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Hydrolysis and recycling of urea formaldehyde resin residues

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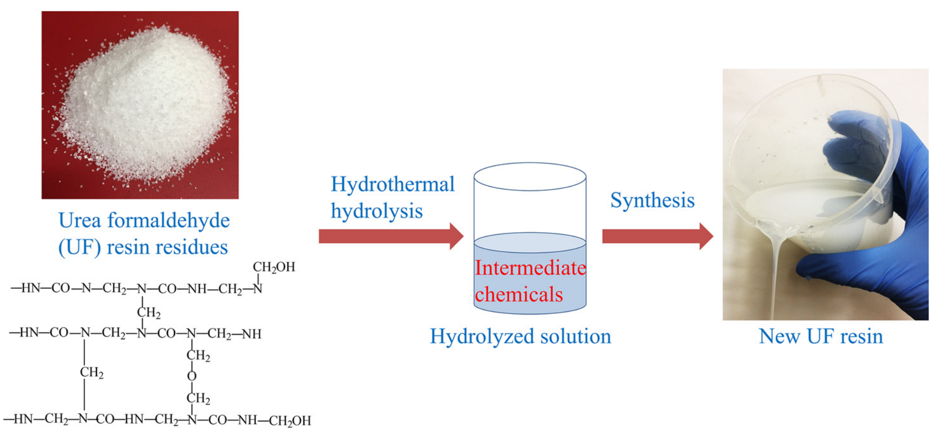
GRAPHICAL ABSTRACT



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ABSTRACT

Urea formaldehyde (UF) resin residues generate many poisonous chemicals during traditional disposal technologies for organic hazardous wastes. In this study, hydrothermal hydrolysis was developed to decompose, remove, and recycle cured UF resin. Under 140 °C and 2 h of hydrothermal process, 20 mL of either 2 M HCl or 30 w.t. % of formaldehyde solutions can decompose as much as 1.7 g of cured UF resin. In addition, from the attenuated total reflection Fourier-transform infrared spectroscopy (ATR-FTIR), gas chromatography–mass spectroscopy (GC—MS), X-ray diffraction (XRD), and ^{1}H nuclear magnetic resonance (NMR) analyses, it confirmed that the hydrothermal hydrolysis could hydrolyze cured UF resin. With 2 M HCl, the hydrolysis of cured UF resin can form NH_4Cl as the final product. Moreover, formaldehyde solution hydrolysis can fully recycle the decomposed UF resin. The hydrolyzed formaldehyde solution can be directly used as a normal formaldehyde solution for UF resin synthesis. The synthesized resin, which contains about 6 w.t. % of decomposed cured UF resin, has similar chemical structures and bonding performance as normal UF resin. These hydrolysis methods generate no harmful gases and pollutants, nor any pre- or post-treatments, which proves its feasibility in UF resin residues safe removal or disposal and recycle.

1. Introduction

Urea formaldehyde (UF) resins are widely used in coatings, molding compositions, and adhesives due to their numerous outstanding features, such as high reactivity, fast cure, relatively low price, and a clear color. Since 2012, the annual production of UF resin is greater than 1

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million metric tons in the world [1]. Meanwhile large amounts of UF resin residues are generated globally every year. These organic resin residues have been identified as hazardous waste in many countries for over 10 years now. Currently, greater than 70% of the total UF resin production is used as a bonding agent by the forest products and wood industry for bonding particle board and medium density fiber board (MDF). The global production of particle board and fiber board was accounted for 228 million cubic meter in 2015 [2]. Each year, a huge amount of these products, after the completion of their service life, need to be discarded or recycled in a safe manner [3]. The recycling of wood becomes much more difficult with the presence of a UF resin binder. Hence, the disposal of either pure UF resin or materials containing UF resin has been attracted numerous attentions in recent years.

The disposal technology of UF resin residue that comes first into mind might be the thermal treatment, such as combustion and pyrolysis, which have been realized as the most available technology to eliminate organic hazardous wastes [4]. In many occasions, combustion of hazardous waste could generate numerous pollutant emissions, which asks for high cost gas purification to meet the discharge standards. Compared to combustion, pyrolysis is an alternative to treat organic hazardous waste, which could even transfer hazardous waste to fuel and other valuable chemical products. Unfortunately, either combustion or pyrolysis alone fails to dispose of the UF resin residue safely. This is caused by the formation of nitrogen-containing gases, such as ammonia (NH_3), isocyanic acid (HNCO), and hydrocyanic acid (HCN) during the thermal disposal of UF resin residue. Hence, low temperature pyrolysis combined with combustion was recommended for the resin disposal [5]. This method was also not adequate because during the second combustion process in oxygen-rich conditions, ammonia could still be oxidized to nitrogen oxides [6], which is a well-known category of harmful wastes [7]. Therefore, thermal disposal of pure UF resin residue or materials containing UF resin residue might not be a good choice. For those reasons mentioned, a safe and economical disposal technology is needed.

Recycling wood-based panels also faces the problems caused by UF resin residue. The prevalent recycling ways for wood-based panels include place in landfill, use gasification, composting, and incineration processes [8,9]. All these available technologies are limited or even prohibited with the existence of UF resin, which usually accounts for 8–10 w.t. % of the panel. A thermal disposal of wood-based panels could generate the same poisonous gases as pure UF resin residue, such as HCN and HNCO [10]. A two-step pyrolysis method, based on the discrepancies of activation energy between UF resin and wood, has been proposed [11]. The efficiency of this method was limited since the decomposition temperatures between wood and UF resin are close to each other, not to mention the possible emission of pollutants. The landfill option was also no longer acceptable for UF resin bonded wood-based panels due to the adverse and chronic effects of the leached resin for subsoil water [12]. The reuse of UF resin was also tried by directly dispersing UF resin residue particles in a new made UF resin to bond wood-based panels. However, the shear strength of the obtained products decreased by 48%, even with only 6 w.t. % of UF resin residue in the new made UF resin [13]. Consequently, the removal of UF resin residue has been considered as the first step to dispose and recycle wood-based panels. Some studies have been focused on hydrolytic decomposition of UF resin residue, based on the reversibility of UF resin synthesis reactions [14]. Compared to thermal disposal, the hydrolysis of UF resin residues was a moderate process, which generates no harmful gases. Indeed, hydrolytic removal of UF resin residues from wood-based panels via acidic solutions has shown high efficiency [15,16]. However, the large quantity of hydrolyzed solution, which contains formaldehyde and other chemicals from hydrolyzed UF resin residues, becomes a new waste and pollutant. To date, there has been no report on the treatment of the hydrolyzed UF resin solution for recycling UF resin residues.

Our study presents a hydrothermal process for hydrolyzing and recycling UF resin residues. The hydrolytic conditions and hydrolyzed solutions have been studied. This process provides not only a feasible way to remove or dispose of UF resin residues, but also a way to produce intermediate materials for synthesizing a new UF resin. The hydrolyzed solution from the hydrolysis of UF resin residues could be directly used in the new UF resin preparation, as an energy efficient and environmentally friendly way to recycle and dispose of UF resin residues.

2. Materials and methods

2.1. Materials

All chemicals used were commercially available, such as paraformaldehyde ($HO(CH_2O)_nH$), deuterium oxide (D_2O, 99.9 atom % D), urea (NH_2CONH_2), sodium hydroxide beads (NaOH), ammonium sulfate ($(NH_4)_2SO_4$), ammonium chloride (NH_4Cl), sodium sulfite (Na_2SO_3), 0.25 M and 0.5 M sulfuric acid (H_2SO_4), 1 M and 2 M hydrochloric acid (HCl). All chemicals were used as received without further purification. Southern yellow pine lumber was purchased from local store.

2.2. UF resin preparation

In this work, cured UF resin was used to mimic the UF resin residues. Liquid UF resin was prepared by following our previous method [17].

2.3. UF resin hydrolysis by acid solution

In this experiment, the influence factors of hydrolysis were determined first. In detail, two types of acid as pH adjusters, two types of hardener, and two types of acid for hydrolysis were tested with a 2^3 full factorial design with three replicates as shown in Table 1.

About 100 g of UF resin from each resin sample listed in Table 1 was cured [17]. Then, the cured UF resins were ground to particles (≤ 28 mesh) and hydrolyzed in assigned acid solutions (1 M HCl or 0.5 M H_2SO_4 for equal concentration of H^+) at 120 °C for 4 h using hydrothermal autoclaves (Teflon lined hydrothermal reactor with a capacity of 50 mL, Hanheng Instrument Co., China). In each run, 2 g of cured UF resin particles were added into 20 mL of acid solution. The efficiency of resin hydrolysis process was measured by the mass loss ratio of solid resin using Eq. (1).

$$Mass\ loss\ ratio\ (\%) = \frac{m_{initial} - m_{hyzdrolyzed}}{m_{initial}} \times 100\% \quad (1)$$

Where:

$m_{initial}$ = weight of resin solid before hydrolysis, and

$m_{hydrolyzed}$ = weight of remaining solid resin weight after hydrolysis.

After the determination of the most efficient approach of cured UF resin hydrolysis, an experiment to optimize hydrolytic operational

Table 1
Cured UF resin hydrolysis design.

Hydrolysis Approach	Acid (pH Control) control)	Hardener	Acid (Hydrolysis)	Replicates
A	H_2SO_4	$(NH_4)_2SO_4$	H_2SO_4	3
B	H_2SO_4	NH_4Cl	H_2SO_4	3
C	HCl	$(NH_4)_2SO_4$	H_2SO_4	3
D	HCl	NH_4Cl	H_2SO_4	3
E	H_2SO_4	$(NH_4)_2SO_4$	HCl	3
F	H_2SO_4	NH_4Cl	HCl	3
G	HCl	$(NH_4)_2SO_4$	HCl	3
H	HCl	NH_4Cl	HCl	3