Instrument Co., Ltd, Shanghai, China), 722 grating spectrophotometer (Shanghai Fine Instrument Co., Ltd, Shanghai, China), Fourier transform-infrared spectrometer (660 FT-IR, Varian Inc., Palo Alto, America), and a mass spectrometer (REFLEX III, Bruker Inc., Germany).

Resin Synthesis Procedure

For the preparation of the SMF resin, 178 g of formaldehyde solution (37 wt %) and 1.3 g of borax (0.3 wt%) were put into a four-necked round-bottom flask with a mechanical stirrer, reflux condenser, and thermometer. The mixture went through a constant stirring until a complete dissolution was achieved. The pH of the mixture was adjusted to 8.5 with sodium hydroxide solution (0.1 M). The temperature was increased to 90 °C and retained for 150 min, followed by the addition of 126 g of melamine and 138 g of sucrose. The solution was then cooled to room temperature. Next, 192 ± 2g of water was added. Finally, sodium hydroxide solution (0.1 M) was added to adjust the pH to 7.5 to 8.5.

Characterization by FT-IR and ESI-MS

SMF resins were purified with methanol-acetic acid ethyl ester as an eluent in a silica gel column chromatograph. The structure of SMF resin was characterized by Fourier transform-infrared spectroscopy (FT-IR) and Electrospray ionization mass spectroscopy (ESI-MS). For the FT-IR characterization, the extracted samples were coated by crystalline ZnSe and each sample was scanned 64 times over a region of 4,000 to 650 cm^{-1} at a resolution of 4 cm^{-1}. For the MS characterization, the spectrum of SMF resin was obtained from matrix assisted laser desorption ionization/time of flight MS with a nitrogen laser and a wavenumber of 337 nm.

Bonding Strength

The bonding strength of the adhesive was tested in accordance with the procedure described in Chinese standard GB/T 17657 (1999). The standard specifies how to evaluate the properties of wood-based panels and their overlays. Three-hour immersion in boiling water method is used to evaluate the durability of the glue bond for the plywood specimens. Plywood (3-layer structure, 30g adhesive on each side of the veneer) with nominal dimensions of 425 mm by 425 mm was glued with the SMF adhesive under a pressure of 0.9 MPa at 150 °C for 7 min, and the specimens with nominal dimensions of 25 mm by 100 mm were made from bonded plywood. The specimens were immersed in boiling water for 3 h and tested in tension using a CMT5504 testing machine. The bonding strength of the specimens was calculated as follows (Eq. 1),

$$X = P_{max}/A \tag{1}$$

where X is the shear strength (MPa), P_{max} is the maximum failing load (N), and A is the bonding surface of the specimen (mm^2).

Shelf-Life of Adhesive

The SMF adhesive in an iodine flask was placed in box with a constant temperature of 23 ± 2 °C. During the conditioning, the viscosity of the sample was measured with a rotational viscometer every five days until the sample was gelled.

Formaldehyde Emission

The formaldehyde emissions of plywood bonded using SMF with various sucrose contents were measured in accordance with the procedures described in Chinese Standard GB/T 17657 (1999). Ten samples (150 mm by 50 mm) were placed in a desiccator with a dish containing 300 mL of water for 24 h at 20 °C. The water samples in the dish were tested by a 722 grating spectrophotometer.

RESULTS AND DISCUSSION

Fourier Transform-Infrared Spectroscopy Analysis

The spectra of SMF and MF obtained from FT-IR are shown in Fig. 1. The peak at 3349 cm^{-1} can be assigned to the stretching vibration of the N-H and O-H bonds, while the peak at 1069 cm^{-1} can be assigned to that of the C-O-C bonds. The absorption peaks at 2957 and 1457 cm^{-1} can be assigned to the stretching vibration and the flexural vibration of C-H in the alkane, respectively. The peaks at 1553 and 1495 cm^{-1} are both attributed to the stretching vibration of C=N in heterocyclic nitrogen. The peak at 814 cm^{-1} can be assigned to the characteristic absorption peak of thiotriazinone. As shown in Fig. 1, the SMF shows enhanced characteristic peaks at 3349 and 1160 cm^{-1}, compared with the MF, indicating the effect of sucrose groups on the structure of SMF resin.

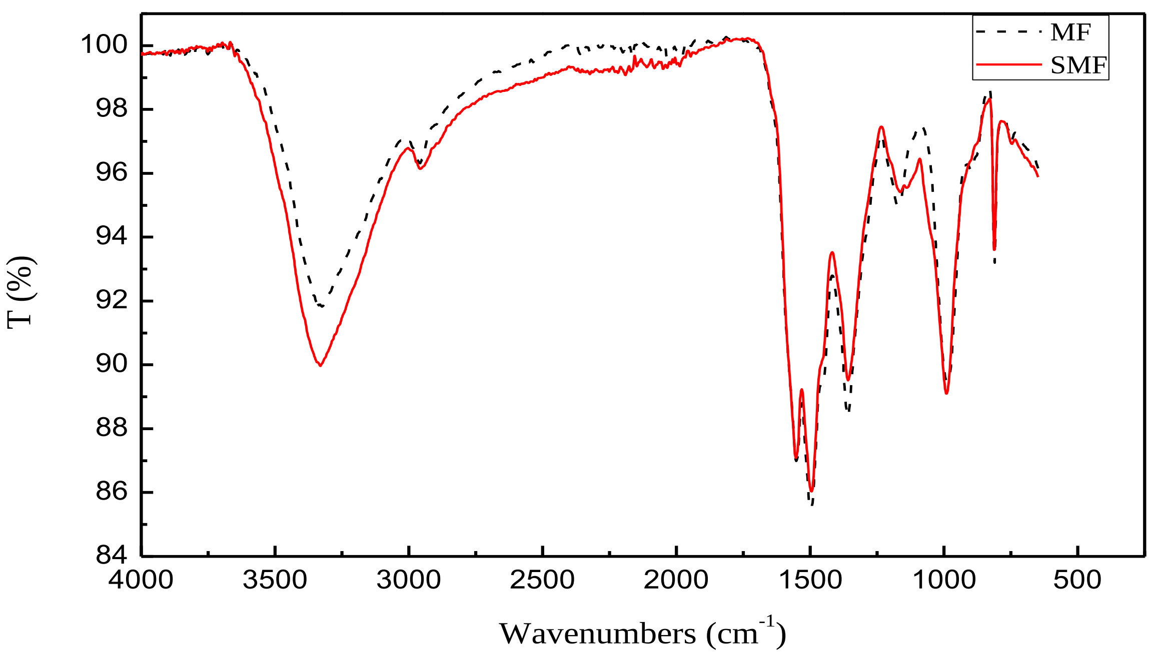

Fig. 1. FTIR spectra of SMF resin and MF resin

Mass Spectrum Analysis

The mass spectrum of SMF resin is shown in Fig. 2. The molecular structures of sucrose at various mass-to-charge (*m*/*z*) ratios are shown in Fig. 3.

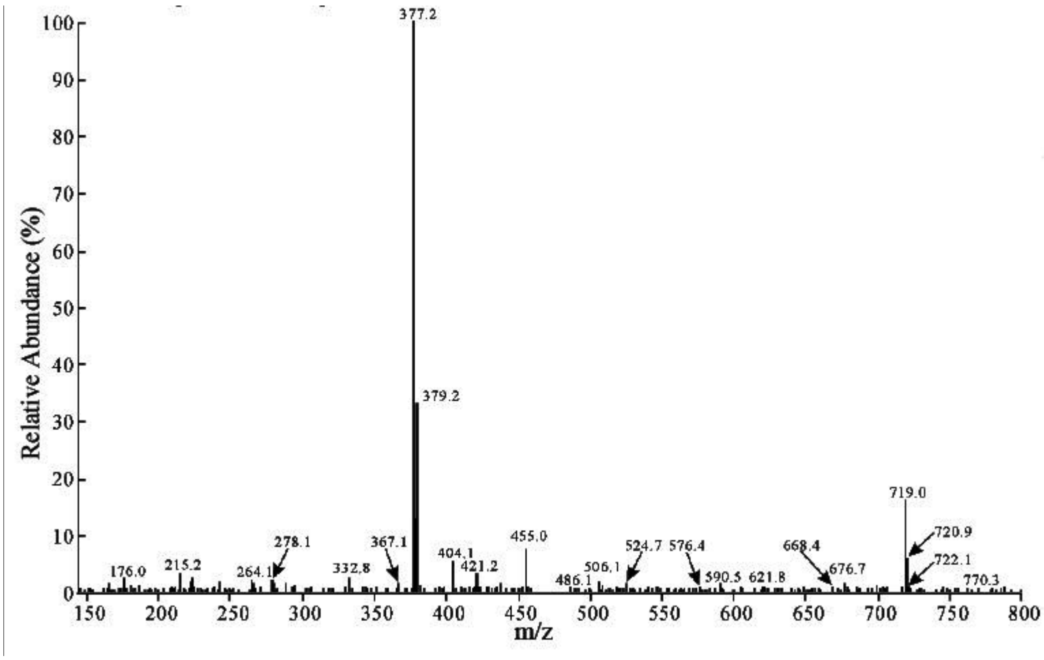

Fig. 2. ESI-MS spectrum of SMF resin

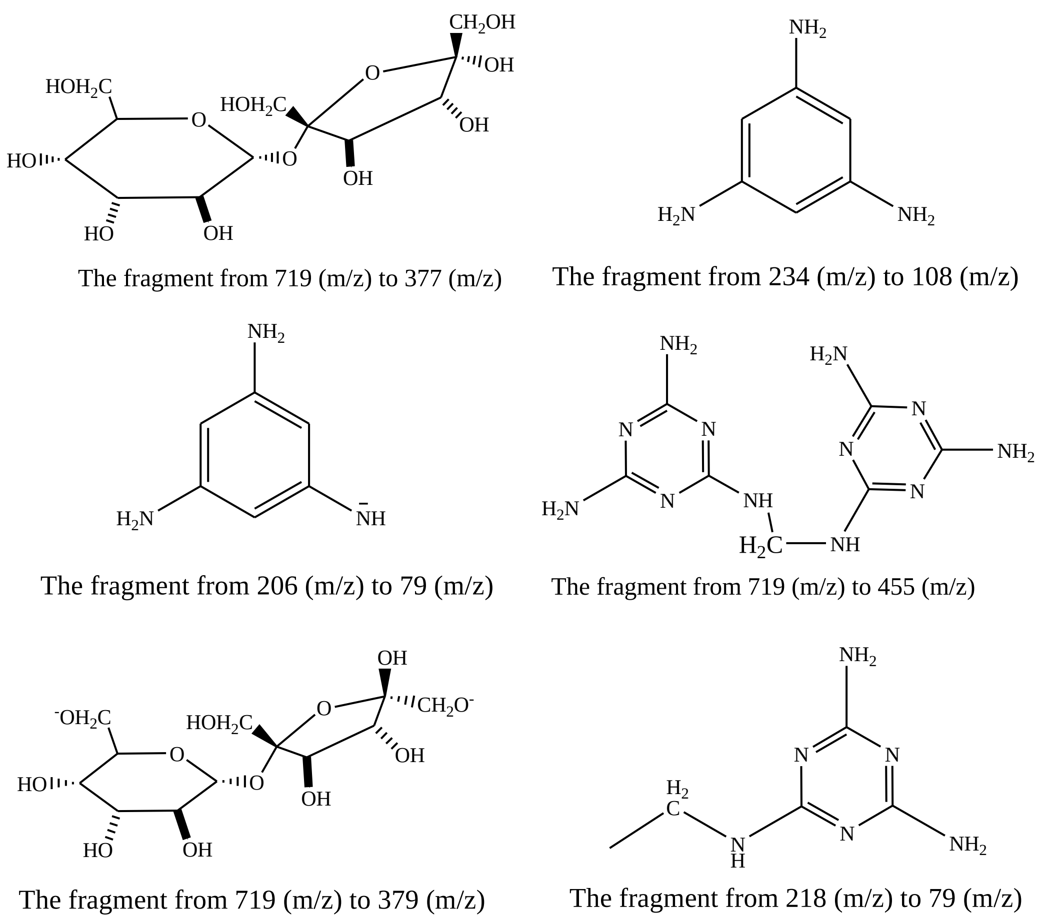

Fig. 3. Structures of fragments speculated from the change of mass-to-charge ratios

From Fig. 2, the molecular weight of sucrose was obtained as 342 from the change in fragment from 719 (*m*/*z*) to 377 (*m*/*z*). The molecular weight of melamine was obtained as 126 from the fragment change from 234 (*m*/*z*) to 108 (*m*/*z*). The molecular structures of sucrose and melamine are shown in Fig. 3. The molecular weight for the melamine with a structure that lost a hydrogen atom was obtained as 125 from the fragment change from 206 (*m*/*z*) to 79 (*m*/*z*). The fragment changes from 719 (*m*/*z*) to 455 (*m*/*z*) (molecular weight of 264), from 719 (*m*/*z*) to 379 (*m*/*z*) (molecule weight of 340), and from 218 (*m*/*z*) to 79 (*m*/*z*) (molecule weight of 139), are assigned chemical structures shown in Fig. 3.

This analysis suggested that the SMF resin was synthesized by the chemical condensation of melamine, formaldehyde, and sucrose. There would be covalent linkages, such as ether and methylene groups, between the monomers. Further tests are ongoing to establish whether there are actual covalent bonds between the sucrose and MF resin.

Bonding Strength

The bonding strength results for plywood bonded using SMF resins with various formulations such as the mole ratios of sucrose to melamine (S/M ratios) and formaldehyde to melamine (F/M ratios) are shown in Fig. 4, and the wood failure percentages of SMF-bonded plywood in the bonding strength test are shown in Table 1.

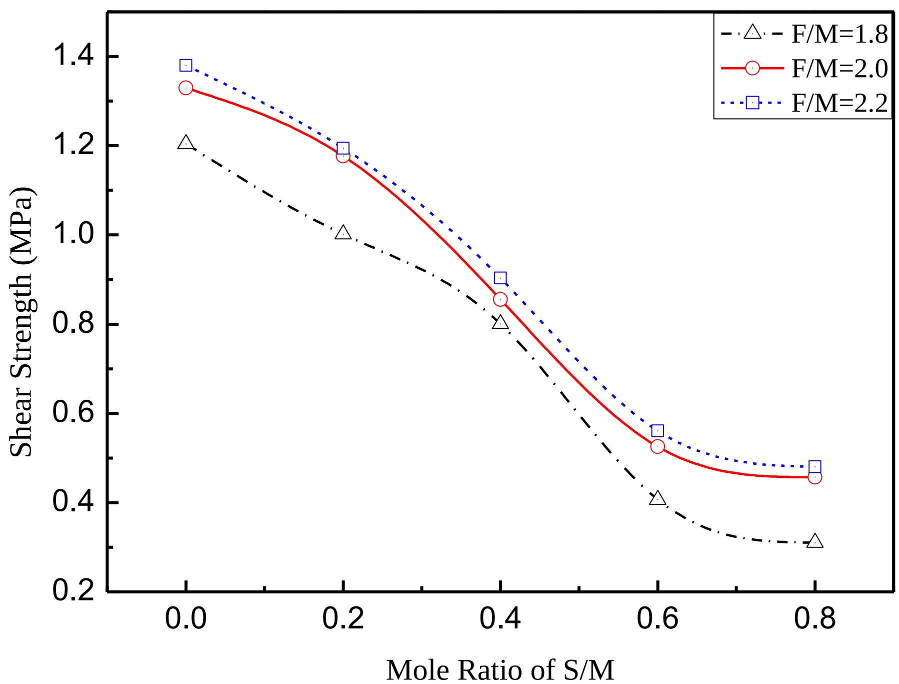

Fig. 4. Effect of sucrose content on bonding strength of SMF-bonded plywood

Compared with the MF adhesive (S/M ratio = 0), the bonding strength of the resins was reduced. As shown in Fig. 4, as the S/M ratio increases, the bonding strength of the plywood decreases. Even though the incorporation of sucrose decreased the bonding strength, at a mole ratio of 0.4 S/M, the bonding shear strengths of the plywood bonded with the SMF adhesive with three F/M ratios (1.8, 2.0, and 2.2) were obtained as 0.80, 0.86 and 0.90 MPa, respectively, which meet the minimum requirements of the Chinese standard GB/T 17657 (1999) (≥ 0.7 MPa). The incorporation of sucrose reduced the water resistance (especially in boiling water) of the resin because of the hydroxyl groups of sucrose.

Table 1. Wood Failure Percentage (%) of SMF-Bonded Plywood in Bonding Strength Test

		Mole ratio of sucrose to melamine (S/M)				
		0	0.2	0.4	0.6	0.8
F/M	1.8	80	60	60	30	10
	2.0	80	50	60	40	10
	2.2	100	80	70	40	20

The mole ratios of formaldehyde to melamine (F/M) are 1.8, 2.0, and 2.2, respectively. The wood failure percentage is assessed according to GB/T 17657 (1999).

Shelf-Life Test

Figure 5 shows the shelf-life of SMF resin as a function of sucrose content. Shelf life is an important parameter for the wood adhesive. It was reported that MF adhesive was not stable in shelf life, especially at low temperatures (Gu 1999). Figure 5 shows that the shelf-life of the MF adhesive with an F/M ratio of 2.0 was only seven days.

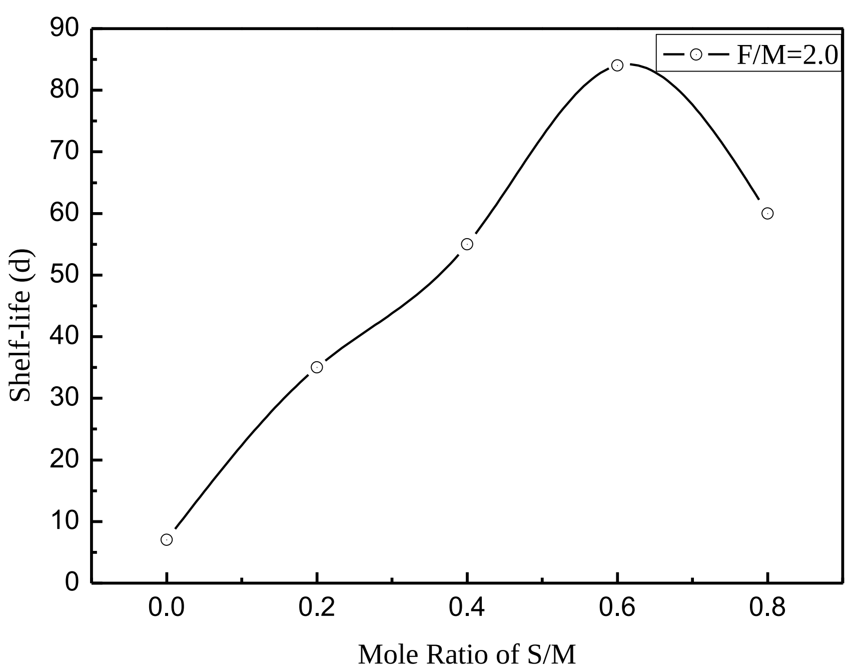

Fig. 5. Effect of sucrose content on shelf-life of SMF resin

Incorporation of sucrose into the MF can markedly increase the shelf life of the adhesive. When the mole ratio of sucrose and melamine is between 0 and 0.6, as the sucrose content increases, the shelf life increases. The longer shelf life of SMF may be due to the efficient reaction of the hydroxyl group of sucrose and the active methylol groups of the resin, so that the number of crosslinking reactions of the active groups of resin is reduced (Wang *et al.* 2012).

Formaldehyde Emission Test

The effect of sucrose content on the formaldehyde emissions of plywood bonded with SMF resin is shown in Fig. 6. The formaldehyde emissions were tested with SMF resins formulated using two different sucrose to melamine mole ratios (2.0 and 1.8). The formaldehyde emissions of the SMF-bonded plywood were measured as between 0.5 and 0.8 mg/L when the sucrose to melamine mole ratios were between 0 and 0.8. When the S/M mole ratio was under 0.4, as the S/M ratio increased, the formaldehyde emissions decreased. However, as the S/M ratio continued to increase (> 0.4), the formaldehyde emission increased. This result indicates that the most efficient reaction for the SMF resin happened when the sucrose and melamine ratio was 0.4. Increasing the sucrose content to a certain point could promote reactions between MF resin and sucrose, which would enhance the stability of the chemical bonds of SMF resin, so that the formaldehyde emissions could be reduced. The formaldehyde emissions level of the adhesives met the requirement of E_1 ($\leq$ 1.5 mg/L) in Chinese standard GB/T 18580 (2001).

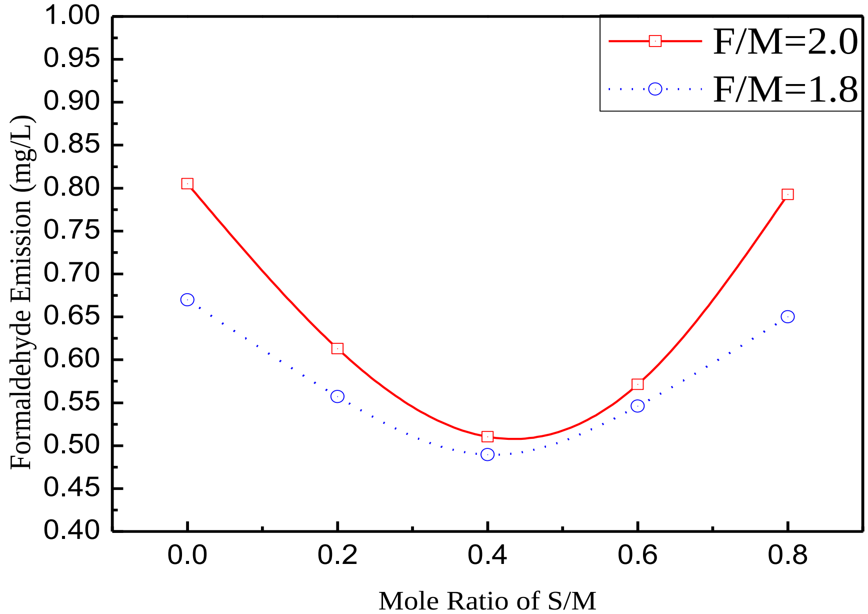

Fig. 6. Effect of sucrose content on formaldehyde emissions from plywood

CONCLUSIONS

1. SMF adhesive was synthesized by a condensation reaction of sucrose, melamine, and formaldehyde.
2. The incorporation of sucrose into MF can improve the shelf life of the resin and reduce the formaldehyde emissions.

3. The optimum sucrose to melamine mole ratio was found to be 0.4:1, with a wet bonding strength of 0.90 MPa and formaldehyde emissions of 0.49 mg/L.

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