

# Effects of Hydrolysis Degree of Soy Protein Isolate On the Structure and Performance of Hydrolyzed Soy Protein Isolate/Urea/Formaldehyde Copolymer Resin

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**ABSTRACT:** The hydrolyzed soy protein isolate (HSPI) with different hydrolysis degree was applied to modify urea-formaldehyde resins (UF) via copolymerization process. The properties of HSPI were characterized by attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) and TGA. The results show that HSPI with different hydrolysis degree is obtained. <sup>1</sup>H NMR and ATR-FTIR spectra indicate that HSPI with different hydrolysis degree can incorporate into the structure of cured and uncured UF. The UF modified with higher hydrolysis degree of HSPI possess more stable units and contribute to the lower exothermic peak temperature in DSC curves. The bonding strength of HSPI modified UF increases as the hydrolysis degree of HSPI increases at the hot-press temperature of 120°C and decreases at the hot-press temperature of 150°C. The best bonding strength is 1.53 MPa at the hot-press temperature of 135°C and improved 56.12% compared with UF. In addition, the formaldehyde emission is dramatically reduced. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41469.

**KEYWORDS:** adhesives; properties and characterization; thermal properties

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## INTRODUCTION

Urea-formaldehyde adhesives (UF) are less costly than other adhesives and have been widely used in wood industry, such as manufacture of plywood, particleboard and medium density fiberboard. UF possess some advantages such as fast curing, good performance in panel, water solubility and lower price. However, the formaldehyde used in the synthesis process will release during practical application. Due to its hazard to health, the emission of formaldehyde has been greatly concerned in the field of wood industry. A lot of works have been carried out to reduce the formaldehyde emission problem associated with this resin system. Some people synthesized UF with acidic catalysts without first using an alkaline catalyst to decrease the formaldehyde emission.<sup>1–3</sup> An effective way is to decrease formaldehyde/urea (F/U) ratio, but the method of decrease the F/U ratio has limitations because this approach resulted in performance degradation.<sup>4,5</sup> In addition, isocyanate, melamine, and acrylamide copolymerization also can be used to modify UF. And the modified resins can give boards of higher physical properties and lower formaldehyde emission.<sup>6–8</sup>

In recent years, many natural compounds can also reduce formaldehyde emission from UF. Moubarik et al. introduced 7% corn flour into UF, the results showed that the mechanical and physi-

cal properties of the boards were improved and their formaldehyde emissions reduced.<sup>9</sup> The cornstarch and mimosa tannin, respectively, up to 10 and 4%, were added to the UF. The performance of these panels is comparable with those of boards made using commercial UF.<sup>10</sup> Essawy et al. used glycolysis as modifiers during the synthesis of urea-formaldehyde resins (UF). It was found that the free formaldehyde was remarkably decreased; the adhesion strength and the moisture resistance were improved.<sup>11</sup> Roumeli applied the prepared UF/SiO<sub>2</sub> resins in wood panels. It was found that the mechanical properties of the panels are enhanced with increasing nanoSiO<sub>2</sub> concentration.<sup>12</sup> Zhang et al. found that nanocrystalline cellulose modified by 3-aminopropyltriethoxysilane improved the wetting property and decreased the formaldehyde emission in fiberboard.<sup>13</sup>

Among the various structures of chemical modifiers, we are interested in hydrolyzed soy protein isolate (HSPI) due to the functional groups, such as primary amine, secondary amine, guanidyl, indolyl etc. Also, the HSPI is sticky, which can be used as adhesives. Soy protein is abundant, inexpensive, renewable, and easy to handle.<sup>14</sup> Soybean products, including soy protein, sodium carbonate hydrolyzed soy protein, soy flour, were mixed with UF to modify the UF. The results showed that the soybean products can reduce formaldehyde emissions from

**Table I.** Formulation of HSPI Modified UF

	I		II		III		IV	
	Urea (g)	HSPI (g)	Urea (g)	HSPI (g)	Urea (g)	HSPI (g)	Urea (g)	HSPI (g)
①	122.5	807	122.5	552	122.5	375	122.5	339
②	87.5	0	87.5	0	87.5	0	87.5	0
③	122.5	0	122.5	0	122.5	0	122.5	0

UF.<sup>15</sup> However, to improve the properties of UF and reduce the formaldehyde emissions, few works use HSPI to partially substitute urea and synthesize the HSPI modified UF by copolymerization. Moreover, the effects of hydrolysis degree of soy protein isolate (SPI) on the structure and performance of HSPI-urea-formaldehyde copolymer resin were also analyzed.

In this work, different hydrolysis degree of HSPI was applied to modify UF by copolymerization. Structures of the HSPI and HSPI modified UF were characterized by using attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR), <sup>1</sup>H nuclear magnetic resonance spectroscopy (<sup>1</sup>H-NMR), thermo-gravimetric analysis (TGA), and differential scanning calorimetry (DSC). The initial standard properties of the unmodified and modified UF were characterized. Moreover, the influences of hot-press temperature on the bonding strength and formaldehyde emission of HSPI modified UF resins were investigated.

## EXPERIMENTAL

### Materials

Urea ( $\geq 99.0\%$ ), formaldehyde (37.5%), sodium hydroxide ( $\geq 96.0\%$ ) and ammonium chloride ( $\geq 99.5\%$ ) were purchased from Shantou Xilong Chemical Factory, Guangdong, China. All chemicals utilized in this study were of analytical reagent grade. SPI was purchased from Anyang Detianli food, Henan Province, China. Poplar panels with 8% moisture content were cut in the size of 350 mm  $\times$  350 mm  $\times$  2.0 mm, which were purchased from Suqian, Jiangsu Province, China.

### Methods

**The Hydrolyzation of Soy Protein Isolate.** Sodium hydroxide aqueous solutions (0.04 wt %, 0.16 wt %, 0.28 wt %, 0.40 wt %) was added and stirred in the reactor. SPI was added gradually when the solution was heated to the temperature of 70°C. The mixture was heated to 90°C and kept for 1 h. The solids content of the HSPI was 13.04%. The SPI hydrolyzed in 0.04 wt %, 0.16 wt %, 0.28 wt %, 0.40 wt % sodium hydroxide aqueous solutions was designated as I, II, III, IV, respectively.

**The Ability to React with Formaldehyde.** The HSPI 100 g and formaldehyde 50 g were added into a four-necked flask equipped with a mechanical stirrer, a thermometer, a condenser, and a septum-seal for feeding. The pH of the mixture was adjusted to 7.8. Then the mixture was heated to the temperature of 90°C and held at 90°C for 2 h. The remaining formaldehyde was determined by a modified sodium sulfite method.<sup>16</sup>

**Synthesis Procedure of the Modified UF.** The HSPI modified UF were synthesized by three steps as described in the following.

**Step I: methylation.** A 2-L four-neck flask equipped with a mechanical stirrer, a thermometer, a condenser and a septum-seal for feeding. 568.05 g formaldehyde was added and the solution was heated slowly until the temperature reached 25–30°C, the first urea and HSPI was added. The pH of the mixture was adjusted to 7.8 by 30 wt % sodium hydroxide aqueous solution. After that, the mixture was heated at a rate of 1°C/min, and the temperature reached 60°C within 30 min. Then the second urea was added, heating was continued to the temperature of 90°C at a rate of 1°C/min within 30 min and held at 90°C for 1 h.

**Step II: Polycondensation.** The pH of the prepared mixture from step I was adjusted to 4.5–5.0 using 25 wt % ammonium chloride aqueous solutions, and maintained until the end reaction point.

**Step III: post-treatment.** After the reactions reached endpoint, the pH of the prepared mixture from step II was finally adjusted to 7.8 by 30 wt % sodium hydroxide aqueous solution. The third urea was added after the temperature decrease to 75–80°C, and kept for 1 h. The obtained resins were cooled to room temperature.

The amount of HSPI was calculated according to its ability to react with formaldehyde. 5% of the urea molar was substituted. The synthesized resins under the same condition without the HSPI were defined as the blank UF. The formulation of HSPI modified UF are showed in Table I.

**Preparation of Plywood Panels.** Three-layer plywood panels were each bonded with prepared resins for the binding strength test according to National Standard of People's Republic of China GB/T 17657-1999.<sup>17</sup> The resins were firstly mixed with 1 wt % of ammonium chloride. Then the resins were applied to two sides of the veneer using a brush. The adhesive-coated veneer was stacked between two uncoated veneers with the wood grain of one layer vertical to its neighbor veneer layer. The plywood panels were prepared under the following conditions: glue spread 16 mg/cm<sup>2</sup>; cold-press under 1.0 MPa for 20 min; hot-press temperature 120°C, 135°C, 150°C; hot-press pressure 1.0 MPa; hot-press time 1 min/mm; the thickness of veneer is 2 mm. Specimens as shown in Figure 1 were cut from the plywood panels along the face-grain axis according to Wood Industry Standard Assemble of China (GB/T 17657-1999).<sup>17</sup>

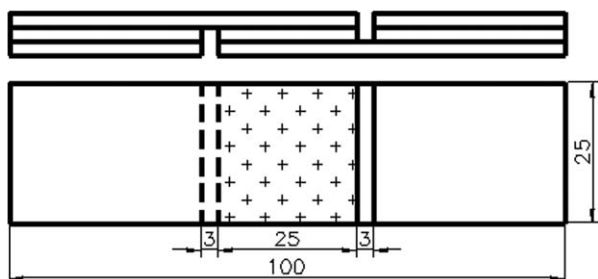


Figure 1. Test specimens size of plywood.

### Characterization

**ATR-FTIR Characterization.** ATR-FTIR spectra were obtained using dried powdered samples (Nicolet iS10, Thermo Scientific, America) in the range of  $4000\text{--}500\text{ cm}^{-1}$ . 32 scans were accumulated at a resolution of  $4\text{ cm}^{-1}$ .

**Thermal Analysis.** The thermal stability of the cured resins was assessed with TGA (SII-7200, Japan). The temperature range was from room temperature to  $800^\circ\text{C}$  at a heating rate of  $10^\circ\text{C}/\text{min}$ . These tests were carried out under nitrogen atmosphere ( $20\text{ mL}/\text{min}$ ) in order to prevent thermoxidative degradations. The sample pan was placed on the Pt basket in the furnace, and approximately  $10\text{ mg}$  of materials was used for each measurement.

DSC curve of samples was carried out using a Mettler Toledo DSC apparatus with a refrigerated cooling system (DSC 823e, Switzerland) and nitrogen as purge gas. The samples for DSC analysis were prepared as followings: the resins were mixed with  $1\text{ wt } \%$   $\text{NH}_4\text{Cl}$ , and then the samples were dried on a freeze-dryer (Alpha1-2 LD plus, Martin Christ, Germany) after frozen in a refrigerator at  $-20^\circ\text{C}$ .

**NMR.** The liquid state  $^1\text{H-NMR}$  spectra of samples were obtained with a Bruker Avance III 500 MHz spectrometer. The HSPI, UF, and modified UF were dissolved in deuterated dimethyl sulfoxide ( $\text{DMSO-d}_6$ ) and tetramethylsilane as internal reference.

**Bonding Strength of Plywood.** Specimens were immersed into  $63 \pm 3^\circ\text{C}$  water for 3 h, and then cooled to room temperature for 10 min before measurement. A tensile testing machine (HY-0580, Shanghai Hengyi Precision Instrument) was used to measure the bonding strength of wood specimens. The bonding strength was conducted at a crosshead speed of  $10\text{ mm}/\text{min}$ . Twenty replicates were tested for each sample to obtain an average value.

**Properties Measurement of Resins.** The pH values were measured by a pH meter (PHS-2F, Shanghai Jingke instrument, China).

The solid content was measured by heating about  $1\text{ g}$  resins sample in a small aluminum pan in an oven at  $120^\circ\text{C} \pm 1^\circ\text{C}$  for  $120 \pm 1\text{ min}$  according to National Standard of People's Republic of China GB/T 14074-2006.<sup>17</sup>

The free formaldehyde content in the resin was determined by a sodium sulfite method.<sup>16</sup>

The viscosity was carried out using a rotating viscometer (NDJ-5S, Shanghai Ande instrument, China).

The density of resins at  $20^\circ\text{C}$  was measured by a densitometer ( $1.000\text{--}1.200\text{ g}/\text{mL}$ , Kairuihe Instrument Factory, Hebei, China).

The curing time of UF and HSPI modified UF was characterized according to National Standard of People's Republic of China GB/T 14074-2006. After  $25\text{ wt } \%$  ammonium chloride aqueous solutions was added as curing agent, the sample was put into boiling water. The hardening time was recorded. Three replications were done for each resin.

The formaldehyde emission of plywood was measured by the 24 h desiccators method according to National Standard of People's Republic of China GB/T 17657-1999.<sup>17</sup> Ten specimens of each sample with dimensional size of  $150\text{ mm} \times 50\text{ mm}$  were placed in the desiccators with a crystallizing dish filled with  $300\text{ mL}$  distilled water. The formaldehyde emission test lasted 24 h at a temperature of  $20^\circ\text{C}$ . The formaldehyde concentration in distilled water was obtained at  $412\text{ nm}$  by using a UV spectrophotometer (Lambda 35, Perkin Elmer, America) based on the Hantzsch reaction.

## RESULTS AND DISCUSSION

### The Ability to React with Formaldehyde

Figure 2 shows the amount of formaldehyde that can be reacted with HSPI. The SPI is a globular protein consisting of a polypeptide chain made up of amino acids as monomeric units. The molecular structures of SPI contain a hydrophobic region that is enclosed within a hydrophilic region, so that many of the polar groups are unavailable. The conformation of the protein is maintained by disulfide bonds and by non-covalent forces, such as van der Waals interactions, hydrogen bonds, and electrostatic interactions. After the SPI was treated with sodium hydroxide solution at  $90^\circ\text{C}$  for 1 h, tertiary and quaternary structures of SPI was partially disrupted due to the breakage of the bonds and interactions between molecular. And the functional groups of the protein for bonding and cross-linking are exposed (Figure 3). The  $-\text{NH}_2$  of HSPI can react with formaldehyde to form methylol derivatives (Figure 4). The formaldehyde react ability of I, II, III, IV is 13, 19, 28, 31 mg HCHO/g HSPI. The higher concentration of sodium hydroxide was applied to hydrolyze the SPI, the more react groups were obtained.

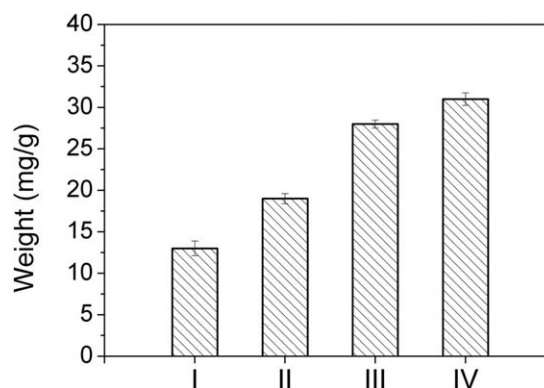


Figure 2. HSPI's ability to react with formaldehyde.

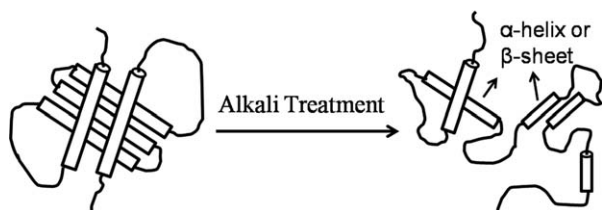


Figure 3. Schematic diagram of SPI denaturation.

### Characterization of HSPI with Different Hydrolysis Degree

Figure 5 shows the spectra of different hydrolysis degree of HSPI. The spectra are analyzed to verify the changes introduced by different concentrations of sodium hydroxide solution. The broad, strong peak of HSPI and SPI at around  $3272\text{ cm}^{-1}$  belongs to the hydroxyl group, amine stretching of the soy protein and hydrogen bond association between molecules.<sup>18,19</sup> The absorption peaks at  $2966\text{ cm}^{-1}$  and  $2901\text{ cm}^{-1}$  are due to the C—H symmetrical stretching vibration. SPI has typical infrared absorption bands at  $1630\text{--}1680\text{ cm}^{-1}$ ,  $1530\text{--}1559\text{ cm}^{-1}$ , and  $1260\text{--}1420\text{ cm}^{-1}$  for amide I, II, and III. The stretching vibration mode of SPI observed at  $1633\text{ cm}^{-1}$  attributes to C=O bonds for amide I. The bending vibration mode of SPI at  $1530\text{ cm}^{-1}$  belongs to the N—H for amide II. The C=O and N—H in peptide bonds form primary backbone of proteins. The amide II band is dominated by chain oscillations, but the correlation between the protein secondary structure and frequency is less straightforward than the amide I vibration. According to the amide I data, the I, II, III, and IV still preserve native-like structure  $\beta$ -sheets ( $1606\text{--}1639\text{ cm}^{-1}$ ).<sup>20,21</sup> The bending vibration mode of SPI at  $1383\text{ cm}^{-1}$  belongs to the C—N for amide III. The absorption bands at  $1236\text{ cm}^{-1}$  and  $1072\text{ cm}^{-1}$  are attributable to the C—C and C—O stretching vibrations.<sup>22</sup>

The peak at  $3272\text{ cm}^{-1}$  decreases with the increasing concentration of sodium hydroxide solution. The reason is that more internal bonds in SPI molecule were disrupted as the concentration of sodium hydroxide solution.<sup>23</sup> The peaks of C=O and N—H in peptide bonds at  $1633\text{ cm}^{-1}$  and  $1530\text{ cm}^{-1}$  also decrease with the increasing concentration of sodium hydroxide solution, which is due to the unfolding of  $\beta$ -sheets.

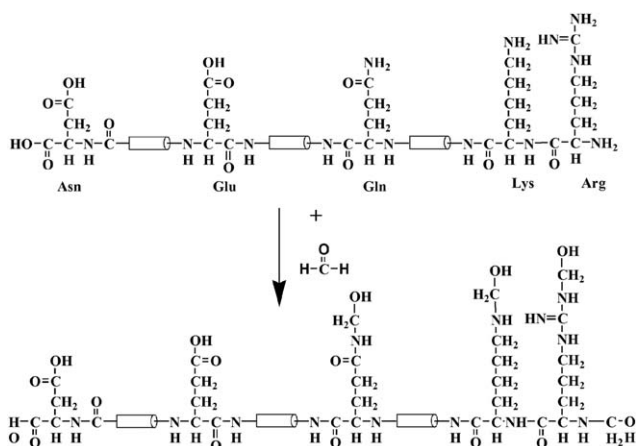


Figure 4. The formation mechanism of methylol derivatives.

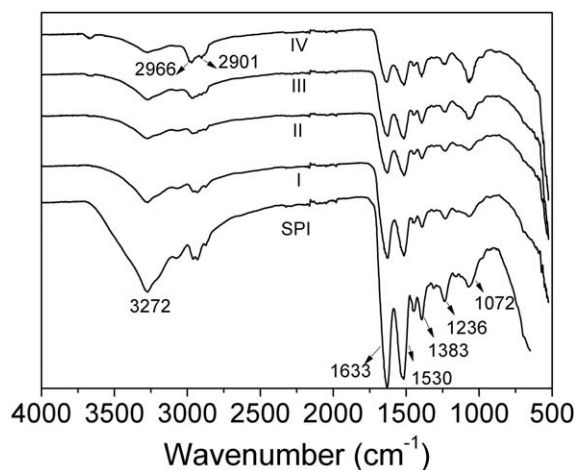


Figure 5. ATR-FTIR spectra of SPI and HSPI.

Meanwhile, a small part of peptide bond was also hydrolyzed and formed carboxyl groups and amino groups. Therefore, the peak of C—O at  $1072\text{ cm}^{-1}$  increases with the increasing concentration of sodium hydroxide solution owing to the formation of carboxyl groups. A conclusion can be drawn from Figure 5 is that HSPI with different hydrolysis degree is obtained.

The formation and structure relationship can be characterized by TGA.<sup>24</sup> The TG, DTG, and DTA curves of SPI and HSPI are shown in the Figure 6. TGA is a curve of the weight loss against temperature, DTG is the first derivative of weight loss, while DTA is the curve of heat flux versus temperature. The minor weight loss observed from room temperature to  $130^\circ\text{C}$  for all samples is likely due to the evaporation of adsorbed moisture.<sup>25</sup> Free water and bound water are lost at this stage. SPI can absorb more moisture than HSPI because many polar groups are exposed after alkaline hydrolysis. It can be seen that the thermal stability of HSPI is better than SPI. The reason is the stronger interactions reformed among the exposed groups in drying process through Van der Waals forces, intermolecular hydrogen bonds and hydrophobic interactions, thereby reducing the segmental motions and creating a barrier that delays the diffusion of heat.<sup>26</sup> The main weight loss of SPI and HSPI is attributed to the degradation of protein involving the scission of intramolecular and intermolecular hydrogen bonds, electrostatic bonds and the random cleavage of peptide bonds in protein backbone.<sup>27</sup> In the DTG curve, the temperature of maximum decomposition rate of SPI, I, II, III, IV is  $313^\circ\text{C}$ ,  $311^\circ\text{C}$ ,  $310^\circ\text{C}$ ,  $299^\circ\text{C}$ ,  $296^\circ\text{C}$ , respectively. In the DTA curves, the peak temperature of I, II, III, and IV is  $320^\circ\text{C}$ ,  $303^\circ\text{C}$ ,  $291^\circ\text{C}$ ,  $287^\circ\text{C}$ , and  $284^\circ\text{C}$ , respectively. The temperature of endothermic peak decreased with increasing hydrolysis degree. The reason is that the higher hydrolysis degree the more groups are exposed and the stronger interactions are reformed. The difference in the DTA curves indicates the chemical structure of I, II, III, IV is different. The result is consistent with the results of FTIR.

### Chemical Structure of HSPI Modified UF

Typical  $^1\text{H}$  NMR spectra of pure UF and modified UF are given in Figure 7. The  $^1\text{H}$  NMR chemical shifts (ppm) and the

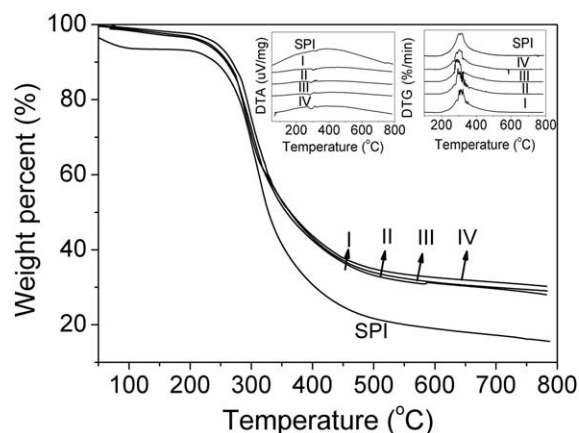


Figure 6. TGA, DTG, and DTA curves of SPI and HSPI.

corresponding functional groups assigned to them are given in Table II. The first two peaks, with chemical shifts at 6.6 and 5.5 ppm, are assigned to substituted ( $-\text{NH}$ ) and nonsubstituted ( $-\text{NH}_2$ ) amide groups, respectively; the peak areas at 4.5 and 3.1 ppm are attributed to  $-\text{O}-\text{CH}_2-\text{O}-$  and  $-\text{CH}_2-\text{OH}$ ; the absorption due to  $-\text{N}-\text{CH}_2-\text{OH}$ ,  $-\text{N}-\text{CH}_2-\text{N}-$ ,  $-\text{N}-\text{CH}_2-\text{O}-\text{CH}_2-\text{N}-$  give peak at 4.2–4.5.<sup>28</sup> HSPI has nearly the same functional groups with UF. Therefore, the  $^1\text{H}$  chemical shift of UF and HSPI-UF is similar. After HSPI copolymerized with urea and formaldehyde, the peak at 2.8 ppm disappeared. The results indicate that the HSPI is reacted with formaldehyde to form methylol derivatives. Methylolated proteins react with other methylolated compounds to form HSPI modified UF resins.

Figure 8 illustrates the ATR-FTIR spectra of cured unmodified and modified UF. Comparing the spectra of the control UF with modified UF, high similarity is noticeable. It could be seen from Figure 8 that a strong absorption peak appeared at around  $3316\text{ cm}^{-1}$  and it is recognized that this peak is stretching vibration band of the  $\text{N}-\text{H}$  functional group. In the spectra of HSPI modified UF, the absorption peaks at  $2968\text{ cm}^{-1}$  and  $2896\text{ cm}^{-1}$  become stronger, which are due to the  $\text{C}-\text{H}$  symmetrical stretching vibration band of HSPI. The absorption peaks of bending vibration band of the  $\text{N}-\text{H}$  functional group appear at  $1531\text{ cm}^{-1}$  and  $1379\text{ cm}^{-1}$ . The stretching vibration band of the  $-\text{C}=\text{O}$  functional group is measured at  $1630\text{ cm}^{-1}$ . The characteristic absorption peak of the stretching vibration band of the  $\text{C}-\text{N}$  functional group appears at  $1235\text{ cm}^{-1}$ .<sup>6</sup> The absorption band at  $1028\text{ cm}^{-1}$  is attributable to the  $\text{C}-\text{O}$  stretching vibrations.<sup>22</sup> The peak related to the  $\text{C}-\text{O}$  absorption of modified UF is seen to shift from  $1028\text{ cm}^{-1}$  to  $1036\text{ cm}^{-1}$ . The reason maybe that the carboxyl groups in HSPI can react with methylol and formed ester bonds ( $-\text{CO}-\text{O}-$ ), and the  $\text{C}=\text{O}$  have contributed to this shift. The result indicates that free amino groups and carboxyl groups of HSPI are able to copolymerize with urea and formaldehyde, and HSPI with different hydrolysis degree can incorporate into the structure of cured UF.

#### Thermal Properties of UF and HSPI Modified UF

Figure 9 shows the TGA, DTG, and DTA curves of the cured resins. Modified and unmodified samples show one similar pyrolysis process in TGA curves. The first stage in TGA curves, observed at room temperature to  $130^\circ\text{C}$ , is related to the loss of adsorbed and bounded water. The higher hydrolysis degree of HSPI modified UF adsorbed more water than pure UF. The

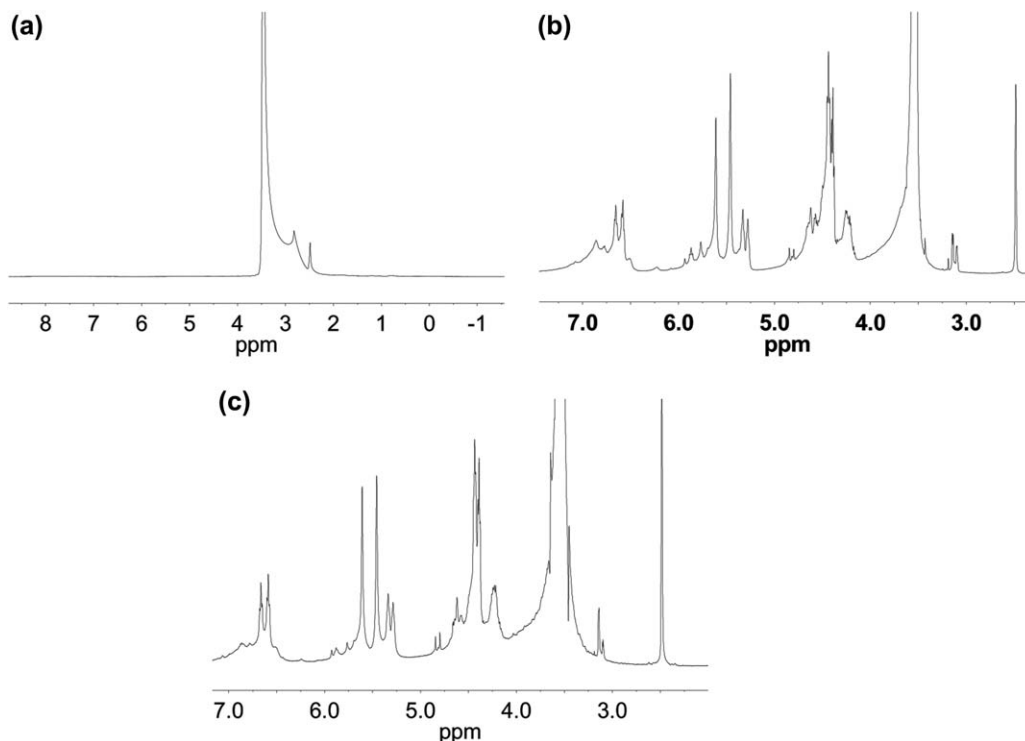


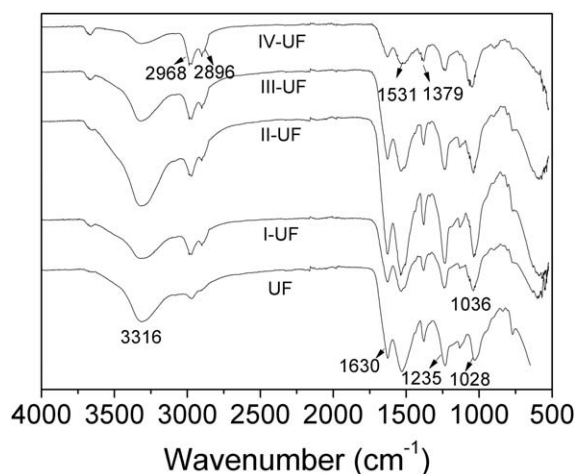
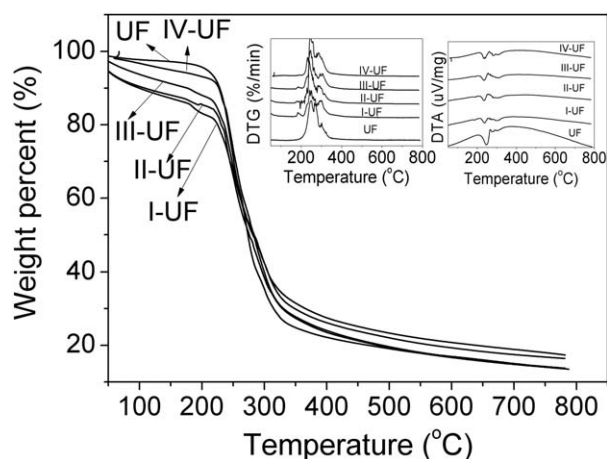
Figure 7.  $^1\text{H}$  NMR spectra of (a) HSPI, (b) UF, (c) HSPI-UF.

**Table II.** Formulation of HSPI Modified UF

Structure	<sup>1</sup> H chemical shift (ppm)
—CO—NH—	6.5–6.7
—CO—NH <sub>2</sub>	5.2–5.6
—O—CH <sub>2</sub> —O—	4.5–4.7
—N—CH <sub>2</sub> —OH, —N—CH <sub>2</sub> —N—,	
—N—CH <sub>2</sub> —O—CH <sub>2</sub> —N—	4.2–4.5
H <sub>2</sub> O	3.4–3.7
—CH <sub>2</sub> —OH	3.1–3.2
DMSO	2.5

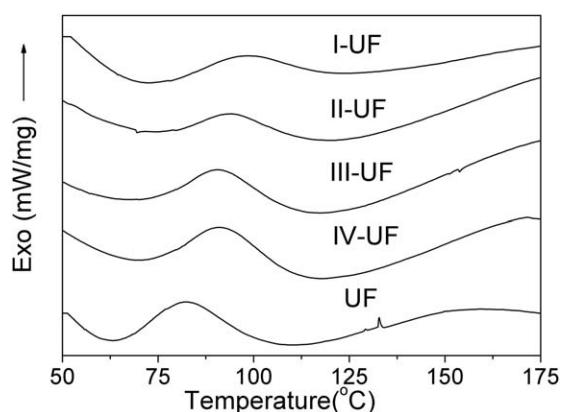
reason is that except the reactive group NH<sub>2</sub>, the hydrophilic groups, —COOH and —OH of hydrolyzed SPI, are also introduced into the UF, which can absorb more water molecules. The higher hydrolysis degree the more hydrophilic groups are exposed. The higher hydrolysis degree of HSPI contributes to the higher thermal stability at the range of 130–250°C, which is consistent with the TG results of HSPI.

In the DTA curves, the endothermic peaks at 246.6, 237.3, 236.4, 234.5, and 232.9°C for UF, I-UF, II-UF, III-UF, and IV-UF are attributed by many authors to the degradation of methylene ether bridges into methylene bridges and branching and cross-linking reactions in the resins network.<sup>29</sup> The endothermic peak temperature of modified UF decreases due to the copolymerization with HSPI. In addition, the endothermic peak temperature of modified UF decreases with the increasing of the hydrolysis degree of HSPI. The results indicate that the activation energy of modified UF is decreased and the methylene ether bridges can convert into methylene bridges easily when the hydrolysis degree of HSPI increases. The first endothermic peaks area of unmodified UF is larger than modified UF, which is ascribed to the less amount of methylene ether bridges in cured HSPI modified UF. The second endothermic peak at about 278.6, 298.2, 307.4, 308.5, 308.6°C for UF, I-UF, II-UF, III-UF, and IV-UF, respectively, belongs to decomposition of the most stable units methylenediurea in the UF.<sup>30</sup> The endothermic

**Figure 8.** ATR-FTIR spectra of cured UF and HSPI modified UF.**Figure 9.** TGA, DTG, and DTA curves of UF and HSPI modified UF.

peak temperature of modified UF increases as the increasing of hydrolysis degree of HSPI. That is to say, the UF modified with higher degree of HSPI possess more stable units.

The thermal transition of samples can be determined using DSC by measuring the amount of energy absorbed or released. Figure 10 present the DSC curves of modified and unmodified UF catalyzed by ammonium chloride at 1 wt % of UF. The exothermic peak observed is due to the cross-linking reaction.<sup>31</sup> The onset temperature, peak temperature and  $\Delta H$  are showed in Table III. Comparing with UF, the onset and peak temperature of modified UF increased,  $\Delta H$  values decreased. These results indicate that the reactivity of modified UF decreased.<sup>32</sup> That is to say, the amount of reactive groups decreased. The reason maybe that molecule chains of HSPI interfere with the cure of UF. Another reason may be that the solid content of modified UF is lower than that of UF. In addition, the higher hydrolysis degree of HSPI contributes to the lower onset and peak temperature and higher  $\Delta H$  values of HSPI modified UF. The higher hydrolysis degree, the less amount needed to substitute the urea. Therefore, the less HSPI molecular chains interfere with the cure of HSPI modified UF. A conclusion can be draw that the amount of HSPI has a greater effect on the thermal properties than the hydrolysis degree of HSPI.

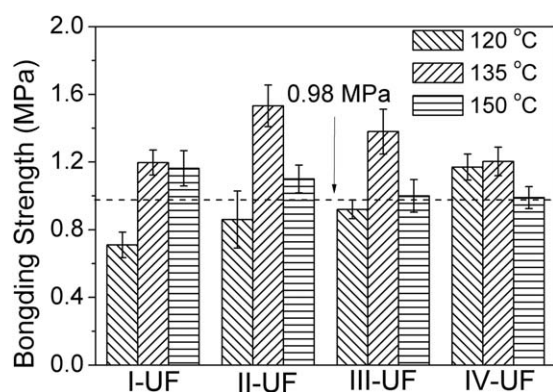
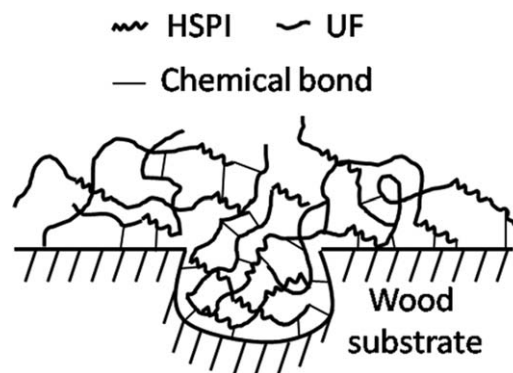
**Figure 10.** DSC curves of modified and unmodified UF.

**Table III.** Data From DSC of Modified and Unmodified UF

	I-UF	II-UF	III-UF	IV-UF	UF
Onset temperature (°C)	75.13	74.86	72.73	69.01	67.18
Peak temperature (°C)	97.86	95.09	91.46	90.78	82.49
$\Delta H$ (J/g)	6.34	7.98	9.22	11.01	11.51

**Bonding Strength of Plywood.** The influence of HSPI additions and hot-press temperature on the bonding strength of the plywood is shown in Figure 11. The best bonding strength of unmodified UF is 0.85 MPa at hot-press temperature of 120°C. The best shear strength of I, II, III, IV is 0.51, 0.55, 0.45, 0.36 MPa at hot-press temperature of 150°C, respectively. For all types of HSPI modified resins, the best bonding strength is obtained at 135°C. The bonding strength of HSPI modified UF increases as the hydrolysis degree of HSPI increases at the hot-press temperature of 120°C and decreases at the hot-press temperature of 150°C. This trend is also consistent with the result of DSC. The higher hydrolysis degree of HSPI contributes to the lower onset and peak temperature of HSPI modified UF. The reason may be that the HSPI modified resins are not fully cured at 120°C. The modified UF may be thermal decomposed at 150°C. The bonding strength can be improved by HSPI at proper hot-press temperature. The best bonding strength of HSPI modified UF is 1.53 MPa and improves 56.12% compared with pure UF, which indicates that the HSPI can copolymerize with urea and formaldehyde and form network structure. The higher bonding strength at higher temperature might be due to less remained moisture when the resin with higher solid content was applied.

Figure 12 shows the bonding mechanism of HSPI modified UF resins. The HSPI chains were block copolymerized with urea-formaldehyde in the synthesis process. In the process of hot press, the following reactions can occur: the condensation reaction occurred between the  $-\text{NH}_3^+$  and  $-\text{COO}^-$  in HSPI chains; the  $-\text{NH}_3^+$  and  $-\text{COO}^-$  also can react with the hydroxyl groups of the cellulose. Except the HSPI chains, the methylol of urea-formaldehyde chains can react with the hydroxyl groups of the cellulose. The chemical bonds also can be formed between

**Figure 11.** Bonding strength of plywood bonded with HSPI modified UF.**Figure 12.** The bonding mechanism of HSPI-UF.

the molecular chains of HSPI-urea-formaldehyde block copolymers. The formed bridges results in an extremely strong wood to adhesive bond which is resistant to water. In addition, the bonding mechanism of the resin to the wood substrate also includes weaker forces such as van der Waals forces and hydrogen bonding, or mechanical interlocking.

**Properties of Different Kinds of Resins.** The initial standard properties of the control and modified resins are showed in Table IV. The pH and density of unmodified and modified UF are similar. The viscosity of modified UF is higher than unmodified UF because of the higher viscosity of the added HSPI. The decrease of solids content of HSPI modified UF is due to the lower solids content of HSPI. The higher hydrolysis degree, the more reactive groups exposed and the less amount of HSPI needed to substitute the 5% urea. Therefore, the solids content of HSPI modified UF increases as the increasing of hydrolysis degree. To compare the reactivity of modified UF, the curing time of UF and HSPI modified UF was characterized. The curing time of modified UF is more than the control UF. The curing time of modified UF decreases as the hydrolysis degree increases. The result suggests that the reactivity of modified UF decreases after adding HSPI, which is consistent with the result of DSC.<sup>32</sup>

Except for the bonding strength, formaldehyde emission, as indicated in Table V, is another important parameter for the practical application of plywood bonded by UF. The formaldehyde emission decreases as the increasing of hot-temperature. The reason is that the cross-linking degree increases at higher temperature. Also, more formaldehyde can migrate with the water vapor evaporation. There is no significant difference between formaldehyde emissions of plywood made from HSPI modified resins at the

**Table IV.** Properties of Different Kinds of Resins

	Viscosity 20°C pH	Viscosity (mPa s)	Solids content (%)	Density 20°C (g/cm <sup>3</sup> )	Curing time (s)	Free formaldehyde (%)
UF	7.6	25.5	51.55	1.182	155	0.160
I	7.5	73.9	35.95	1.173	208	0.157
II	7.6	64.1	38.32	1.181	194	0.134
III	7.7	51.2	40.98	1.170	189	0.126
IV	7.5	38.5	43.02	1.179	174	0.139

**Table V.** Formaldehyde Emission of Plywood at Different Hot-Press Temperature (mg/L)

Hot-press temperature (°C)	UF	I-UF	II-UF	III-UF	IV-UF
120	1.47	1.38	1.27	1.26	1.13
135	1.32	0.84	0.82	0.98	1.06
150	1.23	0.67	0.64	0.61	0.71

same hot-press temperature. However, according to the bonding strength, the best hot-press temperature for UF is 120°C and the formaldehyde emission is 1.47 mg/L; the best hot-press temperature for HSPI modified UF is 135°C and the formaldehyde emission is 0.84–1.06 mg/L. Therefore, the formaldehyde emission of plywood made from HSPI modified resins decreased. One reason may be ascribed to the valid resin amount of HSPI modified UF used is less than that of unmodified UF when the glue spread is the same. Another reason is the reversibility of the reaction between HSPI and formaldehyde is lower than the reaction between urea and formaldehyde.

## CONCLUSIONS

The HSPI with different hydrolysis degree can be used to substitute 5% urea to synthesis modified UF via copolymerization process. HSPI with different hydrolysis degree can incorporate into the structure of uncured and cured UF. The UF modified with higher degree of HSPI possess more stable units. The higher hydrolysis degree of HSPI contributes to the lower exothermic peak temperature in DSC curves. The reactivity of modified UF decreases as the hydrolysis degree increases. The bonding strength of HSPI modified UF increases as the hydrolysis degree increases at the hot-press temperature of 120°C and decreases at the hot-press temperature of 150°C. The best bonding strength is obtained at the hot-press temperature of 135°C and improved 56.12% compared with UF. In addition, the introduction of HSPI in the synthesis of UF resins can effectively reduce the formaldehyde emissions during their usage. The HSPI modified UF can reduce the dependency on petroleum-based chemicals.

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