

## Study of Glycidyl Ether as a New Kind of Modifier for Urea-Formaldehyde Wood Adhesives

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**ABSTRACT:** In this work, the multipoxy functional glycidyl ether (GE) modified urea-formaldehyde (UF) resins were synthesized via a traditional alkaline-acid process under low formaldehyde/urea (F/U) molar ratio. The synthesized resins were characterized by  $^{13}\text{C}$  magnetic resonance spectroscopy ( $^{13}\text{C}$ -NMR), indicating that GE can effectively react with UF resins via the ring-opening reaction of epoxy groups. Moreover, the residual epoxy groups of GE could also participate in the curing reaction of UF resins, which was verified by Fourier transform infrared spectroscopy. The storage stability of GE-modified UF resins and the thermal degradation behavior of the synthesized resins were evaluated by using optical microrheology and thermogravimetric analysis, respectively. Meanwhile, the synthesized resins were further employed to prepare the plywood with the veneers glued. For the modification on bonding strength and formaldehyde emission of the plywood, the influences of addition method, type, and amount of GE were systematically investigated. The performance of UF adhesives were remarkably improved by the modification of GE around 20–30% (weight percentage of total urea) in the acidic condensation stage during the resin synthesis. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 128: 4086–4094, 2013

**KEYWORDS:** adhesives; ring-opening polymerization; crosslinking; rheology; resins

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### INTRODUCTION

Urea-Formaldehyde (UF) resins have been widely used as adhesives, especially in wood industry, such as the manufacture of plywood, particleboard, and medium density fiberboard. However, the UF adhesives have an obvious disadvantage for the practical application because of the emission of formaldehyde.<sup>1,2</sup> The emission of formaldehyde has been greatly concerned in the field of wood industry due to its hazard to health. Therefore, for UF resins, it is quite significant to investigate an effective method to depress the amount of formaldehyde emission.

Great works have been carried out to depress the formaldehyde emission. The works focus on improving the synthesis and curing process such as the strong acid process<sup>3,4</sup> and decreasing the formaldehyde/urea (F/U) molar ratio.<sup>5,6</sup> As the latter would cause the deterioration on the performance of the UF adhesives, the exploration for effective modifiers on UF resins has attracted great attention. Melamine is one of the most generally employed modifiers in the synthesis of UF resins, which can reduce the formaldehyde emission and improve water resistance of the adhesives.<sup>7–10</sup> Phenol and polyvinyl acetate were also applied as formaldehyde scavengers.<sup>11,12</sup> In the current works,

application of natural compounds such as casein, catechin, and vanillin has been proved to effectively suppress the formaldehyde emission from plywood.<sup>13,14</sup> In addition, the reutilization of plant wastes with multifunctional structures such as almond shell and sugarcane bagasse can also be used to modify UF adhesives.<sup>15,16</sup>

Among the various structures of chemical modifiers, we are interested in the multifunctional molecules with the functional groups, such as amine, hydroxyl, and acrylic groups etc., spaced by long alkyl or alkoxy chains.<sup>17–21</sup> As the original blank UF resins synthesized with low F/U molar ratio are brittle and tend to crack after cured, it is doubtless that the incorporation of multifunctional molecular with flexible molecule chains to UF resins can induce the cross-linking structures, so that the mechanical performance such as the bonding strength of the adhesives can be in turn enhanced. There is a typical research in this field as reported by Ebewele et al., in which the UF resins were blended with alkyl and alkylene oxide as flexible backbones with di- or tri-functional amines. It was found that the modification by flexible di- or tri-amines on UF resins can decrease the dissociative formaldehyde, reduce the internal stress, and improve the

**Table I.** Chemical Structures of GE in This Study

Modifier	Chemical structure	Abbr.	Epoxy value	Purity (%)
1,4-Butanediol diglycidyl ether		BDE	0.75	≥99
Ethylene glycol diglycidyl ether		EDE	0.76	≥99
Polyglycol diglycidyl ether		PDE	0.37 n: 8-10	≥99
Trimethylol propane Triglycidyl ether		TPTE	0.73	≥99

stability of UF bonded wood products.<sup>18–20</sup> The enhanced performance of the modified resins can be explained by the formation of a more flexible, random, three-dimensional cured network. Mariusz et al., attempted to modify UF resins by a hydroxyl-terminated hyperbranched polyether obtained from glycerol. By addition of this polyether at 3%, the hardness and compressive shear strength of UF resins can be improved.<sup>21</sup> However, comparing the studies of melamine, phenol, and polyvinyl acetate, there are few reports describing the investigation of multifunctional molecules with flexible long chain structures to modify UF adhesives. Therefore, it is absolutely necessary to further extend the study on modification of UF adhesives by using multifunctional molecules.

Glycidyl ether (GE) is a widely known reactive diluent and has been used in many applications, especially in epoxy adhesives.<sup>22–24</sup> The commercially available GE are generally multifunctional chemicals containing optional numbers of epoxy rings attached by different length of ether linkages. Leon et al.,<sup>25</sup> reported that the epoxy ring of GE initial reacts with amine. The resulting nucleophile then reacts with other epoxy groups to produce hydroxyalkyl group and ether linkages. Kawamura<sup>26,27</sup> reported the modification of UF resins by reaction of urea, formaldehyde, and polyethylene glycol diglycidyl ether at temperature around 85–95°C. The as-prepared resins were in turn mixed with some other additives and molded by hot-pressing at temperature around 165°C for 2 h, so as to increase its impact strength and hardness. However, a few works are reported detailed results on the use of GE to improve the properties and to reduce the formaldehyde emission of UF resins. Therefore, the GE modified UF resins were investigated by our group. We hope to significantly improve the bonding performance of UF resins and decrease the formaldehyde emission of plywood made from the UF resins.

In this work, the modification of UF resins by GE was investigated in details. The commercially available GE was employed, which is functionalized by di- or tri-epoxy groups spaced by alkyl or alkyl ether with different molecule chains, to incorpo-

rate the UF resins with the F/U molar ratio at 1.05. Structures and properties of the modified resins were characterized by using <sup>13</sup>C magnetic resonance spectroscopy (<sup>13</sup>C-NMR), Fourier transform infrared spectroscopy (FTIR), optical microrheology, and thermogravimetric analysis (TGA). The as-modified UF resins were further applied as wood adhesives to prepare plywood. For study of the bonding strength and formaldehyde emission of the bonded plywood, the influences of addition method, type, and amount of GE for the modification were investigated in detail. Moreover, the plywood with low formaldehyde emission and enhanced bonding strength were successfully obtained by using this technology.

## EXPERIMENTAL

### Materials

Formaldehyde in 37 wt % aqueous solution form was purchased from Tianjin Fuchen Chemical Reagents Factory. Urea (nitrogen content ≥46.4%) was purchased from China Petroleum. All the other chemicals were used as received at commercially analytical grade. The basswood veneer with 5% moisture content was cut in the size of 300 × 300 × 1.2 mm, which was purchased from Mudan River Mingfeng Wood Industry. Four kinds of GE purchased from Anhui Hengyuan Chemical were employed in this study, whose chemical structures are listed in Table I. Among them, the molecule chains of EDE, BDE, and PDE are linear structure with GE groups at both end of the molecule chains spaced by ethylene, butane, and poly(ethylene oxide), respectively. TPTE is typical for its branched structure with three epoxy groups for each molecule chain.

### Synthesis of UF-GE Resins

The UF-GE resins were synthesized by three steps as described below.

**Step A: Methylolation.** Formaldehyde 140 part (wt) and urea 60 part (wt) were added into a 500 mL four-neck flask equipped with a mechanical stirrer, a condenser, a thermometer, and a septum-seal for feeding during the reaction. The pH of the mixture was adjusted to 9.0 by using 20 wt% of sodium hydroxide

**Table II.** Different Addition Methods of GE During UF Resins Synthesis

Code	Method
I	Added at the beginning of Step A
II	Added together with the 30 part (wt) of urea in Step B
III	Post-added together with the 10 part (wt) of urea in Step C

aqueous solution. The mixture was heated to 90°C in an oil bath and held at 90°C for 45 min.

**Step B: Condensation.** For the as-prepared mixture from Step A, the pH of it was further adjusted to 5.0 by using 30 wt % of formic acid solution with temperature at 90°C for 15 min. Subsequently, urea 30 part (wt) was added into the reaction system with the constant temperature. The reaction proceeded until the viscosity of the resin reached 350 cp.

**Step C: Post-treatment.** After the viscosity of the resin reached about 350 cp, the pH of the reaction mixture was finally adjusted to 7.5 by using 20 wt % of sodium hydroxide solution. Ten part (wt) of urea was added into the flask. The reaction temperature was decreased to 70°C and kept for 15 min. The obtained resin was cooled to room temperature. The F/U molar ratio of the final resin was 1.05.

GE was employed as modifier and added via three different methods to investigate the influence of addition method for the performance of UF resins as shown in Table II. Different amounts of GE were added from 10 to 40 %, where the amount of urea was defined as 100 wt %. Meanwhile, another synthesized resin under the same condition without the addition of GE was defined as the blank UF resin for comparison.

For the sake of convenience, the as-prepared samples with different addition methods and amounts are designated hereafter as UF-GE (X–Y) where GE stands for different types of modifiers, such as BDE, EDE, PDE, and TPTE, X stands for addition method, such as I, II, and III, and Y means the percentage of addition amount, such as 10, 20, 30, and 40. For example, in UF-PDE (II-10), PDE after the hyphen means the modifier is PDE, II means the PDE is added by method II, and 10 means the addition amount of PDE is 10% in the weight percentage of total urea. Thus the samples studied in this work can be expressed as UF-BDE (I-10), UF-PDE (II-20), UF-TPTE (III-30), etc.

### Plywood Preparation

Three-layer plywood and seven-layer plywood were prepared by using the basswood veneers and the as-synthesized UF resins as adhesive for the bonding strength and formaldehyde emission test, respectively, according to National Standard of People's Republic of China GB/T 17657-1999.<sup>28</sup> The adhesive was firstly mixed with 5 wt % of ammonium chloride solution (20 wt %, aq.) and then spread on the double faces of each piece of veneer. The spread rate was 15 mg/cm<sup>2</sup>. After the spreading, the veneer boards were subsequently lapped together in a manner with the wood grain of one layer vertical to its neighbor veneer

layer. Finally, the plywood was hot-pressed at 120°C with the pressure of 10 kg/cm<sup>2</sup>. The thickness-dependent pressing time was applied for this process at 1 min/mm.

### Characterizations

The transmission FTIR spectra of samples were measured by using a Bruker Tensor 37 Fourier transform IR spectrometer. Thirty-two scans were accumulated with a resolution of 4 cm<sup>-1</sup>. <sup>13</sup>C-NMR spectra were recorded at 400 MHz at ambient temperature by using Bruker Fourier Transform AVANCE 400, and (methyl sulfoxide)-d<sub>6</sub> was used as the solvent. The TGA characterization was carried out on PerkinElmer TGA-4000, heating the samples from room temperature to 300°C at a heating rate of 10°C/min under a 20 mL/min nitrogen flow.

### Storage Stability

The storage stability of the synthesized resins was evaluated by an optical microrheology (Rheolaser LAB from Formulacion, French). In the experiment, 20 mL of liquid resin specimen was injected by a syringe in a flat-bottomed cylindrical glass tube (height 70 mm, external diameter 27.5 mm). The tube was immediately placed in the sample chamber of the Rheolaser LAB preheated to 60°C. During the test, the speckle pattern of the sample, which was generated by the interfering backscattering wave of the incident laser at 650 nm caused by the Brownian motion of the particles, was collected by a multipixels detector every 5 min for 40 h. The generated speckle image is treated to plot the decorrelation curve, which can quantify the particles mobility and displacement, and in turn be used to characterize the viscoelastic structure of the liquid resin.<sup>29</sup> Moreover, the fluidity index (FI) of the resin reflecting the storage stability of resins was calculated directly from the decorrelation curve.

### Bonding Strength of Plywood

The bonding strength of plywood was measured by using a universal material testing equipment (CMT 4304 from Shenzhen, Xinsansi Material Testing), according to National Standard of People's Republic of China GB/T 17657-1999.<sup>28</sup> The three-layer plywood was cut into 25 × 100 mm of specimens with a notch of 20 × 25 mm in each piece. These specimens were merged into 63 ± 3°C water for 3 h, and then cooled to room temperature for 10 min before measurement. The measurement was carried out in tension mode with the test loading speed of 10 N/mm<sup>2</sup>. Twenty specimens were tested for each sample and the results were averaged.

### Formaldehyde Emission

The formaldehyde emission of plywood by using the synthesized UF resins as adhesives was tested according to National Standard of People's Republic of China GB/T 17657-1999.<sup>28</sup> After the produced plywood was cooled down to room temperature, the seven-layer boards were immediately cut into 10 specimens with three-dimensional size of 10 × 50 × 150 mm<sup>3</sup>. Within 30 min after production, these samples were put into a 10 L of covered glass desiccator together with a petri dish filled with a specified amount of deionized water. The formaldehyde emission test lasted 24 h under 20°C. The emitted quantity of formaldehyde was obtained from the concentration of formaldehyde absorbed in the water by using a UV-3150 SHIMZDZU UV-vis-NIR spectrometer based on the Hantzsch reaction, in which the

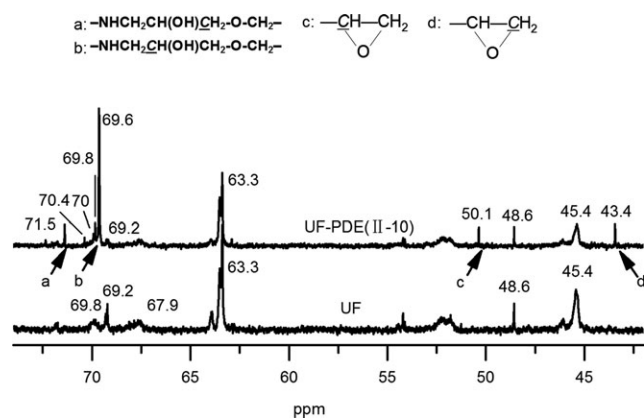


Figure 1.  $^{13}\text{C}$ -NMR spectra of UF resin and UF-PDE (II-10).

formaldehyde can react with ammonium acetate and acetylacetone and the yield of diacetyldihydrolutidine (DDL) was quantified by evaluating the characteristic UV peak centered at 412 nm.

## RESULTS AND DISCUSSION

### Characterization of UF-GE Resins

The  $^{13}\text{C}$ -NMR spectra of blank UF resin and UF-PDE (II-10) are shown in Figure 1, and the assignment of each peak is listed in Table III. The blank UF resin had a chemical shift at 45.4 ppm, which was assigned to the carbon of methylene linkages. The chemical shift at 48.6 ppm was assigned to the carbon of methanol. The chemical shift at 63.3 ppm was assigned to various methylol carbons of the resins. The chemical shifts at 67.9, 69.2, and 69.8 ppm were assigned to various methyl ether carbons.<sup>30</sup> Meanwhile, these peaks are all emerged in the spectra of UF-GE (II-10) in Figure 2.

For UF-PDE (II-10), some new peaks appeared in the spectrum due to the modification of PDE. The chemical shifts at 69.6 and 71.5 ppm were assigned to different alkyl ether carbons, indicating

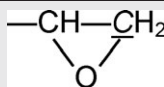
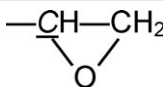
that the epoxy rings on the PDE molecule chain were opened via the reaction with the active hydrogen attached mainly on  $-\text{NH}_2$  groups in the chemicals such as the primary amide in urea, the mono- or di- methylolurea under acid condition as shown in Scheme 1. The chemical shifts at 70.0 and 70.4 ppm were assigned to the carbons on the backbone of PDE. To other GE modified resins, similar chemical shifts were shown in the spectra but with some tiny differences caused by the different molecular structures of GE modifiers. Moreover, the ring-opening reaction between the epoxy ring and hydroxyl cannot be ruled out in this way.

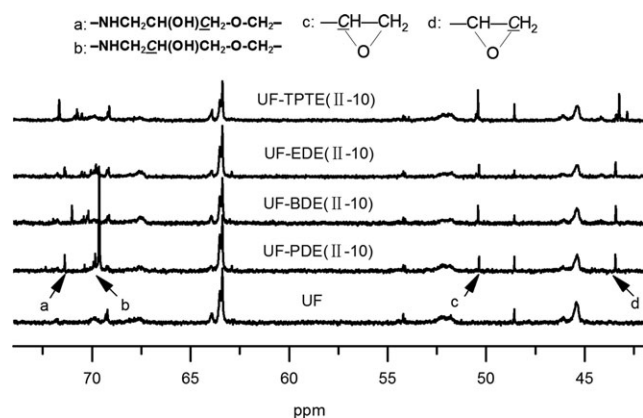
In addition, the peaks around 50.1 and 43.4 ppm were all existed in the spectra of UF-GE (II-10), which were attributed to the chemical shifts of the two carbons on epoxy ring. The existence of these two peaks indicated the survival of unreacted epoxy groups existing in liquid UF-GE (II-10) resins.

FTIR spectra of the three samples of UF-PDE (II-10) at different reaction stages are compared in Figure 3, where Sample 1 is the liquid resin in the condensation stage just after the addition of PDE in step B; Sample 2 is the final liquid resin obtained after step C; Sample 3 is the solid resin cured in the existence of 5%  $\text{NH}_4\text{Cl}$  aqueous solution (20 wt %) under  $120^\circ\text{C}$  for 3 min.

For the spectra in Figure 3, the peak at  $3340\text{ cm}^{-1}$  was assigned to the stretching vibration of N—H and O—H bonds in the primary amines and hydroxyl groups. Besides, for Sample 3, the absorption intensity of this peak was much lower than those of the other two samples, which was due to that the active hydrogen groups were consumed during the crosslinking reaction for the formation of network. The peak at  $1650\text{ cm}^{-1}$  was assigned to the C=O stretching vibration of primary amide. The peak at  $1580\text{ cm}^{-1}$  was assigned to the N—H stretching of secondary amide. The peak around  $1020\text{ cm}^{-1}$  was the stretching vibration of C—O—C bonds.<sup>31</sup> The peaks mentioned above are all observed in the three spectra with small variation on the exact position and relative intensity caused by the condensation and crosslinking reactions.

Table III. The Assignment of UF and UF-PDE (II-10)  $^{13}\text{C}$ -NMR Spectra

Blank UF	UF-PDE(II-10)
/	43.4 (d) 
45.4 $-\text{NHCH}_2\text{NH}-$	45.4 $-\text{NHCH}_2\text{NH}-$
48.6 $\text{CH}_3\text{OH}$	48.6 $\text{CH}_3\text{OH}$
/	50.1 (c) 
63.3 $-\text{NHCH}_2\text{OH}$	63.3 $-\text{NHCH}_2\text{OH}$
67.9 $-\text{N}(\text{CH}_2)\text{CH}_2\text{OCH}_2\text{NH}-$	/
69.2 $-\text{NHCH}_2\text{OCH}_2\text{NH}-$ 69.8 $-\text{NHCH}_2\text{OCH}_2\text{OH}$	69.2 $-\text{NHCH}_2\text{OCH}_2\text{NH}-$ 69.6 (b) $-\text{NHCH}_2\text{CH}(\text{OH})\text{CH}_2\text{OCH}_2-$ 69.8 $-\text{NHCH}_2\text{OCH}_2\text{OH}$
/	70.0 $-\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{O}-$
/	70.4 $-\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{O}-$
/	71.5 (a) $-\text{NHCH}_2\text{CH}(\text{OH})\text{CH}_2\text{OCH}_2-$

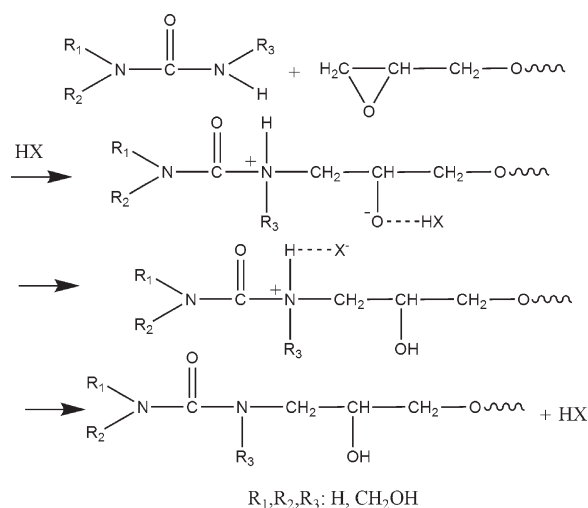


**Figure 2.**  $^{13}\text{C}$ -NMR spectra of UF resin and UF-GE (II-10).

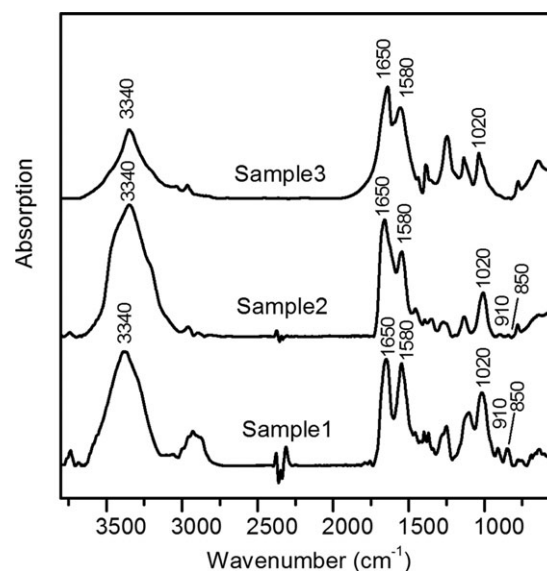
The absorption peak at  $910\text{ cm}^{-1}$  was assigned to the epoxy skeleton vibration, and that at  $850\text{ cm}^{-1}$  was attributed to the C—O—C stretching vibration of epoxy ring. The peak intensity of these two peaks of Sample 1 was the strongest, which was caused by that PDE had not reacted yet. These two peaks were also found in the spectrum of Sample 2, but the peak intensity showed apparent weakening further supporting the result of  $^{13}\text{C}$ -NMR for the ring-opening reaction of epoxy. After curing process, these two peaks became neglectable in the spectrum for Sample 3, indicating that the residual epoxy groups in the liquid resin could participate in the curing process by the ring-opening reaction with the active hydrogen on —OH and —NH— groups under weak acid condition.

### Storage Stability of UF-GE Resins

The synthesized resins were stored in the sample chamber of the rheolaser at a constant temperature of  $60^\circ\text{C}$ . The decorrelation curves of UF-PDE (II-10) were recorded with different time intervals as shown in Figure 4. As the initial (0 min) time, only short linear line was obtained. With the storage time prolonged from 0 to 15 h, both shape and position of the curves (left part of the graph) showed obvious variation. In the range of short decorrelation time, the curve shifted to the lower values



**Scheme 1.** The ring-opening reaction of epoxy ring under acid condition.



**Figure 3.** FTIR spectra of UF-PDE (II-10). Sample 1: the liquid resin just after the addition of PDE in Step B; Sample 2: the final liquid resin after Step C; Sample 3: the solid resin cured in the existence of 5%  $\text{NH}_4\text{Cl}$  solution (20 wt %) under  $120^\circ\text{C}$  for 3 min.

of  $d_2/d_{2\text{max}}$ , indicating the increasing elasticity of the resin (right part of the graph). Meanwhile, in the range of long decorrelation time, the curves shifted right to the longer decorrelation times. However, these variational trends were inverted at the time around 15 h with the curves move up and to the left of the figure indicating the disability of the resin samples caused by crosslinking reaction.

As the storage stability is always judged by the apparent fluidity of the resin, the relationship between the FI versus the storage time can be clearly plotted as shown in Figure 5 of UF-PDE (II-10), which was calculated based on decorrelation curve in Figure 4. The curve can be divided in different stages. The first stage is in the time range from 0 to 0.12 h. The FI rises up from 0 to 10 Hz. The increasing fluidity can be explained by that the sample was experienced the thermal equilibrium process during the period as it was just transfer from ambient condition to a preheated sample chamber. The second stage is from 0.12 to 6.0 h in which the curve declined and reached a plateau. The sample was stable at that time and reached viscoelastic equilibrium by the recovery from the shear flow caused by the injection. The plateau was last until the time of 6 h when the FI curve showed a sudden increase. From then on, the curve came to the third stage and the sudden increase point was defined as the starting point of the losing of fluidity. After the starting point, the FI curve quickly decreased to a valley at the point of 13.5 h, which was defined as the solidification point. The resin was actually hardly to flow even under shaking in apparent observation. After that, with the water separating out, the FI fluctuates up and down for a period of time, and then the FI slowly went down as the storage time further prolonged. It is obviously that the longer the time needs to reach the starting point, the better the storage stability of the resin would be. The resin lost its storage stability during the period from the starting point to

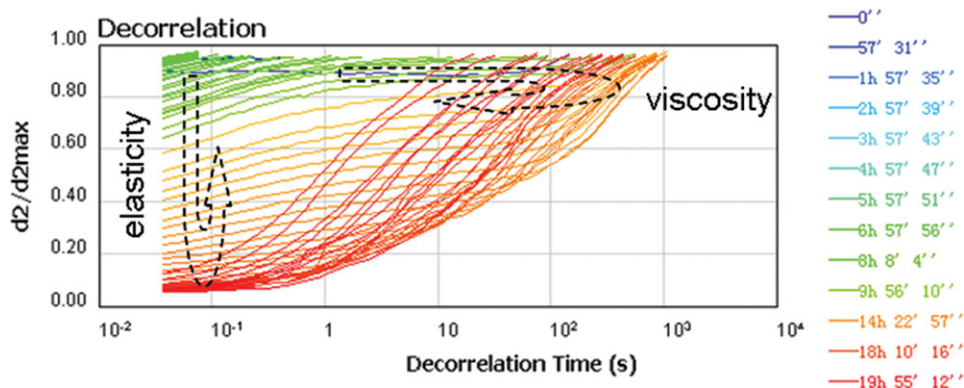


Figure 4. Decorrelation curves of UF-PDE (II-10). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

solidification point with the decreasing fluidity due to the cross-linking reaction of the resin particles.

The time needed to reach the starting point, solidification point, and the time interval between the starting point and solidification point were defined as  $t_{st}$ ,  $t_{so}$ , and  $t_{ss}$  with the value listed in Table IV, respectively. It can be observed that the GE modified resins reached the starting point slowly as compared to the blank UF resin except UF-TPTE whose  $t_{st}$  is 5.3 h similar to 5.5 h of blank UF resin. The longest  $t_{st}$  is found in the curves of UF-BDE (II-20) and UF-EDE (II-20), which is 13.3 and 14 h, respectively. The elongation of  $t_{st}$  can be illustrated by the increasing concentration of hydroxyl groups coming from the ring-opening reaction of epoxy rings as shown in Scheme 1, which could improve the hydrophilicity of the resin. Moreover, the ring-opening reaction consumed N—H, which is more active in the curing reaction so that the instability process is delay. The latter can be used to explain the longer  $t_{ss}$  of UF-GE resins as compared to blank UF resin.

The UF-BDE and UF-EDE had the similar  $t_{st}$  and  $t_{ss}$  because of their similar molecular structure and epoxy value. The  $t_{st}$  and  $t_{ss}$  of UF-PDE were comparable to the value of blank UF resin because PDE has lower epoxy value as compared to BDE and

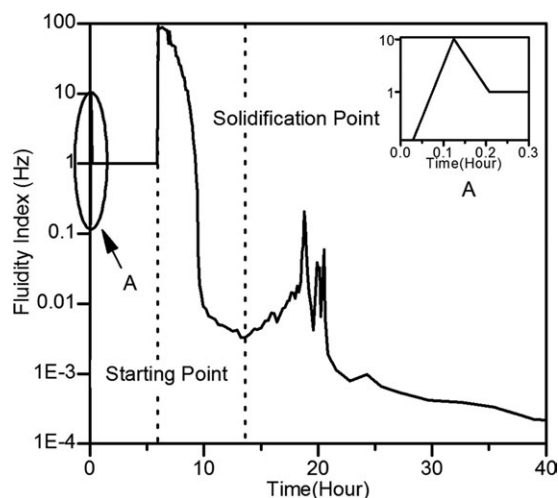


Figure 5. Fluidity curve of UF-PDE (II-10).

EDE. The UF-TPTE has the similar epoxy value to BDE and EDE, but it had lower  $t_{st}$  and  $t_{ss}$  because TPTE has more functionality than other GE modifiers, which increased the cross-linking degree of the resin but resulted in the instability.

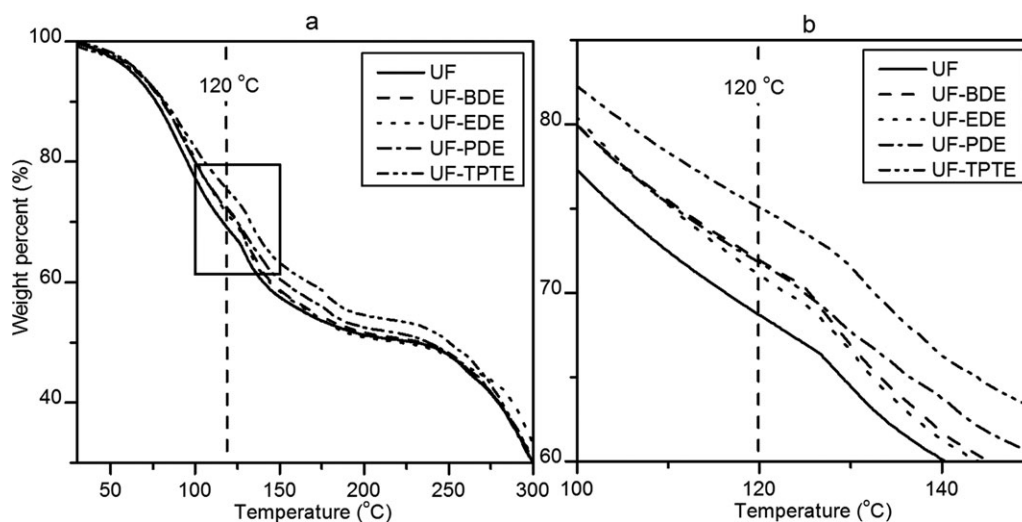
#### Thermo-Gravimetric Analysis of UF-GE Resins

The TGA curves of the synthesized blank UF and UF-GE (II-10) were simultaneously displayed in Figure 6(a) for the comparison. It is quite obvious that all the curves present as the similar shapes with three steps due to the typical degradation of UF resins. The first step (20–100°C, 25% weight loss) and the third step (200–300°C, 25% weight loss) are corresponding to the water evaporation and the main chain scissions, respectively. While, the second step (100–200°C, 20% weight loss) is due to the release of formaldehyde accompanied with water.<sup>31</sup> The released formaldehyde in second step is partly coming from the crosslinking reaction. The degradation of unstable hydroxymethyl and methylene ether groups also can contribute to the formaldehyde emission.

The modification by GE can effectively reduce the weight loss of UF resins during the second step. At a given temperature such as 120°C as shown in Figure 6(b), the weight loss decreased as the following sequence: UF (31.35%) > UF-EDE (29%) > UF-PDE (28.23 %) ≈ UF-BDE (28.1%) > UF-TPTE (25%). The less weight loss of GE modified resins is attributed to the formation of hydroxyalkyl and alkyl ether groups coming from the ring-opening reaction of epoxy ring, which is more stable than the hydroxymethyl and methylene ether groups and can notable reduce the formaldehyde emission. UF-TPTE shows the lowest weight loss because the branch structures of TPTE, which may result in higher crosslinking degree. The PDE modified resins also show better performance as the lower formaldehyde emission than blank UF resin. The TGA curve of UF-BDE

Table IV. The Starting Point and Solidification Point of Blank UF Resin and UF-GE (II-10) Resins

Time	UF(h)	UF-BDE(h)	UF-EDE(h)	UF-PDE(h)	UF-TPTE(h)
$t_{st}$	5.5	13.3	14	6	5.3
$t_{so}$	11.5	23.6	31	13.5	11.4
$t_{ss}$	6	10.3	11	7.5	6.1

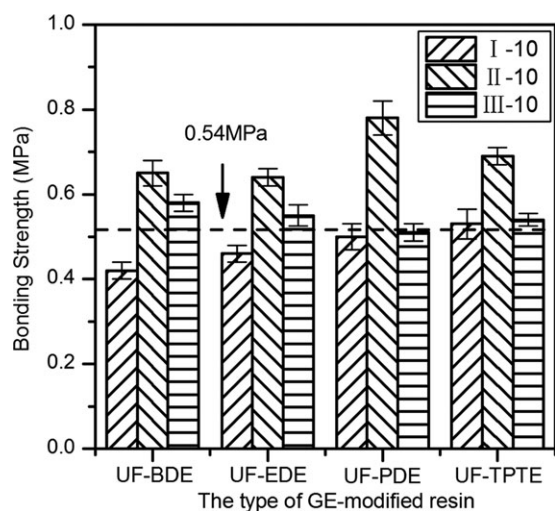


**Figure 6.** TGA curves of blank UF resin and UF-GE (II-10) resins. (b) is the magnification graphs of (a) at the temperature range from 100 to 150 °C.

almost over-lapped in the temperature range between 100 and 120 °C; however, a sudden inflection can be observed around 125 °C toward the higher weight loss direction. While, the difference among the TGA curves for the UF resins modified by the three linear GE molecules is not quite obvious. Moreover, the slightly improved thermal stability of UF-GE resins contributes to less formaldehyde emission of plywood.

#### Properties of Plywood Bonding by UF-GE Resins

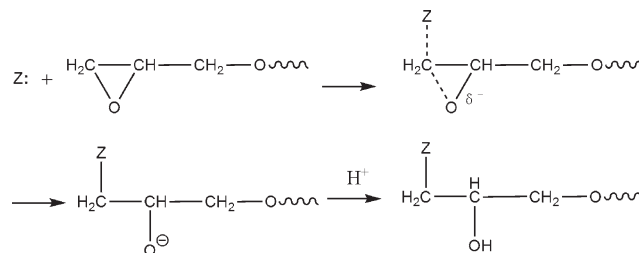
Plywood was prepared by using the synthesized UF resins serving as adhesives.<sup>32</sup> The influences of the addition methods as well as the types of GE on the bonding strength of the prepared plywood are compared in Figure 7. For all types of GE modified resins, the plywood prepared by method I shows the worst bonding strength than that of blank UF resin, which is labeled as the dash line in Figure 7. The plywood made from resins prepared via method III showed the comparable bonding strength to that made from blank UF resin. The bonding strength pre-



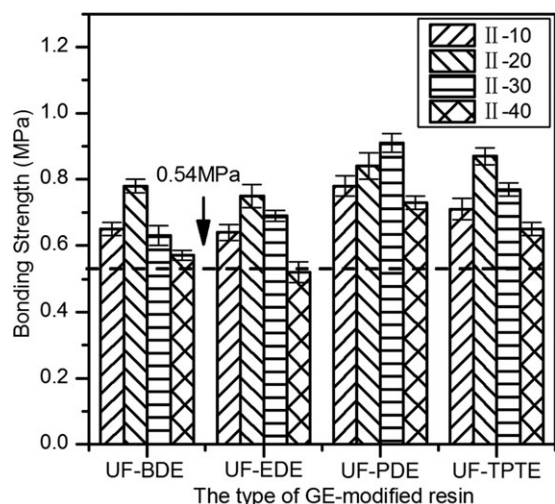
**Figure 7.** Bonding strength of plywood bonding by UF-GE resins synthesized by different addition methods.

pared by method II for all types of modified resins is superior to that of blank UF resin. UF-PDE has the best result of 0.78 MPa up to the standard of 0.7 MPa from National Standard of People's Republic of China GB/T 9846-2004.<sup>33</sup>

According to these results, the best addition method can be confirmed to be method II with the GE ingredient added in step B together with the second batch of urea. The GE molecules can be chemically linked onto the UF backbones via the ring-opening reaction catalyzed by acid as shown in Scheme 1, so that the bonding strength of the corresponding plywood can be much enhanced by the flexibility of alkyl ether with long chains. The prominent bonding strength of UF-PDE can also be attributed to the special poly (ethylene oxide) structure introduced by PDE molecules. Although the ring-opening reaction can also happen at alkaline condition as shown in Scheme 2, no good results was obtained when GE was added in step A. Actually when the methylation stage was finished, the pH of the system should be adjusted from basic to acidic for the further condensation stage. However, more HCOOH had to be used in the system where GE was added in step A, and the pH of the mixture went down slowly. We suppose that the GE added in step A is served as the buffer with negative O<sup>-</sup> consumed H<sup>+</sup> for the formation of stable —OH structures. The large amount of acid and the prolonged reaction time of methylation stage resulted in the inferior performance of the final resin. In method III, when GE was postadded in the resin, GE was served only as a crosslinking agent. Although ring-opening



**Scheme 2.** The ring-opening reaction of epoxy under alkaline condition.



**Figure 8.** Bonding strength of plywood made from UF-GE resins of different GE addition amount.

reaction of epoxy can also happen in the curing of the adhesive, the enhancement on the bonding strength is limited and less obvious than method II.

The influence of GE additional amount (10%, 20%, 30%, and 40% in weight percent versus total urea) on the bonding strength of prepared plywood was studied, and the testing results of bonding strength are shown in Figure 8. For UF-PDE resin, the bonding strength was significantly improved with the increasing additional amount of PDE from 0 to 30%. However, for the further increase of additional amount up to 40%, the bonding strength of plywood was obviously dropped down. The declining bonding strength is probably due to the exceeded hydroxyl content, which in turn resulted in the decreasing water resistance of the prepared plywood. The variations of bonding strength as a function of GE additional amount of BDE, EDE, and TPTE showed the similar trend as that of PDE. However, the maximum bonding strength was reached at 20% additional amount.

The molecular structure and epoxy value of BDE and EDE are similar, and hence, the UF-BDE and UF-EDE have the almost same bonding strength with the same amount of GE. The correspondingly bonding strength reached the standard of 0.7 MPa only at the additional amount of 20%. For TPTE, there is branched structure and more functionality, indicating higher crosslinking degree of UF-TPTE. Therefore, with the same additional amount, UF-TPTE behaves as a little higher bonding strength than UF-BDE and UF-EDE. Although the epoxy value of PDE is only a half of the other GE modifiers, the best bonding strength results can be obtained for its longest molecular chain, which endows the modified resin with the desirable flexibility. PDE is a so effective modifier that the bonding strength of the correspondingly plywood reached 0.78 MPa (>0.7 MPa) only at the 10% additional amount. As the additional amount increased to 30%, the bonding strength can even reach 0.91 MPa.

Except for the bonding strength, formaldehyde emission is another important parameter for the practical application of

plywood bonded by UF adhesives. The measurements of formaldehyde emission for the UF-GE resins were carried out in 30 min after plywood production as listed in Table V. Meanwhile, the formaldehyde emission of plywood made from blank UF resin is 2.12 mg/L tested under the same condition. As indicated in Table V, the amount of formaldehyde emission for UF-GE (II-10) and UF-GE (II-20) are about half of that of blank UF resin and can be further reduced with the increasing GE additional amount. Moreover, with the same additional amount, UF-BDE, UF-EDE, and UF-PDE showed nearly the same formaldehyde emission, and the UF-TPTE showed the lowest value. This trend is consistent with the TGA characterization results. Therefore, the introduction of stable structures as hydroxyalkyl and alkyl ether groups can effectively reduce the formaldehyde emission during their usage. The plywood made from UF-TPTE resin has the best result with the amount of formaldehyde emission less than 1.0 mg/L as the additional amount of GE equal to 20% in step B. Meanwhile, for UF-PDE, the formaldehyde emission reached nearly 1.0 mg/L with the same amount.

## CONCLUSIONS

UF resins were modified by using four different types of long chain multifunctional GE. Through the ring-opening reaction mechanism, the chemical reaction can occur between the epoxy groups within the GE chains and the functional groups within the UF resins such as the amine, hydroxyl, etc., so as to form the hydroxyalkyl and the alkyl ether structures in the GE-modified UF resins as indicated by the results of <sup>13</sup>C-NMR and FTIR, which can confirm the storage and thermal stability of the as-prepared liquid resins. With the plywood prepared by the resin adhesives, the influences of the addition method, type and the amount of GE used in the modification on the bonding strength as well as the formaldehyde emission of the plywood were investigated. The best way to introduce GE modifiers into UF resins is adding GE in the acidic condensation stage. With the increasing addition amount of GE, the bonding strength of plywood first improved and then decreased, and a maximum value was observed at the addition amount of 20 or 30% in the weight percentage of total urea. The formaldehyde emission of plywood was decreased significantly with the addition of GE. Considering the cost and performance, the PDE with more flexible molecular chain is the most effective modifier. The 10% of PDE (in the weight percentage of total urea) added in the UF resin by method II can improve the bonding strength of the plywood to 0.78 MPa, and decrease the formaldehyde to 1.29 mg/L, which is 0.54 MPa and 2.12 mg/L of the corresponding value of the blank UF resin, respectively. Moreover, the performance of the PDE modified adhesive would further enhance with more amount of PDE used. The branched TPTE modified

**Table V.** Formaldehyde Emission of Plywood Made from UF-GE Resins

Addition	UF-BDE (mg/L)	UF-EDE (mg/L)	UF-PDE (mg/L)	UF-TPTE (mg/L)
II 10	1.27	1.31	1.29	1.13
II 20	1.07	1.05	1.02	0.98



resin shows better results in the formaldehyde emission test than UF-PDE, and the bonding strength of the plywood is also remarkable in 20% addition amount.

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