Synthesis of Functionalized Ionic Liquids and Their Straw Dissolution System for the Modification of Phenolic Resin (Postprint)

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Date: 2023-03-18T00:00:00+00:00

Abstract

Three functionalized imidazolium ionic liquids, namely 1-(2-hydroxyethyl)-3-methylimidazolium chloride [HeMIM]Cl, 1-(ethylamino)-3-methylimidazolium bromide [AeMIM]Br, and 1-(carboxyethyl)-3-methylimidazolium chloride [CeMIM]Cl, were synthesized and structurally characterized by infrared spectroscopy and ^{1}H NMR. These three ionic liquids were utilized to dissolve straw, and the dissolution systems were in-situ blended with phenol and formaldehyde to prepare phenolic composites. The influence of ionic liquid type on straw dissolution rate and phenolic resin properties was investigated. The results indicated that the properties of phenolic composites prepared using the ionic liquids and their straw dissolution products were significantly improved. [CeMIM]Cl demonstrated the best dissolution performance, and the phenolic composite prepared using its straw dissolution product exhibited the lowest free aldehyde content. The phenolic composite prepared using the straw dissolution product from [AeMIM]Br displayed the best mechanical properties, with tensile strength increasing from 3.28 MPa to 9.48 MPa and impact strength increasing from 0.93 kJ/m^2 to 5.88 kJ/m^2.

Full Text

Synthesis of Functional Ionic Liquids as Solvent for Straw and Application in Modification of Phenolic Resin

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Supported by the National Natural Science Foundation of China (No. 51203091), Liaoning Province Education Department Project (No. L2014037), and College Students' Innovation and Entrepreneurship Training Project.

Manuscript received July 13, 2014; in revised form August 19, 2014

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Abstract

Three functional imidazolium ionic liquids—1-(2-hydroxyethyl)-3-methylimidazolium chloride ([HeMIM]Cl), 1-(ethylamino)-3-methylimidazolium bromide ([AeMIM]Br), and 1-(carboxyethyl)-3-methylimidazolium chloride ([CeMIM]Cl)—were synthesized and characterized by FTIR and ^{1}H NMR. Straw was dissolved in these ionic liquids, and the resulting solutions were in-situ blended with phenol and formaldehyde to prepare phenolic resin composites. The effects of ionic liquid type on straw dissolution rate and on the properties of phenolic resin were investigated. The results demonstrate that the properties of phenolic resin composites were significantly improved by incorporating the ionic liquid-straw dissolution systems. Among the three ionic liquids, [CeMIM]Cl exhibited the best dissolution performance for straw, yielding composites with the lowest free formaldehyde content. The composite prepared with the [AeMIM]Br-straw dissolution system showed the best mechanical properties, with tensile strength increasing from 3.28 MPa to 9.48 MPa and impact strength rising from 0.93 kJ/m^2 to 5.88 kJ/m^2.

Keywords: organic polymer materials, functionalized ionic liquid, dissolution, straw, phenolic resin composites, free formaldehyde content, tensile strength, impact strength

Introduction

Ionic liquids have been widely applied in organic synthesis, catalytic reactions, separation and extraction, and composite preparation due to their excellent properties [1-5]. The emergence of ionic liquids provides a reaction environment distinct from traditional solvents, facilitating enhanced control over polymer structure and polymerization reactions at a higher level. Introducing ionic liquids into organic polymer materials enables the preparation of high-performance, environmentally friendly modified polymers.

Phenolic resin exhibits excellent mechanical properties, heat resistance, electrical insulation, dimensional stability, processability, and flame retardancy, finding extensive applications in automotive, electronics, electrical, transportation, and military fields, gradually replacing some engineering plastics, metals, and alloys [6]. With the development of the wood-based panel industry and increasing environmental demands, the performance of existing phenolic resin adhesives can no longer meet the requirements of many high-tech applications. Meanwhile, production costs for petroleum-based phenolic resin continue to rise. Additionally, toxic free formaldehyde generated during phenolic resin production is difficult to remove, making environmental concerns a persistent issue. Therefore, research on substituting petroleum-based phenol and formaldehyde to prepare high-performance, low free formaldehyde-releasing green phenolic resins with functional and refined characteristics is extremely necessary.

Recent modification efforts for phenolic resins have focused primarily on environmental performance, curing behavior, high-temperature resistance, and mechanical property optimization. Du et al. [7] used a two-stage alkali addition and single reflux method to modify phenolic resin with organosilicon and sucrose, reducing free formaldehyde release and improving film flexibility. Wang et al. [8] investigated the relationship between curing kinetics and mechanisms of standard phenolic resin, analyzing the complete curing process through kinetic modeling. Hoong et al. [9] prepared modified phenolic adhesives using fast-growing dicotyledonous wood, systematically studying physicochemical properties and improving mechanical strength. Tabarsa et al. [10] prepared phenolic resin from wheat straw and examined its physical and mechanical properties. These studies have laid a theoretical foundation for further phenolic resin modification. This paper employs functionalized ionic liquids and their straw dissolution products to modify phenolic resin, investigating the effects of several key factors on composite performance.

1. Experimental

1.1 Materials and Instruments

Main materials: N-methylimidazole, chloroethanol, chloroacetic acid, 2-bromoethylamine hydrobromide, phenol, formaldehyde, sodium hydroxide, organic solvents (ethanol, ethyl acetate), and straw.

Main instruments: MAGNA-IR750 Fourier transform infrared spectrometer (FTIR), AVANCE AV-400 superconducting Fourier digital NMR spectrometer, D/max-2400 automatic X-ray diffractometer, TM3000 scanning electron microscope, XLB-D400\$×400×\$2 plate vulcanizing machine, CMT4304 electronic universal testing machine, DJF-20 dynamic impact analyzer, and SFX-2L rotary evaporator.

1.2 Synthesis and Characterization of Functionalized Ionic Liquids

N-methylimidazole was mixed with chloroethanol, chloroacetic acid, or 2-bromoethylamine hydrobromide at a molar ratio of 1.2:1 in a round-bottom flask equipped with a reflux condenser. The mixture was stirred in an 80°C water bath for 8-36 hours to synthesize three functionalized imidazolium chloride/bromide ionic liquids with hydroxyl, carboxyl, or amino groups on the side chain. As the reaction progressed, the system gradually changed from a colorless transparent solution to a light yellow viscous liquid. After completion, the synthesized ionic liquids were transferred to a separatory funnel and washed three times with diethyl ether to remove unreacted N-methylimidazole. The ether-treated ionic liquids were then dried in a vacuum oven at 80°C and 0.08 MPa for 24 hours to obtain the final products. The structures were characterized by infrared spectroscopy and NMR spectrometry. The chemical structures of the three functionalized ionic liquids are shown in [Figure 1: see original paper].

[HeMIM]Cl analysis:
IR (KBr, cm^{-1}): 3410 (O-H), 3146 (C-H), 2956 (C-H), 2876 (C-H), 1644 (C=C), 1574 (C=N), 1167 (C-O), 755 (imidazole ring).
^{1}H NMR (400 MHz, DMSO): 5.40 (d, 1H, OH-a), 3.88 (d, 3H, CH$_3$-b), 7.76 (d, 1H, CH-c), 7.71 (s, 1H, CH-d), 9.23 (s, 1H, CH-e), 4.23 (s, 2H, CH$_2$-f), 3.71 (s, 2H, CH$_2$-g), 2.50 (DMSO).

[AeMIM]Br analysis:
IR (KBr, cm^{-1}): 3455 (N-H), 3163 (C-H), 2957 (C-H), 2870 (C-H), 1616 (C=C), 1579 (C=N), 744 (imidazole ring).
^{1}H NMR (400 MHz, CDCl$_3$): 4.01 (d, 2H, NH$_2$-a), 4.03 (d, 3H, CH$_3$-b), 7.10 (d, 1H, CH-c), 7.37 (s, 1H, CH-d), 9.09 (s, 1H, CH-e), 4.02 (s, 2H, CH$_2$-f), 3.75 (d, 2H, CH$_2$-g), 7.26 (CDCl$_3$).

[CeMIM]Cl analysis:
IR (KBr, cm^{-1}): 3426 (O-H), 3079 (C-H), 2976 (C-H), 2850 (C-H), 1732 (C=O), 1635 (C=C), 1560 (C=N), 1166 (C-O), 763 (imidazole ring).
^{1}H NMR (400 MHz, CDCl$_3$): 2.58 (d, 1H, COOH-a), 3.81 (d, 3H, CH$_3$-b), 7.16 (d, 1H, CH-c), 6.96 (s, 1H, CH-d), 8.01 (s, 1H, CH-e), 3.72 (s, 2H, CH$_2$-f), 7.26 (CDCl$_3$).

1.3 Dissolution of Straw in Ionic Liquids and Preparation of Phenolic Resin Composites

Straw was crushed and sieved; particles smaller than 80 mesh were washed with 20% alkaline solution to remove impurities and fatty substances, then rinsed with water to neutrality, and dried at 70°C for 12 hours. The dried straw was collected for later use.

The three synthesized ionic liquids were mixed with straw at a specific mass ratio in a round-bottom flask and stirred at 90°C. Samples were taken periodically to observe dissolution morphology under a polarizing microscope. After 3 hours of dissolution, the system was cooled to room temperature, transferred to centrifuge tubes, and centrifuged for 3 minutes. The supernatant was removed, and the residue was repeatedly washed with methanol, filtered, dried, and weighed to calculate the dissolution rate [11].

1.4 Preparation and Performance Testing of Phenolic Composites

Phenol, formaldehyde, and sodium hydroxide catalyst were added to the dissolution system at a molar ratio of 1:2:0.5, with a mass ratio of phenol to ionic liquid of 5:1. The blend was heated to 70°C within 20 minutes, held for 30 minutes, then slowly heated to 95°C and maintained for 1-2 hours. When the system turned into a brown-red viscous state, it was cooled to 70°C, dehydrated under vacuum, and ethanol was added to adjust viscosity to 380-400 mPa • s. The mixture was poured into a mold and cured on a plate vulcanizing machine at 80-130°C for 4-5 hours to obtain the final product.

Free formaldehyde content was measured according to reference [12]. Tensile and impact properties were determined using a CMT4304 electronic universal testing machine and DJF-20 dynamic impact analyzer, respectively. Relative hardness was measured with a Shore hardness tester.

2. Results and Discussion

2.1 Effect of Ionic Liquid Type on Straw Dissolution Rate

The dissolution of straw was conducted using the three functionalized ionic liquids at 90°C with a mass ratio of ionic liquid to straw of 20:1. The results are shown in [Figure 2: see original paper].

Figure 2 compares the dissolution effectiveness of the three functionalized ionic liquids on straw. All three ionic liquids demonstrated good dissolution performance, but [CeMIM]Cl containing a terminal carboxyl group showed the best performance, achieving a dissolution rate exceeding 30% with rapid dissolution kinetics. This superior performance is attributed to the acidic self-catalytic effect of the hydroxyl group in its structure. Additionally, the terminal carboxyl group makes this ionic liquid the most polar among the three. The cation $[\text{CeMIM}]^+$ more readily forms coordination complexes with oxygen atoms of hydroxyl groups in straw cellulose compared to $[\text{HeMIM}]^+$ and $[\text{AeMIM}]^+$. Furthermore, the free Cl^- anion has strong electronegativity, exerting a strong pulling effect on hydrogen atoms in the cellulose structure, which more effectively weakens intra- and intermolecular hydrogen bonds in cellulose, disrupts its aggregated structure, and leads to molecular chain cleavage and dissolution. Therefore, [CeMIM]Cl provides the best dissolution effect.

2.2 Polarizing Microscope Observation of Straw Dissolution Process

Straw dissolution was performed using [CeMIM]Cl at 80°C, and the process was observed under a polarizing microscope at different time intervals, as shown in [Figure 3: see original paper].

Figure 3 presents polarized light micrographs at 0, 20, 50, 80, and 120 minutes of dissolution. Initially, the fibrous structure of straw swelled and became loose.

With increasing time, the supramolecular structure of fibers was disrupted by the ionic liquid, and straw gradually dissolved. After 120 minutes, the dissolution process was essentially complete, with virtually no fibrous material visible and the solution appearing nearly transparent. This demonstrates that functionalized imidazolium ionic liquids exhibit excellent dissolution performance for straw.

2.3 Effect of Ionic Liquid Type and Mass Ratio on Phenolic Resin Properties

The three functionalized imidazolium ionic liquids and their straw dissolution products were in-situ blended with phenol and formaldehyde to prepare modified phenolic composites. The effects of ionic liquid type and mass ratio on resin properties were investigated, with results summarized in .

Table 1 shows that modification with ionic liquids and their straw dissolution products significantly improved mechanical properties while reducing free formaldehyde content. Comparing samples 2-6, as the mass ratio of hydroxyl-terminated [HeMIM]Cl to straw increased, the properties of modified phenolic resin gradually improved, stabilizing when the ratio exceeded 20:1. Comparing samples 4, 7, and 8, the amino-terminated [AeMIM]Br system exhibited the best mechanical performance, increasing tensile strength from 3.28 MPa to 9.48 MPa and impact strength from 0.93 kJ/m^2 to 5.88 kJ/m^2, though hardness decreased slightly. The carboxyl-terminated [CeMIM]Cl system produced composites with the lowest free formaldehyde content, decreasing from 3.64% to 0.92%. This indicates that both the structural characteristics and dosage of ionic liquids influence phenolic resin performance.

The mechanism involves the hydrophilic functional polar groups and lipophilic alkyl side chains in the ionic liquid structures, which provide good compatibility with phenolic resin and act as coupling agents during composite preparation, uniformly dispersing in the polymer matrix without migrating to the surface during curing. Simultaneously, strong interactions between ionic liquids and phenolic resin form more stable polar conjugated structures, enhancing intermolecular forces and thereby improving tensile strength and impact toughness. However, excessive ionic liquid prolongs curing time and yields diminishing performance improvements, making a 20:1 mass ratio optimal. The amino-terminated [AeMIM]Br provided superior coupling during curing, creating more stable polar conjugated structures and thus the best mechanical properties. The carboxyl-terminated [CeMIM]Cl showed the best straw dissolution due to its carboxyl group' s acidic self-catalytic effect and the cation' s stronger coordination with cellulose hydroxyl oxygen atoms, which disrupts cellulose hydrogen bonding and exposes numerous hydroxyl groups that can partially replace phenol in reacting with formaldehyde, resulting in the lowest free formaldehyde content.

2.4 Chemical Structure of Phenolic Composites

The chemical structures of unmodified phenolic resin (Sample 1 in Table 1), raw straw, and [HeMIM]Cl-dissolved straw modified phenolic resin (Sample 4) were characterized by MAGNA-IR750 FTIR, with results shown in [Figure 4: see original paper].

In spectrum 4a (original phenolic resin), the peak at 3407 cm^{-1} corresponds to hydroxyl stretching vibrations, 1611 cm^{-1} and 1465 cm^{-1} to aromatic ring skeleton vibrations, 1218 cm^{-1} to aromatic ether stretching, and 617 cm^{-1} to out-of-plane bending of benzene ring C-H bonds—these are characteristic phenolic resin absorptions. In spectrum 4b (straw), the 3442 cm^{-1} peak represents cellulose hydroxyl groups, while the distinct peak at 2902 cm^{-1} indicates crystallinity, confirming the presence of crystalline regions in straw cellulose. The 1633 cm^{-1} peak is the C=C vibration of cellulose, and the broad, strong peak at 1060 cm^{-1} is characteristic of C-O-C ether bonds in cellulose structure, clearly distinguishing it from spectrum 4a. Spectrum 4c (composite) shows features of both phenolic resin and straw, plus new characteristic peaks at 3146 cm^{-1}, 1590 cm^{-1}, 1019 cm^{-1}, and 753 cm^{-1} from [HeMIM]Cl. The peak at 1469 cm^{-1} intensified, the cellulose ether peak at 1060 cm^{-1} weakened significantly, and the crystallinity-related peak at 2910 cm^{-1} became smaller and broader, indicating destruction of straw cellulose crystalline regions. These results confirm that hydroxyl groups in straw cellulose reacted with formaldehyde.

2.5 Crystalline Structure of Phenolic Composites

The crystalline structures of raw straw and [HeMIM]Cl-dissolved straw modified phenolic resin (Sample 4) were analyzed by D/max-2400 automatic X-ray diffractometer, with results shown in [Figure 5: see original paper].

Figure 5 shows that raw straw exhibits diffraction peaks at 31.4°, 45.7°, 56.1°, and 66.2°, characteristic of straw cellulose crystalline regions. While theoretically cellulose dissolved in ionic liquids still contains crystalline regions with altered crystal form and microcrystalline dimensions, curve b shows no diffraction peaks in this angular range, indicating complete disappearance of the cellulose crystalline structure. This confirms that after straw dissolution, the exposed hydroxyl groups in cellulose reacted with formaldehyde to form amorphous phenolic resin.

2.6 Morphology of Phenolic Composites

The surface morphologies of original phenolic resin (Sample 1) and modified phenolic resin (Sample 7) were observed using TM3000 scanning electron microscope, as shown in [Figure 6: see original paper].

Figure 6 presents SEM images at 1000× magnification: Figure 6a shows unmodified phenolic resin with a loose, porous, brittle surface prone to cracking; Figure 6b shows [AeMIM]Br-dissolved straw modified phenolic resin with a smooth, dense, crack-free surface. The 零星点缀的白色物质 (sporadic white specks) are sodium hydroxide catalyst particles. The improved morphology results from incorporation of imidazolium ionic liquid and straw cellulose structures, creating a dense, pore-free structure consistent with the enhanced mechanical properties.

Conclusions

1. The three functionalized ionic liquids synthesized—1-(2-hydroxyethyl)-3-methylimidazolium chloride ([HeMIM]Cl), 1-(ethylamino)-3-methylimidazolium bromide ([AeMIM]Br), and 1-(carboxyethyl)-3-methylimidazolium chloride ([CeMIM]Cl)—are target products with high purity and yields above 90%.
2. All three functionalized ionic liquids demonstrated excellent dissolution performance for straw, achieving dissolution rates greater than 25% at 90°C, with [CeMIM]Cl showing the best performance (30.25% dissolution rate) followed by [AeMIM]Br.
3. Phenolic resin composites prepared using ionic liquid-straw dissolution systems exhibited significantly improved properties. As ionic liquid dosage increased, composite performance gradually improved, stabilizing when the ionic liquid to straw mass ratio exceeded 20:1. At a 20:1 ratio, [CeMIM]Cl produced composites with the lowest free formaldehyde content, while [AeMIM]Br yielded the best mechanical properties with minimal hardness change. The modified phenolic resins showed smooth, pore-free, crack-resistant surfaces.

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