Production of Melamine Formaldehyde Resins Used in Impregnation by Incorporation of Ethylene Glycol and Caprolactam with High Flexibility, Storage Stability, and Low Formaldehyde Content

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Ethylene glycol and caprolactam were added during the synthesis process of melamine formaldehyde (MF) resins to develop a new MF formulation with high flexibility, storage stability, and low formaldehyde emissions that can be used for the impregnation of papers. It was demonstrated that the MF resins with amounts of ethylene glycol (molar ratio of ethylene glycol to melamine was 1.0) and caprolactam (molar ratio of caprolactam to formaldehyde was 0.12) achieved higher storage stability, flexibility, and lower free formaldehyde content. The impregnated papers made from these MF resins displayed good dry and wet tensile strength and passed the relevant standard specifications for decorative paper on wood-based panels. The size exclusion chromatography (SEC) and Fourier transform-infrared spectrometry (FT-IR) studies showed that the MF resins produced *via* incorporation of ethylene glycol and caprolactam had a different molecular weight distribution and polymeric structure.

Keywords: Melamine formaldehyde resins; Impregnated paper; Size exclusion chromatography; Ethylene glycol; Caprolactam

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INTRODUCTION

Melamine-formaldehyde (MF) resins are synthesized by the methylolation and condensation reaction of melamine with formaldehyde under the action of a catalyst. Similar to other wood adhesives, such as urea-formaldehyde resins (UF) and phenol-formaldehyde resins (PF), MF resins are used in the production of semi-exterior and exterior grade wood-based panels. Meanwhile, with the added advantage of excellent water and weather resistance, vivid wood texture, and brilliant color, nearly half of MF resins are used for the impregnation of both low- and high-pressure paper laminates and overlays applied in furniture, flooring, the construction industry, and exterior cladding (Pizzi 1983, 1994; Gindl *et al*. 2003; Kandelbauer *et al.* 2009; Kohlmayr *et al*. 2012; Paiva *et al.* 2016; Shao *et al.* 2016).

Melamine-formaldehyde resins are widely used in many fields, but there are still some deficiencies in their performance. First, formaldehyde emission is unavoidable due to the use of formaldehyde as the raw material. Second, the cured MF resins have high hardness and brittleness because of the large steric hindrance of melamine's triazine groups. Third, MF resins exhibit low storage stability due to the presence of a large amount of

reactive imino and methylol groups. Therefore, most of the modifications of MF resins have concerned improving the performance of these three aspects (Gu 1999; Lubczak *et al*. 2000; Siimer *et al*. 2010; Chen *et al.* 2011; Xiong *et al*. 2013; Zeng *et al*. 2014; Zhang *et al*. 2014; Sun *et al*. 2018). Lukowsky (2002) reduced the formaldehyde content of water-based MF resins by adding aromatic sulfonyl compounds, urea, and thiourea. Kim and Kim (2005) discovered that polyvinyl actate had a good function in decreasing the formaldehyde emission level of MF resins. Lian *et al.* (2014) obtained a long storage period for MF resins through modification with diglycol-caprolactam, which was successfully used in the preparation of wear-resistant decorative paper. Zhou *et al.* (2018) investigated the blending modification of melamine formaldehyde resins using hyperbranched polymer polyamidoamines; the results showed that polyamidoamines reduced the viscosity of MF resins, shortened the curing time, and prolonged the storage period.

In this work, the addition of ethylene glycol and caprolactam during MF resins' synthesis process developed a new MF formulation with good flexibility, storage stability, and low formaldehyde emissions that can be used for the impregnation of paper sheets. The evolution of ethylene glycol and caprolactam in the synthesis process of MF resins was also recorded by size exclusion chromatography (SEC) and Fourier transform-infrared spectrometry (FT-IR).

EXPERIMENTAL

Materials

Melamine (≥ 99.8%) was purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd., Shanghai, China. Formaldehyde (37%) was purchased from Shanghai Jiuyi Chemical Reagent Co., Ltd., Shanghai, China. Ethylene glycol and triethanolamine were purchased from Nanjing Chemical Reagent Co., Ltd., Nanjing, China. Caprolactam was purchased from Sinopec Co., Ltd., Baling branch, Yueyang, China. *N*,*N*-Dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) were purchased from Sigma-Aldrich Co., Ltd., Shanghai, China. Impregnated base papers (the base weight is 80 $g.m^{-2}$) were provided by Lodgi Wood Industry Co., Ltd., Changzhou, China.

Methods

Synthesis of MF resins

The MF resins were synthesized in a round bottom flask equipped with mechanical stirring (S312-60; Shanghai Meiyingpu Instrument Co., Ltd., Shanghai, China) and a thermometer. The synthesized temperature was controlled by a heating water bath (DF-101S; Gongyi Gaoke Instrument Co., Ltd., Gongyi, China).

The formaldehyde, ethylene glycol, and water were added in to the flask at a basic pH of 9.0, which was obtained by adding an appropriate amount of 30% triethanolamine solution. Approximately 80% of the total mass of melamine was added into the above solution, and the reaction temperature was raised from the initial 60 °C to 80 °C, and maintained for 40 min. The rest of melamine and caprolactam were added to continue the condensation reaction, which kept the basic pH of the reaction solution between 8.5 and 9.0. The reaction was continued until a desired water dilution capacity (WDC) was attained between 2.3 and 2.5. Then, the reaction was terminated by cooling the mixture to the temperature of 40 °C.

The molar ratio of formaldehyde to melamine was 2.5. The molar ratio of water to melamine was 9.0. The major difference among all the produced MF resins was the added amount of ethylene glycol and caprolactam during the reaction.

Properties determination of MF resins

The WDC was used to determine the end point of the condensation reaction of MF resins. It was determined by how much possible water can be added to 5 g of MF resins at room temperature until this solution turns hazy and precipitates (Gu 1999). The reaction time of MF resins was calculated starting from the reaction temperature and up to 80 °C until the desired WDC of the reaction solution was obtained. The storage stable time was monitored according to the color change of MF resins, from colorless to milky white, accompanied by the phenomena of turbidity, stratification, and precipitation. The properties of the MF resins, such as appearance, viscosity, pH, gel time, solids content, and free formaldehyde content, were determined according to the Chinese national standard GB/T 14074 (2006).

Manufacture and properties determination of melamine-impregnated papers

The base paper was cut into pieces having a size of 350 mm × 350 mm. The melamine-impregnated papers were produced by impregnating the base papers in the MF resins for 2 min, then removing the excess resins on the paper surface using two glass rods to ensure the impregnation amount was 200 $g.m^{-2}$. The papers were dried at 130 °C for 8 min. The properties of dry/wet tensile strength of the impregnated papers were determined by the Chinese forestry industrial standard LY/T 1831 (2009).

SEC and FT-IR analysis

A SEC (G1311; Agilent Technologies Inc., Santa Clara, USA) equipped with a G1329B 1260 automatic injector (Agilent Technologies Inc., Santa Clara, USA), a G1362A differential detector (Agilent Technologies Inc., Santa Clara, USA), and a 5-µm MIXED-C column (Agilent Technologies Inc., Santa Clara, CA, USA) was used. The DMF was used as the mobile phase and the flow rate was 1 mL. min^{-1}. Samples were prepared by dissolving a small amount of MF resin in DMSO with vigorous stirring, and then it was filtered through a 0.45-µm filter.

The FTIR experiment was carried out using a Nicolet 380 FT-IR instrument (Nicolet Corp., Madison, USA) with the KBr method. The scan wavenumber range was from 500 to 4000 cm^{-1}. Approximately 0.2 mg dried MF resins were added into 30 mg KBr powder, mixed, ground to a particle size with 2-µm diameter, and then pressed into a small sample in a press machine (HY-12; Tianjin Optical Instrument Co., Ltd., Tianjin, China).

RESULTS AND DISCUSSION

Effects of Ethylene Glycol on Properties of MF Resins and Impregnated Papers

A series of MF resins were produced using the same process, varying only by the different molar ratio of ethylene glycol to melamine, between 0 (MF1) and 2 (MF5). All the MF resins were colorless liquids with a solid content between 51.3% and 53.9%, viscosity between 52 mPa.s and 63 mPa.s, and pH value between 8.7 and 9.1. The important properties of the MF resins are presented in Table 1.

Table 1. Properties of the MF Resins with Varied Addition of Ethylene Glycol

MF Resins Number	Ethylene Glycol/Melamine Molar Ratio	Properties of MF Resins			
		Reaction Time (min)	Gel Time (s)	Storage Stability (d)	Free Formaldehyde Content (%)
MF1	0	101	156	2	1.15
MF2	0.5	105	231	7	1.23
MF3	1	116	259	10	1.36
MF4	1.5	121	278	14	1.40
MF5	2	139	281	23	1.72

As expected, the reaction time of MF resins depended on the rate of the methylolation and condensation reaction of melamine with formaldehyde. The gel time and storage stability were largely related to the content of active amino ($-NH_2$), imino (-NH), and methylol ($-CH_2OH$) groups in the MF resins. More active groups in the MF resins resulted in easier crosslinking reactions among the intermediate products, shorter gel time, and worse storage stability. It could be concluded from Table 1 that reaction time, gel time, and storage time increased noticeably with ethylene glycol addition due to the effect of hindering condensation of ethylene glycol. The hydroxyl groups (-OH) in the ethylene glycol reacted with methylol groups ($-CH_2OH$) by an etherification reaction to consume some of the methylol groups ($-CH_2OH$) in the MF resins (Fig. 1), which would slow down the condensation reaction (Lian *et al*. 2014).

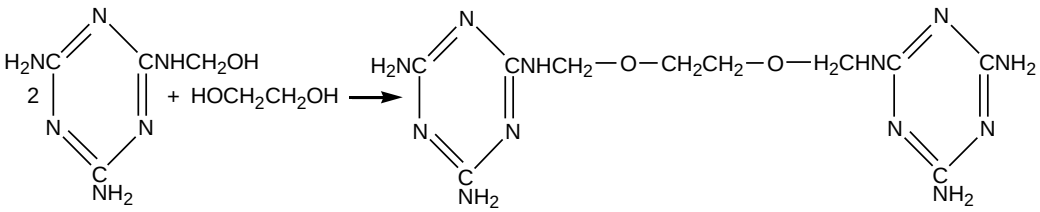

Fig. 1. Etherification reaction of ethylene glycol with melamine

The tensile strength of impregnated papers refers to the maximum tension that impregnated papers can withstand. Better toughness of the MF resins after curing resulted in a higher tensile strength of the impregnated papers. Figure 2 shows the dry and wet tensile strengths of MF resin-impregnated papers as a function of molar ratio of ethylene glycol to melamine. It is apparent from Fig. 2 that dry/wet tensile strength of MF resin-impregnated papers was improved considerably when ethylene glycol was added. These results showed that ethylene glycol had a good toughening effect on MF resins due to the condensation reaction of the hydroxyl groups (-OH) in ethylene glycol or self-condensation polyethylene glycol with amino groups ($-NH_2$) in melamine (Fig. 3), which introduced linear flexible segments to increase the distance between adjacent melamine's triazine, thus improving the flexibility of the MF resins after curing (Antunes *et al*. 2018a). The best values of dry and wet tensile strength were obtained when the molar ratio of ethylene glycol to melamine was 1.0.

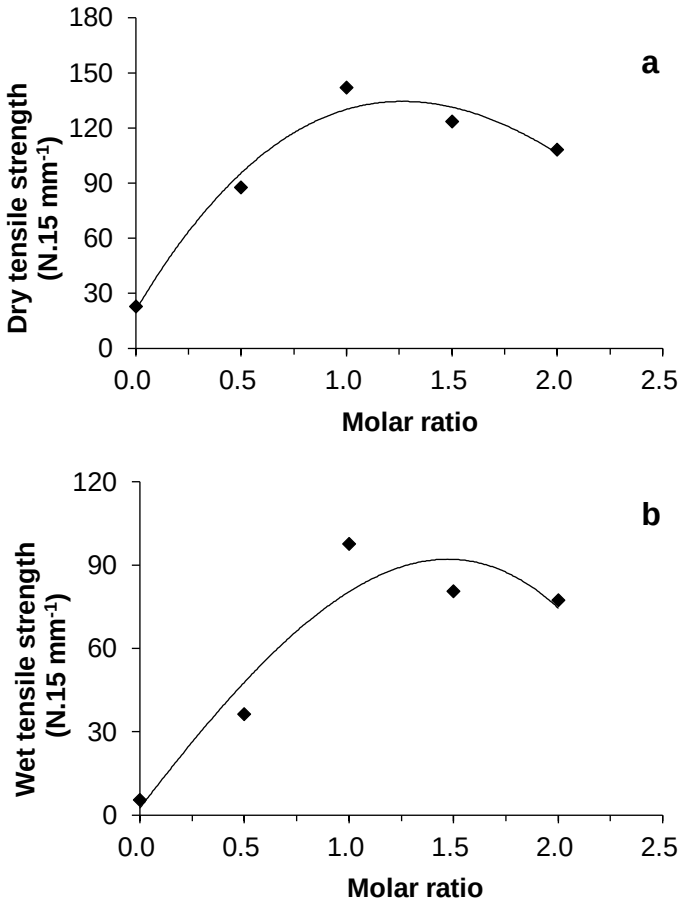

Fig. 2. Effects of the ethylene glycol/melamine molar ratio on the dry tensile strength (a), and wet tensile strength (b) of MF resin-impregnated papers

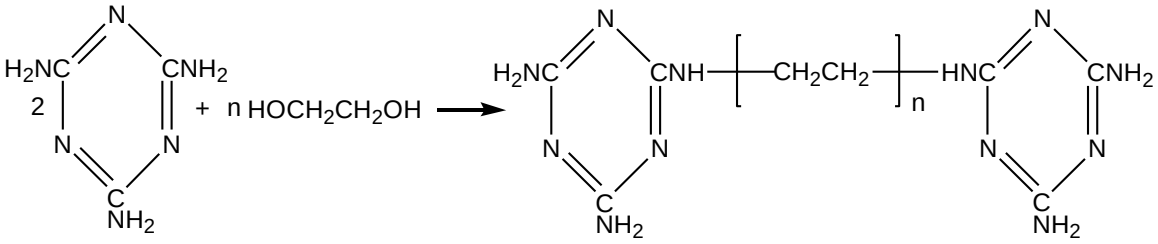

Fig. 3. Condensation reaction of ethylene glycol with melamine

Effects of Caprolactam on Properties of MF Resins and Impregnated Papers

It is well known that formaldehyde has a negative influence on human health because of its high toxicity. Free formaldehyde content is an important parameter to consider in MF resins. Ethylene glycol is a perfect toughener and stabilizer that can improve the toughness and storage stability of MF resins, but Table 1 shows that the free formaldehyde content in MF resins gradually increased with increased ethylene glycol content.

To decrease formaldehyde emissions, a series of MF resins with different quantities of caprolactam were studied by fixing the molar ratio of ethylene glycol to melamine as

1.0, and changing the molar ratio of caprolactam to formaldehyde as 0.02 (MF6), 0.04 (MF7), 0.08 (MF8), 0.12 (MF9), 0.16 (MF10), 0.20 (MF11), and 0.24 (MF12).

The curves of the storage time and free formaldehyde content of MF resins as a function of increasing molar ratio of caprolactam to formaldehyde are presented in Fig. 4. The dry and wet tensile strengths of impregnated papers are given in Fig. 5. The results clearly show that the storage stability of MF resins and tensile strength of impregnated papers increased noticeably with the addition of caprolactam; conversely, the free formaldehyde content steadily declined. These results were obtained as a result of the possible reactions of caprolactam with formaldehyde and methylolmelamine in MF resins (Fig. 6). First, caprolactam reacted with formaldehyde to form *N*-methylol-caprolactam, which will reduce free formaldehyde content in MF resins (Fig. 6a) (Normand *et al*. 2002). On the other hand, caprolactam and its methylolation adduct reacted with hydroxymethyl group in methylolmelamine, leading to the formation of methylene and methylene-ether linkages in the resins (Fig. 6b and 6c). Since caprolactam is a monofunctional compound that has only one reactive group, these reactions lead to partial blocking of reactive end groups in methylomelamine monomers and oligomers. This will reduce the polymer's reactivity and prolong its storage time. In addition, it will decrease the cross-linking density of the resins after curing and therefore improve its flexibility (Antunes *et al*. 2018b; Pereira *et al*. 2019).

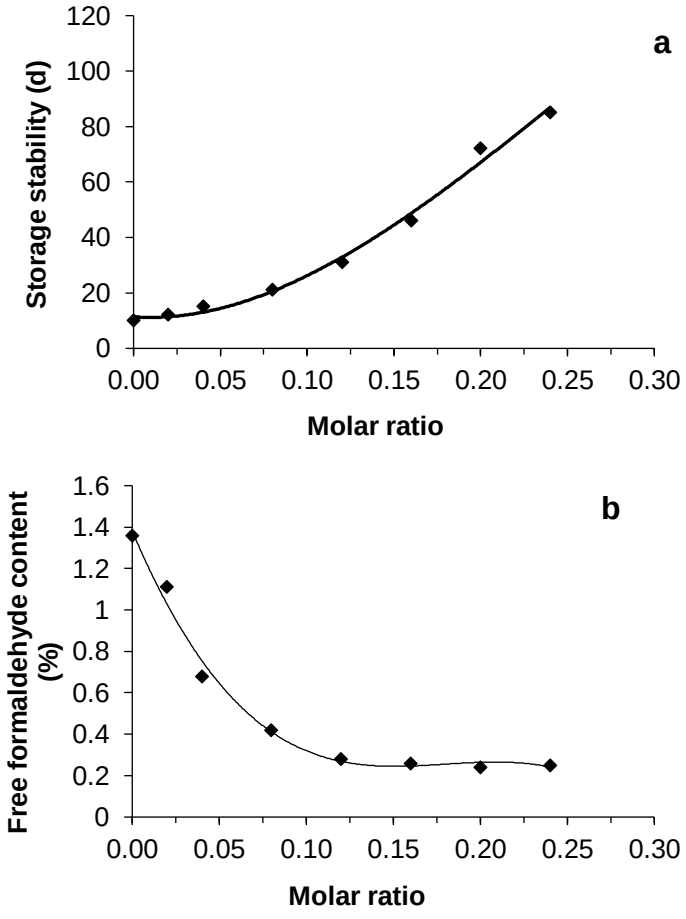

Fig. 4. Effects of caprolactam to formaldehyde molar ratio on the storage stability (a) and free formaldehyde content (b) of MF resins

Generally, the optimal molar ratio of caprolactam to formaldehyde was 0.12 (MF9) after comprehensively considering all properties. Compared to MF resin without ethylene glycol and caprolactam (MF1), the improved MF resins' storage time was prolonged from 2 days to 1 month, and free formaldehyde content decreased from 1.15% to 0.28%, respectively. The free formaldehyde content passed the relevant Chinese national standard GB/T 14732 (2006) specifications for wood adhesives (free formaldehyde content ≤ 0.3%). Meanwhile, the dry tensile strength of impregnated paper was improved from 22.7 to 146.6 N·15 mm^{-1}, and wet tensile strength was increased from 5.5 to 101 N·15 mm^{-1}. These values also passed the relevant Chinese forestry industrial standard specifications for decorative paper on wood-based panels (dry tensile strength ≥ 25.0 N·15 mm^{-1}; wet tensile strength ≥ 6.0 N·15 mm^{-1}).

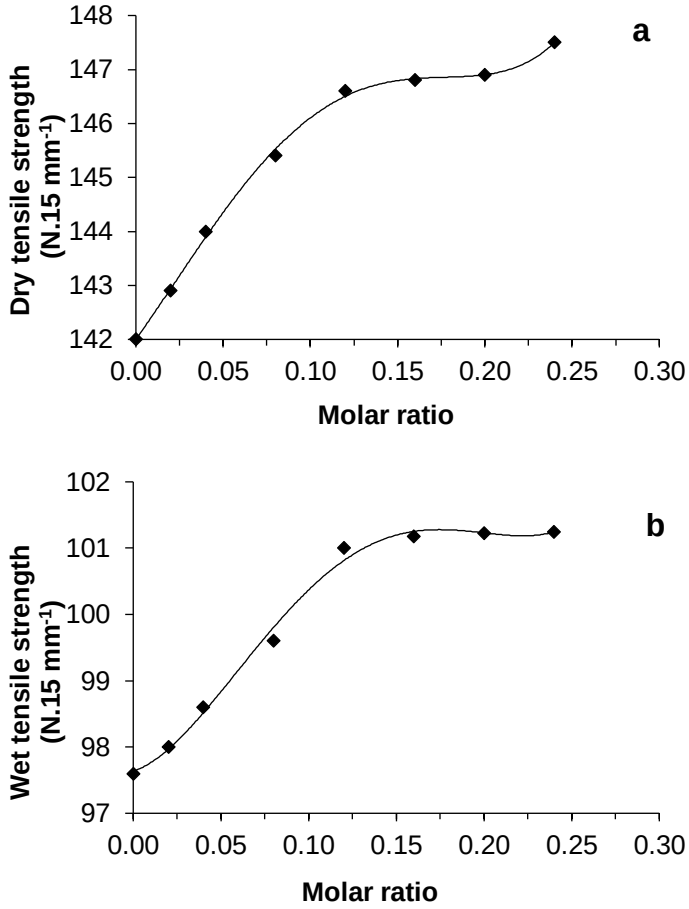

Fig. 5. Effects of caprolactam to formaldehyde molar ratio on the dry tensile strength (a) and wet tensile strength (b) of impregnated papers

SEC and FT-IR Characterization

The SEC and FT-IR results are considered in this section to observe the evolution of ethylene glycol and caprolactam in the synthesis process of MF resins. The molecular weight distribution of MF1 without ethylene glycol and caprolactam, MF3 with ethylene glycol, and MF9 with ethylene glycol and caprolactam were examined by SEC chromatography. The results are shown in Fig. 7.

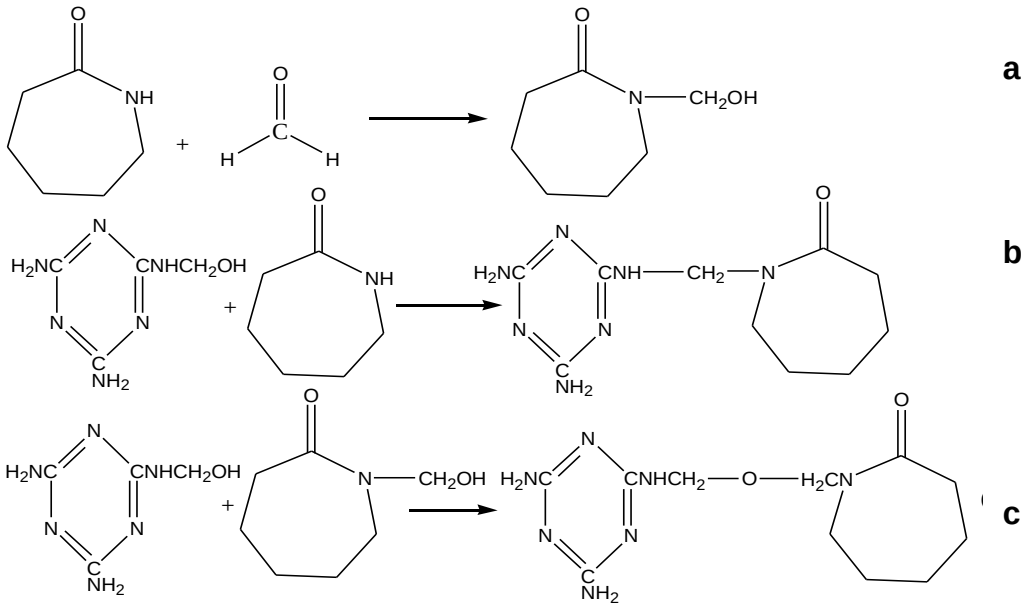

Fig. 6. Possible reaction of caprolactam with formaldehyde and methylolmelamine in MF resins

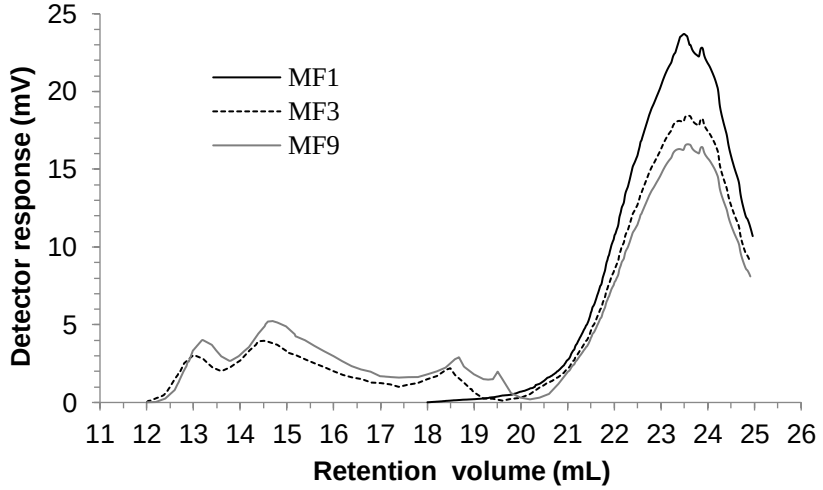

Fig. 7. SEC chromatograms of MF resins

It is worth noting that the resin (MF1) without ethylene glycol and caprolactam presented only on large retention volumes (between 18 mL to 25 mL), which can be assigned to lower molecular weight substances such as unreacted melamine, methylolmelamine, and intermediate oligomers. The curves for the other two resins (MF3 and MF9) exhibited more complex peaks at the lower retention volumes (from 11 mL to 20 mL), which corresponds to polymers with medium molecular weight (Paiva *et al*. 2012a,b). This difference is a result of the higher molecular weight aggregating in MF1 that never actually enter the SEC column due to their retention on the filter during sample preparation (Ferra *et al*. 2010). For MF3 and MF9, a section of intermediate molecular weight products were generated with the addition of ethylene glycol and caprolactam that can be detected by the SEC detector. It can be concluded from Fig. 7 that ethylene glycol and caprolactam participated in the chemical reaction of MF resins. These reactions lead

to a different molecular weight distribution of MF resins. Compared to MF1 resin, the MF resins with ethylene glycol and caprolactam have more intermediate molecular weight products.

The functional groups of the MF resins were analyzed by FT-IR. The spectra are presented in Fig. 8, and the assignments are given in Table 2. The large band at 3320 cm^{-1} was assigned to the stretching vibration of hydroxyl (-OH), amino (-NH_2), and imine (-NH) groups. The band at 1629 cm^{-1} was due to the N-H bending vibration that was assigned to amino (-NH_2) and imine (-NH) groups (Li 2003). All of these groups mainly come from melamine, methylolmelamine, ethylene glycol, and caprolactam. A weak signal at 1730 cm^{-1} was assigned to aldehyde groups (HC=O) from formaldehyde. The bands located at 1556 cm^{-1}, 1360 cm^{-1}, and 812 cm^{-1} were assigned to C=N-C, N-C-N stretching vibration, and C_3N_3 out-of-plane bending vibration of melamine's triazine, respectively. The band at 2930 cm^{-1} was due to the C-H stretching vibration assigned to methylene bridges (-CH_2-) between melamine's triazines. The band at 1150 cm^{-1} was due to the C-O stretching vibration assigned to ether bridges (C-O-C) between melamine's triazines (Kandelbauer *et al*. 2007). In addition, another C-O stretching vibration was displayed at 1028 cm^{-1}, assigned to primary alcohol (R-CH_2-OH) from methylolmelamine, ethylene glycol, and methylol-caprolactam. The band at 874 cm^{-1} was due to ring bending of caprolactam.

It is important to note that an obviously double peak at 725 cm^{-1} was detected that was assigned to saturated C-C stretching attributed to multiple methylene bridge (-$(CH_2)_n$- $n \geq 4$), which belongs to self-condensation of polyethylene glycol and caprolactam in MF3 and MF9 resins. Meanwhile, compared to one weak single peak at 1730 cm^{-1} in MF1, another signal at 1750 cm^{-1} was determined that was assigned to C=O stretching attributed to cyclic ketone (caprolactam). This FT-IR observation was in accordance with the SEC chromatography analysis, indicating that ethylene glycol and caprolactam participated in the chemical reaction of resins synthesis process and changed their chemical composition and structure.

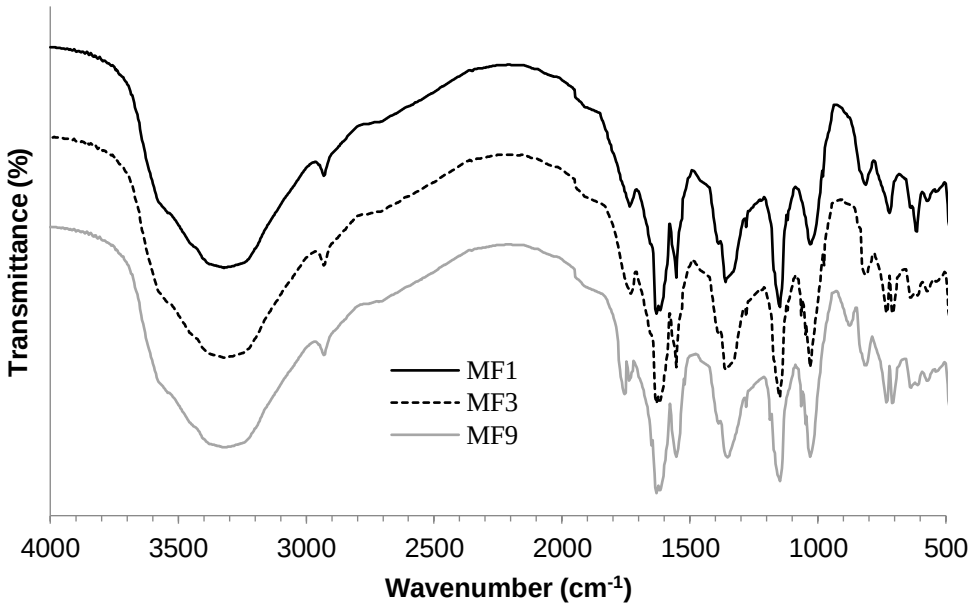

Fig. 8. FT-IR spectra of MF resins

Table 2. Assignment of FT-IR Spectra of MF Resins

Wavenumber (cm^{-1})	Assignment
3320	-OH, $-NH_2$, -NH stretching
2930	C-H stretching of $-CH_2-$ between triazine
1750	C=O stretching of caprolactam
1730	C=O stretching of RCHO (formaldehyde)
1629	N-H bending of amide $–NH_2$ and –NH
1556	-C=N-C bending of triazine
1360	N-C-N stretching of triazine
1150	C-O-C stretching of $–CH_2-O-CH_2-$ between triazines
1028	C-O stretching of primary alcohol ($R-CH_2-OH$)
874	Ring bending of caprolactam
812	C_3N_3 out-of-plane bending of triazine
725	C-C stretching of $-(CH_2)_n-$ ($n \geq 4$, double peaks)

CONCLUSIONS

1. Ethylene glycol and caprolactam had a good function on the improvement of the toughness and storage stability of MF resins. Meanwhile, caprolactam was a good formaldehyde scavenger that decreased the free formaldehyde content well. The optimal MF resins were obtained when the molar ratio of ethylene glycol to melamine was 1.0, and the molar ratio of caprolactam to formaldehyde was 0.12.
2. The impregnated papers made from MF resins displayed good dry and wet tensile strengths and passed the relevant Chinese forestry industrial standard specifications for decorative paper for wood-based panels (dry tensile strength $\geq$ 25.0 N·15 mm^{-1}, wet tensile strength $\geq$ 6.0 N·15 mm^{-1}).
3. The results from SEC and FT-IR showed that ethylene glycol and caprolactam participated in the chemical reaction of MF resins synthesis process. The MF resins produced with ethylene glycol and caprolactam had a different molecular weight distribution and polymeric structure.

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