

Preparation and characteristics of Aziridine-Benzoguanamine-Urea-Melanmine-Formaldehyde resins

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Abstract. In this study, the effect of Aziridine (AZ) addition on the properties of the BG-MF and BG-U-MF resin, such as the mechanical strength, tensile strength, moisture adsorption, and limited oxygen index, were studied in details. The best performance was obtained for modified resins with 2 wt. % added AZ. The structure characteristics of the modified MF resins were investigated using Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD). It was found that the characteristic absorption peak of the hydroxyl group and the ring of the three triazine group was significantly reduced, which indicated that the addition of aziridine was beneficial to the curing reaction. It could be seen that the effect of the addition of aziridine on the crystallinity of BG15% modified resin was not obvious, but the crystallinity of BG15%+U20% modified resin was reduced. The tensile strength and elongation at break increased after the addition of 2% aziridine, and resistance to burning and boiling water were also improved.

1. Introduction

Melamine formaldehyde resin (MF) is derived from the polycondensation of melamine and formaldehyde molecules, which is a triazine-rich heteroatom polymer with high content of nitrogen¹. Presently, MF is widely used in many fields. However, the high degree of crosslinking density in cured MF resin makes it inherently brittle, which resulted in limiting its application. Thus, the modification of melamine resin (MF) has become a research hotspot [1-7].

At present, the research on the modification of melamine resin (MF) has been reported. Xu et al^[6] reported that Melamine-formaldehyde resin (MF)/polyvinyl alcohol (PVA) composite fibers were prepared by wet spinning, the experiments results shown that the obtained MF/PVA composite fiber shows a sea-island phase structure, and the best comprehensive properties: the breaking strength and breaking elongation are 4.29 cN/dtex, 13.55%, respectively. Yari et al [7] reported that an acrylic polyol/melamine hardener was modified with a POSS macromolecule, and POSS could enhance toughness. Hang et al [8] reported that using benzoguanamine (BG) as a substitute for partial melamine to synthesize modified resin to improve the heat resistance and toughness.



Aziridine (AZ) is transparent liquid crosslinker. It is a compound containing three membered rings, and three membered ring molecules is an unstable structure, which shows high chemical crosslinking reaction (Fig 1). In this paper, the BG-MF and BG-U-MF resin were both modified by AZ, and the impregnated kraft paper laminate were prepared by using the obtained modified resins as adhesive. The effect of AZ addition on the properties of the BG-MF and BG-U-MF resin, such as the structure characteristics, mechanical strength, tensile strength, moisture adsorption, and limited oxygen index, were studied in details.

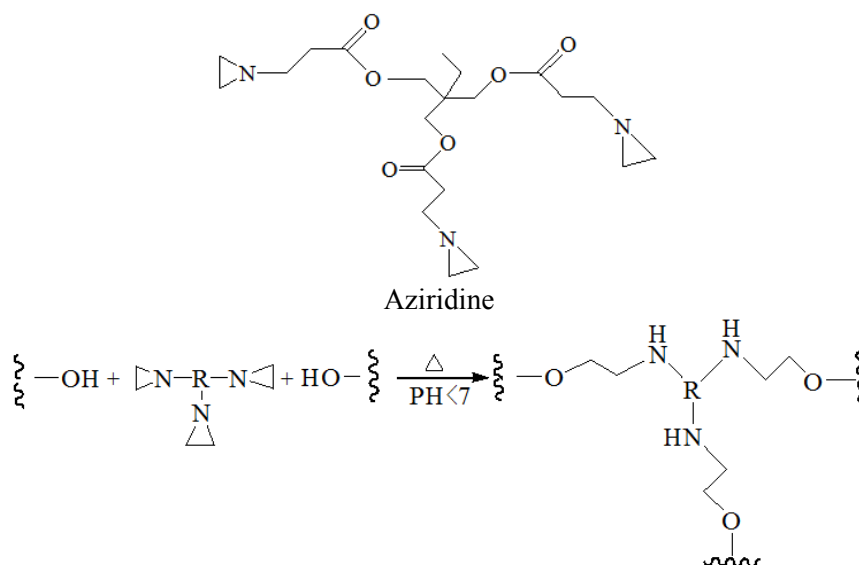


Figure 1. The mechanism of modification by aziridine (AZ)

2. Materials and methods

2.1. Materials

Formaldehyde, melamine, urea, and kraft paper were purchased from Zhejiang linglong decoration material Co. Ltd., benzoguanamine was obtained from Wuhan Organic Chemical Co. Ltd., sodium hydroxide was obtained from Sinopharm Chemical Reagent Co. Ltd.; aziridine was purchased from Dongguan xuyi hua Chemical Co. ltd.

2.2. Characterization

2.2.1. Fourier Transform Infrared (FTIR) Analysis. The modified resin was cured at 120 °C, and then dried in vacuum oven to a constant weight. The FTIR spectra of samples are recorded using a Model Perkin Elmer 1100 series operating in the region of 4000-400 cm⁻¹ using KBr pellet technique.

2.2.2. X-Ray Diffractometer (XRD) Analysis. XRD spectra of the samples were obtained from a Rigaku D/max-RA power diffraction-meter using Cu K α radiation in the 2 θ range of 5°-60°.

2.3 Preparation of modified MF resins

A typical procedure was as followed, certain formaldehyde and melamine were both added into a condensation reflux device three flasks. The pH value was adjusted to about 9.0 by sodium hydroxide solution, and then the mixture was stirred until completely dissolved. After that, the certain amount of benzoguanamine was added to the mixture solution, and the reaction mixture was heat to 85 °C and maintaining for a certain reaction time. The colorless transparent liquid copolymer resin was obtained, with a solid content of 61.4% and a pH value of 8.8. The content of aziridine was 2%.

A certain amount of 37% formaldehyde solution, urea and melamine were added to a condensation reflux device three flasks. The pH value was adjusted to about 8.5 by sodium hydroxide solution, and the reaction mixture was heat to 60 °C and maintaining for a certain reaction time. The rest of the melamine, benzoguanamine, and formaldehyde were added to the mixture solution, and the reaction mixture was heat to 85 °C and maintaining for a certain reaction time. The colorless transparent liquid copolymer resin was obtained, with a solid content of 57.2% and a pH value of 8.5. The content of aziridine was 2%.

2.4. Preparation and properties of impregnated paper laminated board

A typical procedure was as followed, each laminated board was made up of three pieces of kraft paper, and the amount of glue was 80%, and then dried at 60 °C by hot air circulation, which make the adhesive paper uniform dried. Hot-pressing condition was as followed: Temperature 140-150 °C, pressure 6-7 MPa, time 30 min.

The appearance of the obtained hot pressed laminated plate was smooth, uniform color and gloss. The process conditions of tensile properties (GB/T 7911-2013): The tensile mechanical properties of laminated plate were tested by electronic universal testing machine. The temperature was 25 °C, the loading rate was 5mm/min, and the number of each sample was not less than 5. Boiling water resistance test (GB/T 7911-2013): each sample is not less than 3. Determination of combustion performance (GB/T 2406.2-2009): The top ignition method and each sample is not less than 5.

3. Results and discussion

3.1. FTIR and XRD analysis

FTIR spectra were usually employed to identify the structural change of the sample. As shown in Fig 2, the band at near 3350 cm^{-1} was linked to the -OH and -NH- hydroxyl groups. The stretching band appeared at 1010 cm^{-1} was ascribed to the vibration absorption peak C-O and N-H, and the peak at 813 cm^{-1} ascribed to thiotriazinone surface of outer ring vibration absorption peak. From the results, it was concluded that existence of aziridine could accelerate curing reaction of BG15% and BG15%+U20%.

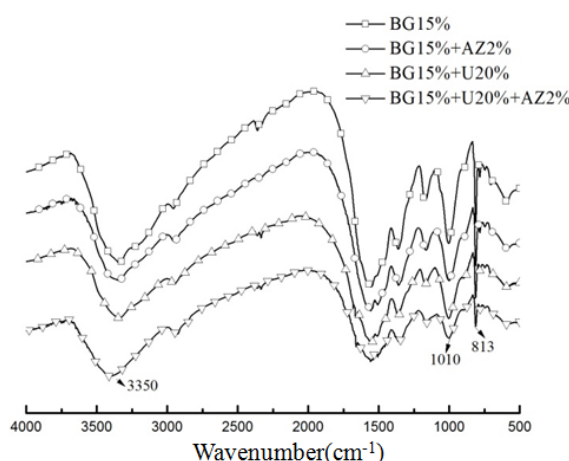


Figure 2. FT-IR of modified MF resin

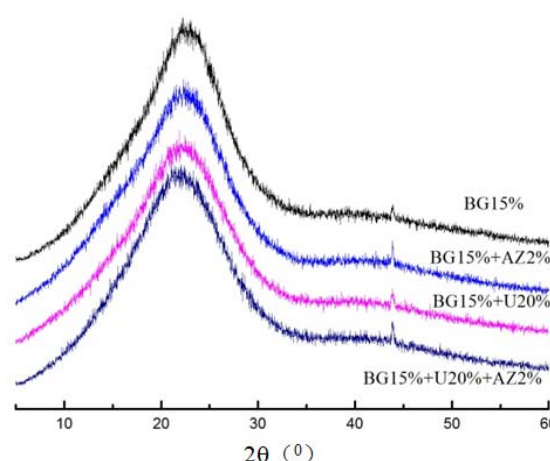


Figure 3. XRD of modified MF resin

As shown in Figure 3, there is no obvious change in the X-ray diffraction pattern of BG15% modified MF resin, and the diffraction peaks appear at 20 and 43 degrees. The relative crystallinity of BG15% modified MF was 39.45% by calculation of crystallinity. But the crystallinity of modified resin by aziridine was changed to 40.20%, this was maybe because that the new cross-linked structure was formed when the aziridine was added. By adding AZ to BG15% and U20% resin, the peak angle was slightly shifted and narrowed. According to the calculation of crystallinity, the relative crystallinity of

urea modified MF was 40.78%, and the crystallinity was reduced by the modification of aziridine. This was because that the addition of aziridine molecules could destroy the regularity of the molecular chain of urea formaldehyde resin.

3.2. Mechanical of properties modified MF resin

Table 1 shown effect of aziridine on the tensile mechanical properties of modified MF resin. As shown in Table 1, In comparison with the MF resin, the tensile strength of BG15% modified MF resin increased, but the elastic modulus decreased. Meanwhile, the elongation at break increased to 3.24%. This may be due to the existence of the the large molecule of the triazine ring. The tensile strength and elastic modulus of MF modified by BG15% and U20% were increased after adding the aziridine, and the tensile strength increased from 86Mpa to 90Mpa, while the elongation at break was not obviously changed.

Table 1. Effect of Aziridine on the tensile mechanical properties of modified MF resin

Samples	Tensile strength (Mpa)	Elasticity modulus (Mpa)	Elongation at break (%)
MF	91.2	11767	2.54
BG15%	99.2	13618	3.10
BG15%+AZ2%	99.8	12593	3.24
BG15%+U20%	86.0	12280	3.47
BG15%+U30%+AZ2%	90.0	12370	3.49

3.3. Oxygen index, thickness swell water adsorption properties of modified MF resin

Fig 4 shown that effect of aziridine on oxygen index of MF modified resin laminated panel (BG15% and BG15% + U20%). The results are shown in Fig 3. There was no obvious change on the oxygen index of BG15% modified MF resin when the addition of 2% aziridine. But the oxygen index was increased to 34.9 when the aziridine added into the BG15% + U20% resin.

Fig 5 and Fig 6 shown that effect of aziridine on thickness swell and water absorption of modified MF resin laminated panel. As shown in Fig 4, it was clearly seen that the thickness swell ratio of BG15% resin was decreased from 7.72% to 7.6% and the water absorption rate was decreased from 8.73% to 8.6% after 2% aziridine adding. Meanwhile, the thickness swell ratio of BG15%+U20% resin was decreased to 7.6% and the water absorption rate decreased to 8.6% after 2% aziridine adding. It was found that the thickness swelling rate and water absorption rate were both decreased.

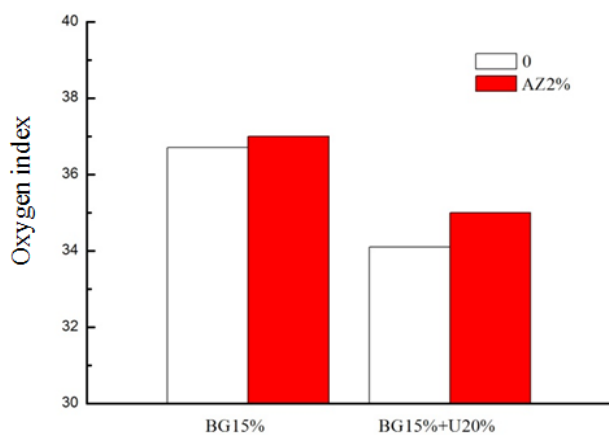


Figure 4. The oxygen index of laminated panel

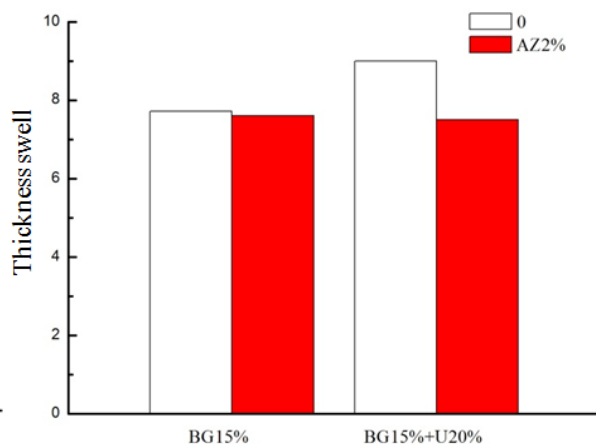


Figure 5. The thickness swell of laminated Panel

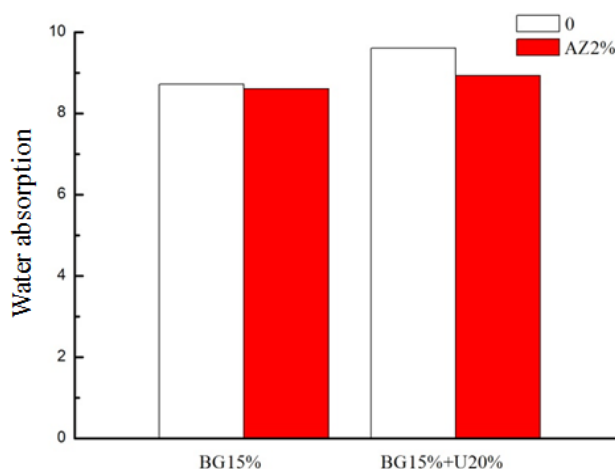


Figure 6. The water absorption of laminated panel

4. Conclusion

(1) Based on the results of FTIR analysis, it was found that the characteristic absorption peak of the hydroxyl group and the ring of the three triazine group were significantly reduced under the same curing condition, which indicated that the addition of aziridine was beneficial to the curing reaction.

(2) Based on the results of XRD analysis, it could be seen that the effect of the addition of aziridine on the crystallinity of BG15% modified resin was not obvious, but the crystallinity of BG15%+U20% modified resin was reduced.

(3) Based on the results of mechanical, oxygen index, thickness swell and water absorption properties of laminated panel, the tensile strength and elongation at break increased after the addition of 2% aziridine, and resistance to burning and boiling water were also improved.

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