# Study on Modification of Phenol Formaldehyde Resin Adhesive with Ionic Liquid

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**Abstract.** Ionic liquid [HeMIM]Cl was prepared and then used to synthesize phenol formaldehyde resin adhesive by in-situ blending with phenol and formaldehyde using base catalyst. The chemical structure of hybrid adhesive was characterized by FT-IR, as well as the effects of the ionic liquid amount, the molar ratio of phenol to formaldehyde and the catalyst dosage on the properties of adhesive were investigated. The results showed that the adhesion properties of phenol formaldehyde resin were improved significantly by the modification with ionic liquid. When the molar ration of phenol to formaldehyde was 1:2, the amount of ionic liquid was over 15%, and the catalyst dosage was no less than 1%, the adhesion properties of phenol formaldehyde resin were the best.

## Introduction

Ionic liquids (ILs) are ambient temperature molten salts and have attracted considerable attention because of their unique properties such as incombustibility, negligible volatility, high ionic conductivity, and thermal stability, etc[1]. ILs are versatile liquids that have recently been utilized in many researches concerned with macromolecules[2-4].

Phenol formaldehyde (PF) adhesive is widely utilized in various industrial fields for its advantages such as high bonding strength, good chemical stability and resistances of water, heat and wear[5]. With the development of economy, further improvement of its quality and performance is required higher and higher. Therefore, many Chinese researchers carried out the modifications of PF with different methods. Li Yi et al.[6] utilized boron and tung oil to modify PF to improve its heat resistance and wear resistance. Wang Chao et al.[7] conducted the modification with maleimide to improve the bonding strength of PF. Wang Jigang et al.[8] improved the carbon residual rate and the bonding strength of PF with inorganic materials such as silicon power and B4C. Zhang Qiaoling et al.[9] used distilled tall oil to improve the compatibility of PF. To make good use of renewable resource, Li Aiyang et al.[10] applied lignin to modify PF, however, the bonding property was not improved significantly. So far, the literature about modification of PF using ionic liquid has not been reported yet.

In this paper, with the purpose to overcome the defects of deep color and cracks after resin curing, and decrease the amount of free formaldehyde to improve adhesion properties, we prepared the ionic liquid [HeMIM]Cl and then blended it in-situ with phenol and formaldehyde to synthesize alcohol soluble adhesive of phenol formaldehyde resin over base catalyst, which offering a new method for the preparation and property optimization of hybrid materials using ionic liquid.

## Experiment

**Materials and Apparatus.** Phenol (AR) was purchased from Tianjin Chemical Agent Factory Three. Formaldehyde (38%, AR) was purchased from Shanghai Su Yi Chemical Agent Limited Company. Hydrochloride, sodium thiosulfate and sodium hydroxide (AR) were all purchased from Shanghai Pilot Chemical Agent Company. The ionic liquid of [HeMIM]Cl was prepared in lab by the method reported in the literature[11].

The viscosity of the hybrid adhesive was determined with NDJ-8-S viscosity meter. The lap samples were prepared using XLB-D plate vulcanization machine (400×400×2). The tensile shear strength of the lap samples was tested through CMT4304 type SANS computer control electronic universal testing machine. The chemical structural characterization was performed using MAGNA-IR750 type FT-IR.

**Preparation of PF Hybrid Adhesive.** The reaction was carried out in a round bottom beaker with a condensation and refluxing device. A certain amount of ionic liquid and aqueous solution of phenol and sodium hydroxyl were charged into the beaker successively, and mixed with stirring. The resulting mixture was heated to 42～45 $^{o}$C using a water bath and kept at this temperature for 10 min. After charging formaldehyde solution into the beaker, the temperature of the reaction mixture was increased to 70 $^{o}$C in 15min and kept at this level for another 20 min, and then increased slowly to 95～98 $^{o}$C. After reaction for another 30 min, the resulting reaction mixture was cooled to 60 $^{o}$C and dehydrated with circulating water vacuum pump for 40 min. After regulation the viscosity to 350～400 mPa*s at 40 $^{o}$C with proper amount of alcohol, the final product was stirred continuously to achieve a uniform system before discharge.

**Curing and Properties Test of PF Hybrid Adhesive.** The tests of solids content and free formaldehyde content were carried out according to national standards HG/T 2793-1995 and HG/T 2622－94, respectively. Those samples prepared through plate vulcanization machineand were shelved for a week to test their tensile and shear properties, namely of adhesion properties, according to the national standard GB/T7124－86. Characterizations of the solidified samples by FT-IR were performed to determine the chemical structure of the PF hybrid adhesive.

## Results and Discussions

**Determination of Curing Temperature of PF Hybrid Adhesive.** The determination and analysis of the curing temperatures of the traditional PF, PF made of wood powder and PF made of wood powder combing with ionic liquid were performed using DSC. The curves obtained are shown in Fig.1.

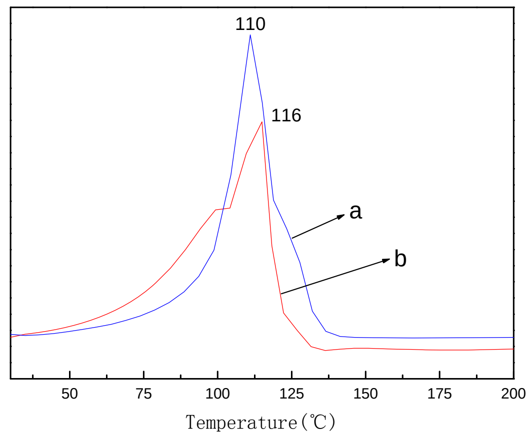


Fig.1. DSC results of (a) original PF and (b) PF modified with ionic liquid.

As shown in Fig.1, the curing temperature of the traditional PF was 116 $^{o}$C, while that of the PF modified with [HeMIM]Cl decreased to 110 $^{o}$C, which proves that the curing temperature can be decreased after modification with the ionic liquid, but not very greatly. The small lower range may be due to the properties of the ionic liquid such as having high boiling point and being non-volotile. However, compared to the original PF, the modified PF has advantages such as lighter color, no cracks, better glossiness and higher transparency.

**Effects of Ionic Liquid Amount on Properties of the Modified PF.** When the molar ratio of phenol to formaldehyde, NaOH and water was 1:2:0.25:0.05, changing the charge of the ionic liquid in the modification, the properties of modified PF were determined and analyzed to investigate the effects of the ionic liquid amount on the properties of the modified PF. The results are shown in Table 1.

Table 1 Effects of ionic liquid amount on the properties of the modified PF.

| Samples | Ionic liquid amount (%) | Solids content (%) | Free formaldehyde content (%) | Tensile shear strength (KN) |
|---|---|---|---|---|
| 1 | 5% | 28.9 | 2.76 | 1.16 |
| 2 | 10% | 30.4 | 1.08 | 2.03 |
| 3 | 15% | 33.5 | 0.86 | 3.08 |
| 4 | 20% | 34.2 | 0.77 | 3.19 |

According to the data in Table 1, it can be seen that when the viscosity varied in the range of 350～400mPa*s, the properties of PF adhesive were different from each other due to the ionic liquid amount used in the modification. With the increase of ionic liquid amount, the apparent solids content increased and the free formaldehyde content decreased significantly, while the tensile shear strength increased from 1.16 KN to 3.19 KN. The reason for this could be that when PF was synthesized in the solvent of ionic liquid, lots of ionic liquid was left in the modified PF as residue, which leads to a bigger apparent solids content. The great reduction of free formaldehyde content is because of the capture capability of ionic liquid to the free formaldehyde. Since the ionic liquid itself has strong polarity, which is convenient to adhesion property of PF, the existence of the ionic liquid can improve the adhesion property of the PF hybrid adhesive. However, when the amount of the ionic liquid exceeded 15%, the properties of the modified PF tended to be stable.

**Effects of Molar Ratio of Phenol to Formaldehyde on the Properties of the Modified PF.** Using 15% ionic liquid and the same catalyst dosages of catalyst and water, the process for the Sample 3 described in Table 1 was applied to investigate the effect of phenol to formaldehyde on the properties of modified PF. The results are listed in Table 2.

Table 2 Effect of molar ratio of phenol to formaldehyde on the properties of the modified PF.

| Samples | Ionic liquid amount(%) | Solids content (%) | Free formaldehyde content (%) | Tensile shear strength (KN) |
|---|---|---|---|---|
| 1 | 1:1.5 | 34.8 | 0.31 | 2.86 |
| 2 | 1:1.8 | 35.4 | 0.69 | 3.01 |
| 3 | 1:2 | 33.5 | 0.86 | 3.08 |
| 4 | 1:2.3 | 37.8 | 1.26 | 3.10 |

From Table 2, we can know that in a certain range of viscosity, with the increase of free formaldehyde content, the apparent solids content tended to increase, but the change was not great, while the free formaldehyde content and the tensile shear strength increased gradually. The reason for this is that with the increase of formaldehyde content, the ionic liquid in the hybrid adhesive only absorbed a certain amount of formaldehyde, which leading to the increases of the free formaldehyde content and the viscosity. When the concentration of formaldehyde is too high, the release amount of free formaldehyde could be too large to achieve any environment protection significance and ideal modification result. According to the experimental data, a relatively good adhesion property can be achieved at the molar ration of phenol to formaldehyde 1:2.

**Chemical Structure Characterization of PF Hybrid Adhesive.** The FT-IR spectra of the original PF and the modified PF with ionic liquid are shown in Fig.2.

As shown in curve a, the adsorption bands centered at 3466 $cm^{-1}$ and 2933 $cm^{-1}$ were attributed to the stretching vibrations of association hydroxyl and methylene, respectively. The characteristic absorption bands at 1609 $cm^{-1}$ and 1452 $cm^{-1}$ were the benzene skeleton vibration. The adsorption band centered at 1205 $cm^{-1}$ was corresponded to the stretching vibration of aromatic ether bond. The characteristic peak at 883 $cm^{-1}$ was attributed to the bending vibration of –CH– in the substituted benzene. All these peaks were typical characteristic peaks of PF. On the other side, two new peaks at 1161 $cm^{-1}$ and 741 $cm^{-1}$ in curve b, which were characteristic peaks of imidazole ring in ionic liquid, indicated that phenolic hydroxyl group had a higher reaction activity in the hybrid adhesive system, which using ionic liquid as reaction medium, and performed condensation reaction with phenol and formaldehyde. The difference of FT-IR spectra was due to that the ionic liquid with a higher boiling point was left in the hybrid adhesive as residue during curing.

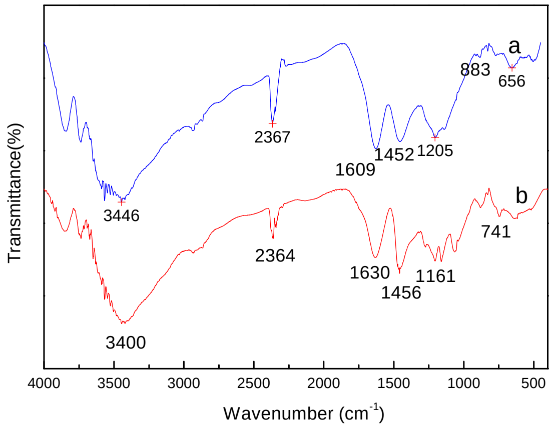


Fig.2. FT-IR Spectra of (a)the original PF and (b)the PF modified with the ionic liquid [HeMIM]Cl.

## Conclusion

In this paper, the ionic liquid [HeMIM]Cl was prepared and blended in-situ with phenol and formaldehyde to synthesize PF adhesive using base catalyst, as well as the properties of the resulting PF were tested. The results showed that the free formaldehyde content in the modified PF produced with this method decreased, while the tensile shear strength was improved significantly. The hybrid adhesive had a low curing temperature, fast curing speed, no cracks, good transparency, light color and good glossiness. When the molar ration of phenol to formaldehyde was 1:2 and the amount of ionic liquid was no less than 15%， both relatively stable properties and good adhesion property can be achieved.

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