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Preparation of a starch-based adhesive cross-linked with furfural, furfuryl alcohol and epoxy resin

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ABSTRACT

Furfural and furfuryl alcohol originating from agriculture were used as crosslinkers to develop a renewable starch-furanic adhesive with good water resistance. Electrospray ionization mass spectroscopy and ^{13}C nuclear magnetic resonance measurements indicated that furfural and furfuryl alcohol reacted with starch under acidic conditions and that the –CH_2–O– groups were involved in the cross-linking of the starch-furfural-furfuryl alcohol adhesive (SFF). The gel time of SFF was longer than that of the starch-furfural adhesive (SF), while the dry shear strength of the SFF-bonded plywood suggested that the cured SFF adhesive acquired a performance better than that of starch (S) and SF adhesives. Moreover, the water resistance of the SFF adhesive cross-linked with 9% epoxy resin was further enhanced with respect to that of the S, SF, and commercial phenol formaldehyde adhesives.

1. Introduction

During the last decades, phenol formaldehyde (PF), as the main oil-derived resin, has been widely investigated in the fields of wood and composite materials [1–3]. However, the PF resin contains harmful substances, such as phenol and formaldehyde, which can seriously harm human health. Starch, originating from forest and agriculture, is a renewable bio-based material [4–8] that has been widely used in the manufacture of wood adhesives to replace the PF adhesive. Nevertheless, its water resistance is insufficient for plywood due to the high number of hydroxyl groups within its structure. Nowadays, the graft co-polymerization of synthetic polymers in starch backbones, such as the cross-linking between starch and cellulose, is the best way to improve the water resistance and bonding properties of starch [9–11]. However, these starch-based wood adhesives are still exhibiting low bonding strength and weak water resistance compared to the PF adhesives. Moreover, when compared with PF-based plywood, starch-based adhesives are typically too weak for practical use in industry [12]. Furfural, as a processing residue of agriculture products, such as crops and sugarcane, is a furfuran derivative whose hydrogen atom is replaced by an aldehyde group and has been widely used in synthetic composite materials and food industry [13–16] owing to the high reactivity of the aldehyde group. The earlier research revealed that the cross-linking between starch and furfural can be easily established for the preparation of a starch-furfural (SF) adhesive. However, the high reaction speed between starch and furfural quickly led to resin curing, which does not favor the storage of the adhesive [17]. In addition, furfuryl alcohol, the monomer of polyfurfuryl alcohol, is the major commodity chemical produced from furfural. Due to its stable furan ring and hydroxymethyl group, it has been widely used to prepare bio-based materials, such as tannin-furanic plastic [18], foams [19–22], and adhesives [23–25]. Therefore, furfuryl alcohol could replace some parts of furfural and react with starch for the preparation of new adhesives. Moreover, it can react with furfural to reduce the speed of the furfural and starch reaction, thus prolong the storage time. Consequently, further research on starch, furfural, and furfuryl alcohol was necessary to verify the feasibility of a

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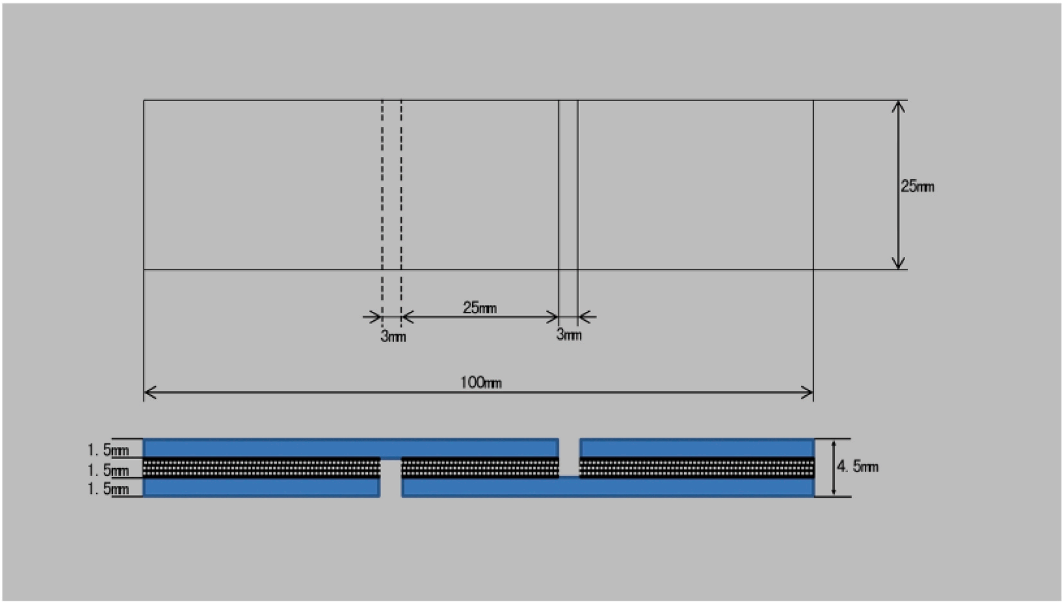


Scheme 1. An illustrative sketch of prepared plywood dimensions.

starch-furfural-furfuryl alcohol (SFF) adhesive that may reveal beneficial bonding, water resistance, and storage prolonged duration. Considering the availability of starch, monosaccharide and/or oligosaccharide derived from hydrolysis of starch, would improve its solubility and enhance its reactivity with furfural or furfuryl alcohol (Note: furfuryl alcohol can be oxidized to furfural in the presence of oxygen while furfural can be converted to furfuryl alcohol and furan-carboxylic acid by a disproportionation reaction in presence of a base), which would contribute to the preparation of new adhesive with integrated performance. In this paper, starch, furfural, and furfuryl alcohol are formulated for use as crosslinkable bio-based adhesive (SFF) under acidic conditions. In addition, the crosslinking was supported by hybridization between SFF resin and a commercial epoxy resin (EPR) in order to establish improvement of the water resistance of SFF. This study is important for the development of novel environmentally-friendly wood adhesives to replace the conventional PF adhesive.

2. Experimental

2.1. Materials

Crops (*Zea mays* L) soluble starch extract powder (S) was purchased from jingshan starch company (Taian, China). Furfural (with a purity of 98%), ammonium chloride (with a purity of 30%) and furfuryl alcohol (with a purity of 98%) were purchased from Acros Organics (Geel, Belgium). Beech veneer (Fagus sylvatica) with 1.5 mm thickness and 9–10% moisture content was supplied by Xin Fei Lin panel Company (Kunming, China). Commercial EPR (E-44) was purchased from Sinopharm Chemical Reagent Company (Beijing, China). PF, as control adhesive (molar ratio F/P = 2.2) was supplied by Xin Fei Lin panel Company (Kunming, China).

2.2. Preparation of the S, SF, and SFF adhesives

The S adhesive was synthesized following a reported method [26]. In order to avoid the formation of high viscosity starch adhesive, it was synthesized under weak acidic condition. In particular, 100 g of starch and 100 mL of distilled water were mixed together in a beaker and stirred with a mechanical stirrer (Model AM300L-H, ONYI, Shanghai, China) at 60 °C for 30 min under acidic conditions to form the S adhesive. During the process, the pH was adjusted to 5.0 using acetic acid solution (40%).

For the preparation of the SF adhesive, 70 g of S, 35 g of furfural, and 100 mL of distilled water were mixed in a beaker and stirred at 60 °C for 30 min under acidic conditions. The reaction process is the same as that of starch adhesive, during the reaction process, the pH was adjusted to 5.0 using acetic acid solution (40%).

For the preparation of the SFF adhesive, 70 g of starch, 17.5 mL of furfural, and 100 mL of distilled water were mixed in a beaker and stirred at 60 °C for 30 min under acidic conditions. The pH was adjusted during the process to 6.0 by acetic acid solution (40%), which was also used to subsequently adjust the pH of the resin system to 4.0. Afterward, 17.5 mL of furfuryl alcohol was added to the resin system followed by stirring at room temperature for 30 min.

The gel time and viscosity of S, SF, SFF, and PF adhesives were determined according to the Chinese norm of GB/T14074 9. For the determination of the gel time, 10 g of each adhesive was placed into a test tube, which was then immersed in a boiling water bath (Model HWS-26, YIHENG, Shanghai, China) at 100 °C and gently, continuously, and rapidly stirred with a muddler using an upward-downward movement until gelation occurred. The gel time was measured from the beginning of the immersion of the adhesive in the boiling water. A tu-4 viscosity cup (Model NDJ-5, YUEPING, Shanghai, China) was then used to test the viscosity of these adhesives. The solid content of the various adhesives was measured by determining the weight of the adhesives before and after oven drying at 120 °C ± 1 °C for 2 h.

2.3. Preparation of plywood

The plywood was prepared using three layers of beech wood veneers. The dimensions of each veneer sheet was 300 mm × 220 mm × 4 mm. The plywood preparation was performed by initially brushing each veneer sheet with consistent 320 g/m^2 load of various adhesives, applied by a manual spreader roll, according to the Chinese national standards GB/T9846-2015. Especially, the S adhesive was mixed with ammonium chloride (with a purity of 30%); the SF and SFF adhesives were mixed individually with EPR resin (the proportion of EPR in SF or SFF adhesive was 9%) under stirring for 3 min, in accordance with the method described by Zhang [24], before being brushed onto the surfaces of the veneers.

Once the adhesive was applied to the contact side of each veneer sheet, the sheets were layered one on top of the other in a standard

Table 1
Performance characteristics of starch-based and PF adhesives.

Adhesive type	Dry shear strength (MPa)	63 °C for 1 h	at 100 °C for 3 h
		Wet shear strength (MPa)	Wet shear strength (MPa)
S	0.63 ± 0.07	0	0
SF	1.53 ± 0.06	0.55 ± 0.07	0.53 ± 0.08
SF + EPR	1.57 ± 0.06	0.76 ± 0.07	0.78 ± 0.08
SFF	1.48 ± 0.05	0.83 ± 0.08	0.69 ± 0.07
SFF + EPR	1.58 ± 0.08	0.93 ± 0.08	0.86 ± 0.08
PF	1.63 ± 0.05	0.85 ± 0.07	0.82 ± 0.08

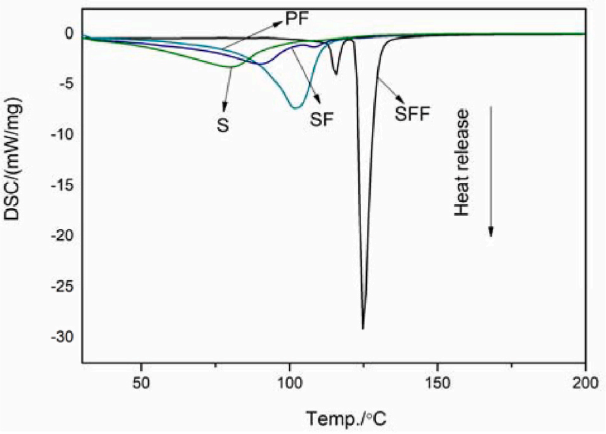


Fig. 1. DSC thermograms of S, SF, SFF and PF adhesives collected under nitrogen atmosphere in the range from 40 °C to 200 °C.

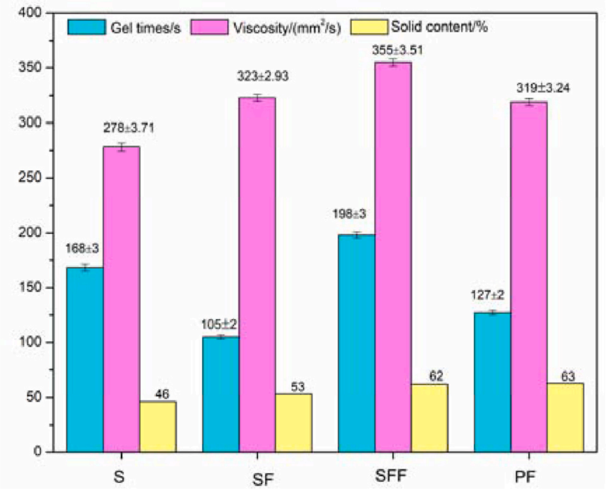


Fig. 2. Gel time, viscosity, and solid content of the prepared S, SF, SFF, and PF adhesives.

plywood configuration, where each adjacent layer had its wood grain rotated 90°. The three adhered layers were then placed in a bonding press for 5 min at a pressure of 1.5 MPa at 170 °C.

After pressing, the plywood was removed from the press and conditioned for 24 h in a climate-controlled laboratory at a constant temperature of 23 ± 0.1 °C and 60% relative humidity.

2.4. Testing of dry and wet shear strength of plywood specimens

Prior to shear strength testing, each plywood specimen was cut into dimensions measuring 100 mm × 25 mm × 4.5 mm by a wood cutting machine (Model 455 AL, LINGTAI, Suzhou, China). Sheer strength of each specimen was tested using Instron 4476 universal testing machine. To provide equal testing, each specimen was tested using a 25 mm × 25

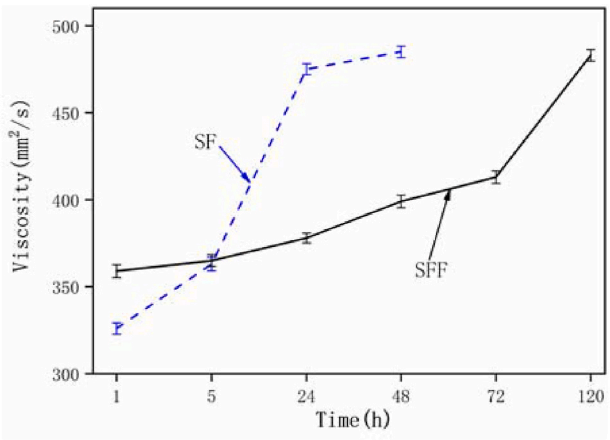


Fig. 3. Viscosity development of SF and SFF adhesives as a function of time.

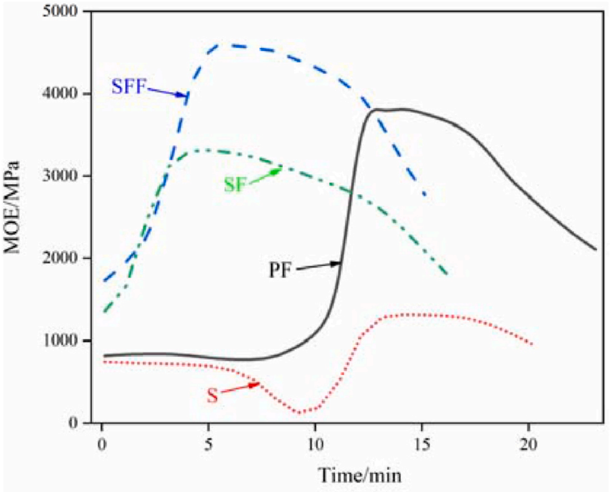


Fig. 4. TMA thermograms of S, SF, SFF and PF adhesives in the range from 0 min to 25 min.

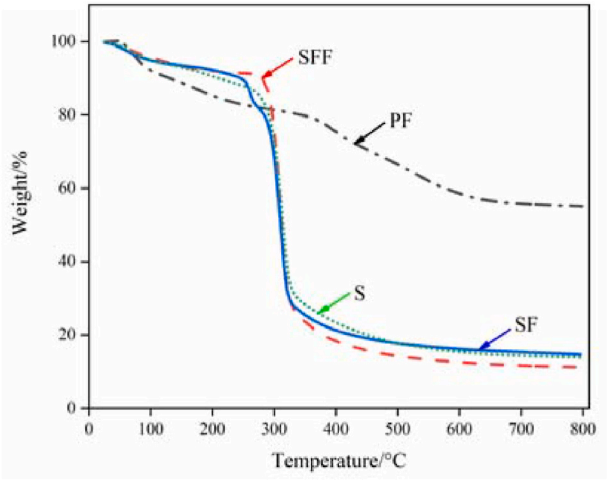


Fig. 5. TGA thermograms of S, SF, SFF and PF adhesives in the range from 0 °C to 800 °C.

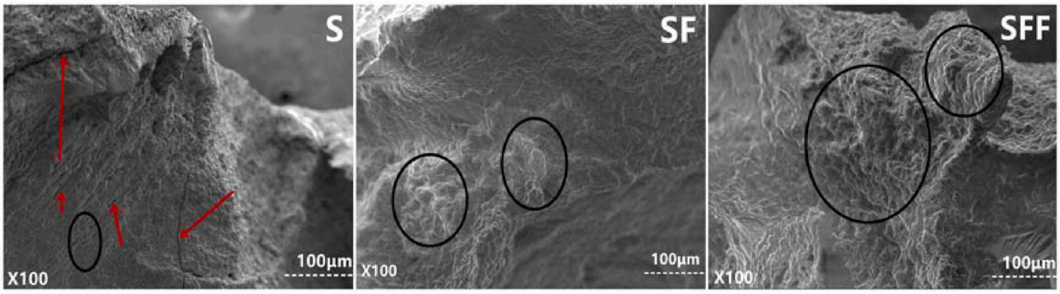


Fig. 6. SEM images for S, SF and SFF adhesives after curing.

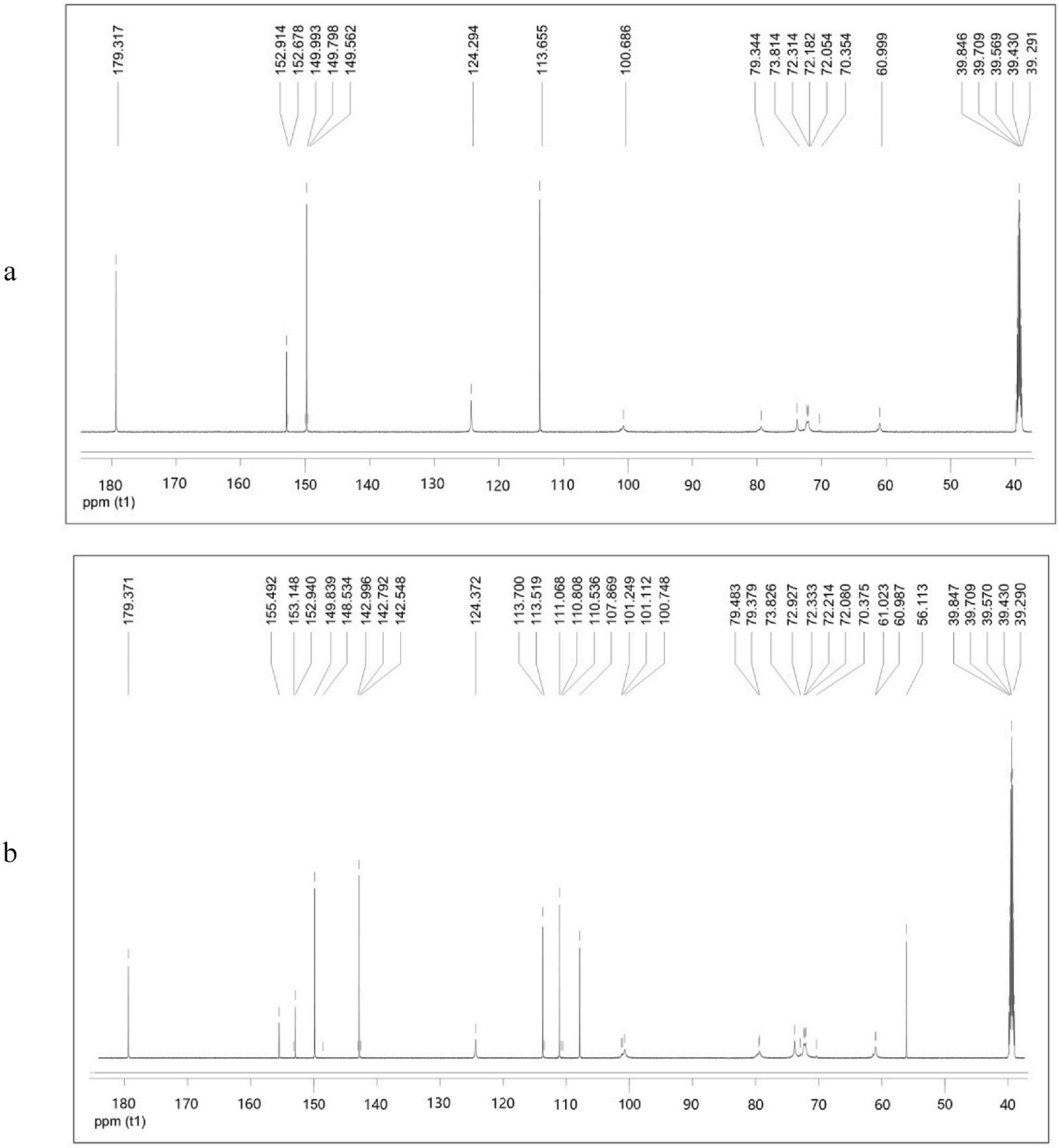


Fig. 7. ^{13}C NMR spectra of the (a) SF and (b) SFF adhesives.

mm bonded area. Two grooves (25 mm × 3 mm × 3 mm) were made in each plywood and the thickness of resin layer was 1.5 mm. These dimensions are illustrated in Scheme 1. Dry and wet shear strength values were assessed in accordance with the Chinese national standards GB/T17657-1999 and CB/T9846.7-2004. For the dry shear testing, the two grooves of each sample were fixed into the testing machine with a load of 5 N at a head rate of 2 mm/min. Wet shear testing was performed under two scenarios: first, specimens were immersed in water at a temperature of 63 ± 3 °C for 1 h prior to testing; second, specimens were immersed in boiling water (100 °C) for 3 h then cooled and the two grooves of each sample were fixed into the testing machine with a load of 5 N at a head rate of 2 mm/min. The final wet shear strength had to equal 0.9 of the remaining strength. Eight replicates were tested in case of the dry as well as the wet strength to allow for calculation of the mean

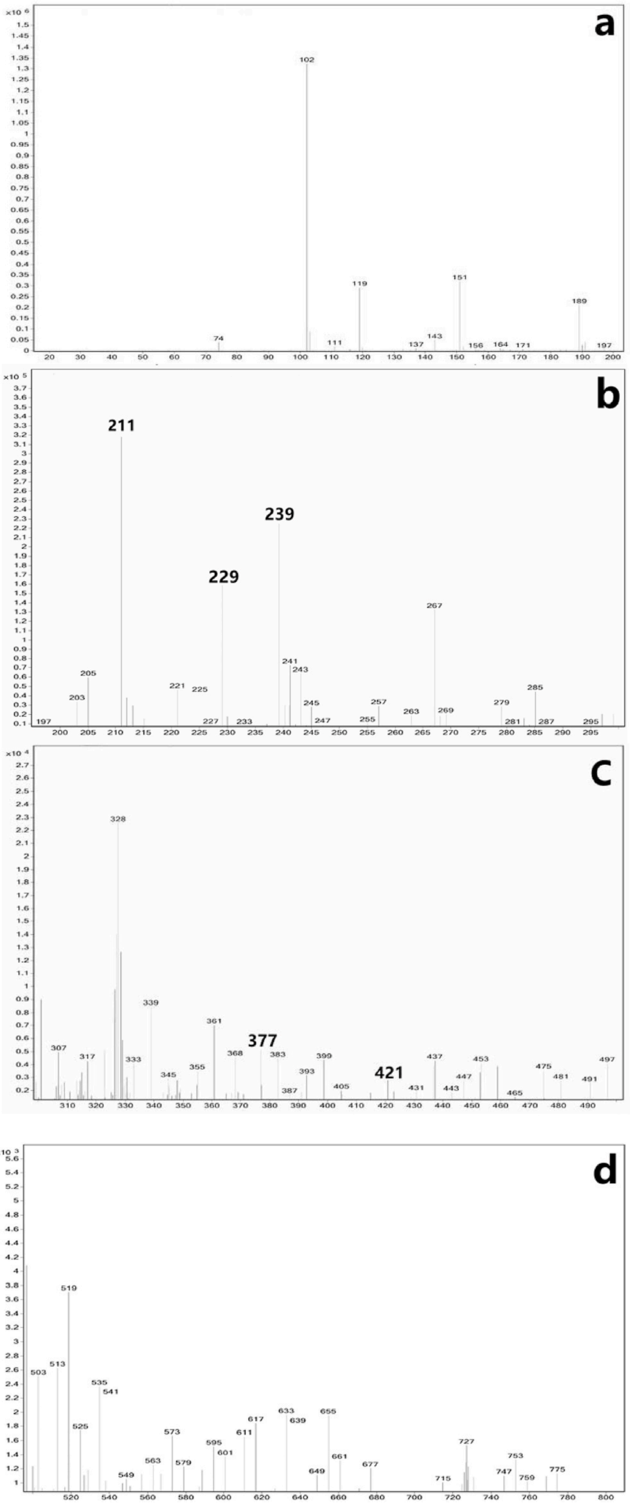


Fig. 8. ESI-MS signals of the SF adhesive at *m/z* (a) 20–200, (b) 200–300, (c) 300–500, and (d) 500–800.

values and standard deviations.

2.5. Differential scanning calorimetry (DSC), thermomechanical analysis (TMA) and thermal gravimetric analysis (TGA)

The curing behaviors of the starch-based adhesive were investigated on a dry basis at a heating rate of 10 °C/min using a DSC analyzer (Model DSC 204 F1, Netzsch, Germany). The measuring temperature range was 30 °C–200 °C with a 50 mL/min flow of N_2.

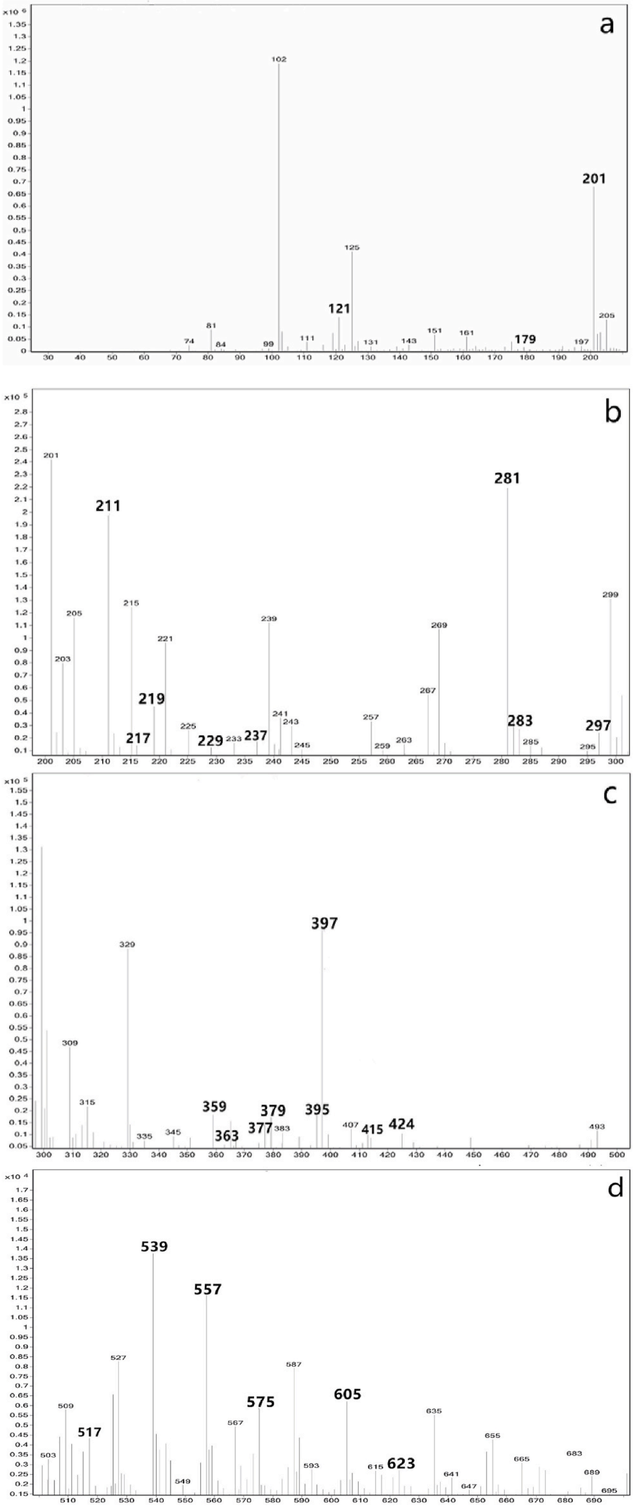
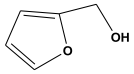
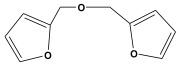
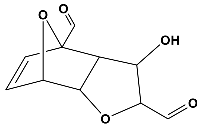
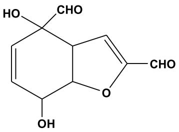
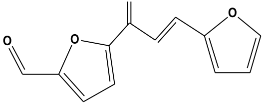
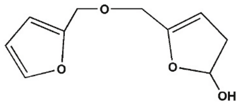
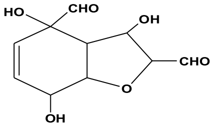
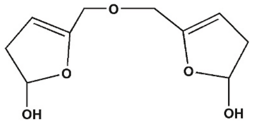
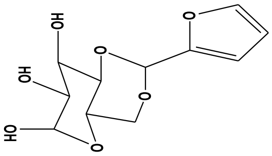
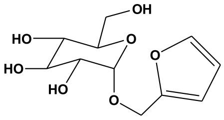
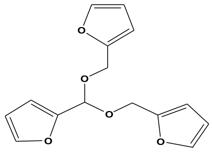
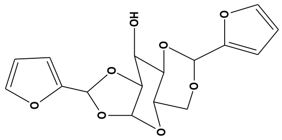
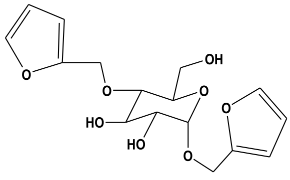


Fig. 9. ESI-MS peaks of the SFF adhesive at *m/z* (a) 30–200, (b) 200–300, (c) 300–500, and (d) 500–700.

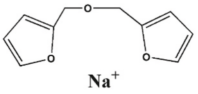
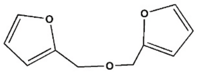
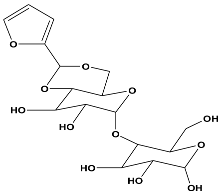
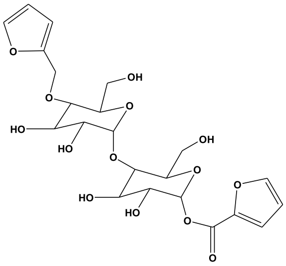
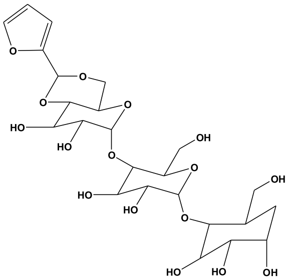
The modulus of elasticity of the different starch-based adhesives was identified using thermomechanical analysis (TMA SDTA840, Mettler-Toledo, NY-USA) processed by STARe software version 14,0 (Mettler-Toledo) for data treatment, Two beech wood veneers were 0.6 mm thick bonded with each adhesive, for a total samples dimensions of 21 × 6 × 1.2 mm. The runs were proceeding from r.t. to 250 °C at a heating rate of 20 °C/min.

Table 2
Oligomers identified by ESI-MS for the reaction of starch, furfural and furfuryl alcohol.

Experimental		Calculated		Chemical species
$[M+H]^+$	$[M+Na]^+$	$[M+H]^+$	$[M+Na]^+$	
	121		121	
179	201	179	201	
211		211		 or 
	217		217	
	219		219	
229		229		
	237		237	
	281		281	
	283		283	
	297		297	
	359		359	
	363		363	
	379		379	

(continued on next page)

Table 2 (*continued*)

Experimental		Calculated		Chemical species
$[M+H]^+$	$[M+Na]^+$	$[M+H]^+$	$[M+Na]^+$	
				
				
421		421		
517	539	517	539	
	605		605	

TGA was performed using a TG 209 F3 thermogravimetric analyzer (Netzsch) operated under a nitrogen atmosphere to identify the thermal resistance of the different starch-based adhesives. The heating rate was 20 °C/min and the run covered a temperature range of 30 °C–800 °C.

2.6. *Scanning electron microscopy (SEM)*

The surface of starch-based cured adhesive with 5 × 5 × 4 mm^3 size was observed using Hitachi scanning electron microscope (model S4800, Tokyo, Japan) at 100× magnification.

2.7. *Electrospray ionization mass spectroscopy (ESI-MS) and ^{13}C nuclear magnetic resonance (^{13}C NMR)*

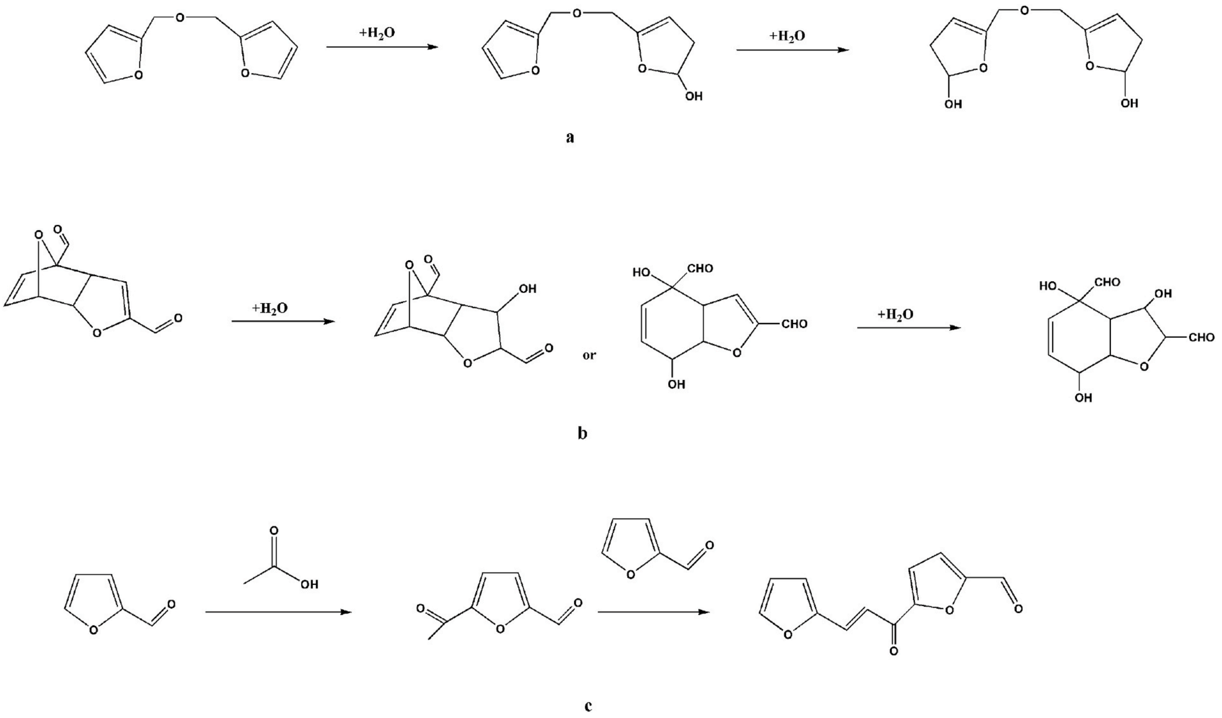
Mass spectrometry detection was undertaken using a Waters Xevo Triple Quadrupole-MS Spectrometer (Waters, Milford, MA, USA) equipped with an electrospray ionization source (ESI). The N- (2)–L–alanyl- L-glutamine, SFF adhesive, and their mixture samples were dissolved in chloroform sequentially at a concentration of approximately 10 μL/mL and injected into the ESI source plus ion trap mass spectrometer (Bruker Daltonics Inc., Billerica, MA, USA) via a syringe at a flow rate of 5 μg/s. The spectra were recorded in a positive mode, with ion energy of 0.3 eV.

A super conducting magnetic resonance apparatus (Bruker-AVANCE 600, Switzerland) was used to detect the presence of SF and SFF adhesives. The resonance frequency employed was 150 MHz. 300 μL of samples and 100 μL dimethyl sulfoxide (DMSO - d6) solvent were mixed and assessed. Test conditions included: relaxation delay time of 6s; scanning accumulative numbers of 800–1200 times; and a temperature of 25 °C.

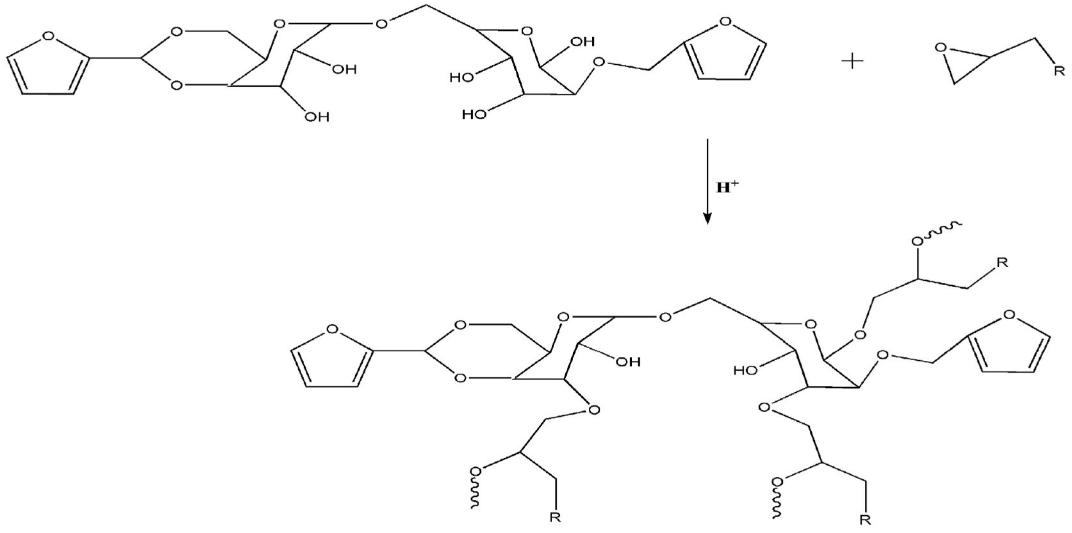
3. Results and discussion

3.1. *Characteristics of the prepared S, SF, SFF, and PF adhesive-based plywood*

The results obtained from testing the plywood panels bonded with the synthesized starch-based adhesives and the PF adhesive are shown in Table 1. The dry shear strength values for the plywood samples, except the one prepared with the S adhesive, met the requirements of the Chinese national standard (GB/T9846.3-2004, ≥0.70 MPa). Although the S adhesive was synthesized under acidic conditions, the S-bonded panel exhibited poor bonding strength and water resistance which is in accordance with the results of Kennedy [26]. Thus, furfural was used as a coupling agent to react with starch under acidic conditions to prepare SF adhesive with improved bonding strength and water resistance. As observed from Table 1, the dry shear strength of the SF-based panel was higher than that of the panel bonded with the S adhesive. Indeed, furfural bears a furan ring, which effectively improves the water resistance of the adhesive, and a highly reactive aldehyde group, which can react with the hydroxyl groups of glucose in starch and form cross-linking between starch and furfural, thus increase its bonding strength. In addition, the SFF-based plywood exhibited even higher wet shear strength than the SF-based plywood. However, its dry strength was



Scheme 2. Proposed reaction routes for the observed ESI-MS data.



Scheme 3. Reaction steps between the oligomers of SFF and EPR during the curing process.

a little lower than that of the SF-based plywood. This result could be attributed to the high rigidity of the resin. Hence, the water resistance of the SF adhesive joint was weaker than that of the SFF adhesive joints is likely due to the more integrated network structure as will be illustrated in the next sections. Further, compared with the SFF and PF adhesive-bonded panels, the SFF + EPR-bonded adhesive exhibited better water resistance when placed in boiling water (100 °C) for 1hr. Thus, the SFF + EPR adhesive appears to be competitive with the PF adhesive in the future; however, further optimization is required for a possible future industrial production.

3.2. *Characteristics of the synthesized starch-based and PF adhesives*

Based on the differential scanning calorimetry (DSC) thermograms of S, SF, SFF, and PF adhesives (Fig. 1), all the synthesized adhesives exhibited one or two exothermic peaks after freeze-drying treatment. Two exothermic peaks were observed for the SFF adhesive, one at 117 °C and another at 125 °C. Moreover, the peak of S was detected at 70°C-80 °C, while the addition of furfural shifted the peak in case of SF to 90°C-110 °C, indicating that the curing temperature of the starch adhesive increased due to higher temperature requirement of the cross-linking between starch and furfural. Furthermore, it was demonstrated that the cross-linking among starch, furfural, and furfuryl alcohol requires a higher temperature than that needed for the cross-linking between starch and furfural indicating more complication of the network structure.

The adhesives synthesized in the current study were also characterized for their gel time, viscosity, and solid content (Fig. 2). Meanwhile, the shelf-life test result of SF and SFF adhesives are shown in Fig. 3. The gel time of SFF adhesive was longer than that of the SF adhesive, which indicates that the addition of furfuryl alcohol led to complication of the cross-linking. It may be caused by the difference in the solubility between furfural and furfuryl alcohol thus leading the reaction to proceed in several steps. From Fig. 3, the addition of furfuryl alcohol in the SF resin system was also beneficial for the adhesive storage during the preparation process. With the increasing of time, the viscosity of SF and SFF adhesive increased, the SF adhesive cured within 48 h, on the contrary, the SFF adhesive cured with a longer time due to the complication of its network structure (within 120 h). In addition, the viscosity and solid content of SFF were higher than that of S and SF, which were close to that of the PF adhesive, implying that the SFF adhesive would be more ideal for the preparation of plywood compared to the S and SF adhesives.

With respect to DSC analysis of SFF, in the beginning, there is phase separation and barrier caused by the poor solubility of furfural with respect to furfuryl alcohol. This makes the reaction slow and unsupported first because of the low reactivity of furfural with starch especially in presence of furfuryl alcohol (minor reaction with small peak). With the temperature goes higher, this formed part between furfural and starch start to melt and all the reactants, including this product, participate in build up of network structure (major peak), which is much more favored. Evidence for this interpretation is the big difference in peaks size and direct inauguration of the second reaction once the first is terminated (note the connection between them).Again, the disfavor ability of the first is related to the poor solubility of furfural while in the second case, the reaction is pushed by the higher solubility of furfuryl alcohol and presence of hydroxyl groups from both starch and furfuryl alcohol, which allows furfuryl alcohol mostly by penetrating into the primary formed network (of the minor peak) and adsorption on the surface as well, for further condensation. This can be more evidenced from the correlation with gel time, which acquires higher value in case of SFF compared with SF because SFF is much more complicated network than the simpler one of SF thus takes longer time to be built. Therefore, the dry shear strength of SFF-bonded plywood is better than the others because of the stronger network structure of the resin in this case, which allows the bonded plywood to bear higher mechanical load.

The thermomechanical analysis (TMA) thermograms of S, SF, SFF, and PF adhesives were shown in Fig. 4. The cross-linking between starch, furfural and furfuryl alcohol can proceed smoothly at a higher modulus of elasticity (MOE) of 4725 MPa as compared to the reaction between starch and furfural (3315 MPa) or to the self-condensation of starch (1293 MPa) to produce an adhesive with reasonable reactivity and balanced strength. Moreover, the MOE value of SFF adhesive was higher than that of PF adhesive. It may be also expected that in case of SFF adhesive and wood, efficient chemical bonding to the network structure can develop through their surface hydroxyl groups, which leads to outstanding strength with respect to the PF adhesive. Detailed information on this point needs further extensive thermal studies.

The thermal degradation profiles of the various adhesives are displayed in Fig. 5. The degradation behavior was almost the same in all cases of starch-based adhesives and for better understanding it can be divided into 2 portions: from r.t. to 300 °C and 300–800 °C. Thus, the degradation of cured SFF adhesive proceeded slowly up to 300 °C as a result of the efficient curing and higher cross-linking density especially when compared with SF and S adhesives, while the counterparts of PF adhesive proceeded faster in the same range. Beyond 300 °C and up to the end of the run at 800 °C, starch-based adhesives almost coincided and showed less resistance to thermal degradation compared to PF adhesives, inferring that the presence of starch as part of the structure is responsible for the higher sensitivity to degradation under the effect of heat. Nevertheless, it can be deduced from TMA and TGA results that SFF adhesive is a good candidate for wood adhesive applications considering balanced properties of reasonable thermal resistance and developed mechanical strength.

3.3. Interfacial properties of starch-based adhesives

Fig. 6 shows the SEM images of fractured cross-sections of cured S, SF and SFF adhesives. It reveals that the curing of S adhesive is incomplete or occurs so quickly that a cracked adhesive is formed (marked with arrow), and the crosslinking intertextures almost do not appear in the S adhesive. For the SF adhesive, a dense section with a smooth surface and few crosslinking structures (marked with circle) are formed due to a full curing of the SF adhesive. In addition, for the SF adhesive, curing is complete and accompanied by a section with crosslinking structures (seen from the circle) and the crosslinking intertextures are almost evenly distributed in the case of SFF adhesive.

3.4. ^{13}C NMR and ESI-MS analysis

To investigate the reaction of starch, furfural, and furfuryl alcohol, the SFF adhesive was examined by ^{13}C NMR spectroscopy, while the ^{13}C NMR spectrum of the SF adhesive was also recorded for comparison (Fig. 7a and b). The abscissa represents the chemical shift values (peaks position). Some peaks showed weak signals due to the very complicated structure. However, the shift of the main structure peaks to the low or high field and the detection of new peaks indicated the possible upgrading of the reaction when comparing between SF and SFF adhesive systems. In case of SF, the signals at 179.3, 152.9, 149.8, 124.3, and 113.7 ppm could be attributed to the structure of furfural, while new weak peaks appeared at 152.7 and 149.6 ppm clearly illustrate the change in the chemical environment, especially the shift of the peaks at 152.9 and 149.8 ppm, respectively. Moreover, new peaks were identified in the spectrum of the SFF adhesive (Fig. 7b) at 155.4, 142.8, 111.1, 107.9, and 56.2 ppm, which reflects more involvement of other reacting species (like furfuryl alcohol) and their effective inclusion into the integrated network structure. This is additionally corroborated by several small new peaks that are detected in the spectrum of SFF adhesive such as the peaks at 153.1, 143.0, 142.5, 113.5, 110.8, and 110.5 ppm, which illustrate shifts of the peaks of the main structure of furfural. Furthermore, the new weak peak at 148.5 ppm was due to a shift in the main structure of furfuryl alcohol, while the signals at 143.0 and 142.5 ppm were caused by shifts of the signal at 142.8 ppm (Fig. 7b). Therefore, all these shifts reveal that both furfural and furfuryl alcohol participated effectively in the build up of the network structure.

The results of the ESI-MS analysis of the different oligomers that were formed during the preparation of the SF and SFF adhesives, generated by the co-polymerization reaction of starch, furfural, and furfuryl alcohol are presented in Figs. 8 and 9. In the mass spectrogram, the abscissa represents the mass to charge ratio (m/z) value of the ion, and the ion value increases from left to right. For the ion with single charge, the abscissa represents the mass of the ion and the ordinate represents the intensity of the ion flow. The main chemical structures of the SF and SFF adhesives are shown in Table 2. All the peak values were based on the molecular weight of the species +23 Da due to the Na $^+$ ion of the NaCl matrix enhancer used or +1 Da due to the H$^+$ protonation, while the obtained results suggested the formation of several possible products or intermediates. More specifically, the formation of 2,2′-oxybis (methylene) difuran was proposed by the positive ions at m/z 179 ([M+H]$^+$) and 201 ([M+Na]$^+$) (Fig. 9a), which could be produced by the dehydration of two furfuryl alcohol monomers, as can be seen in Fig. 8. Furthermore, under the present reaction conditions, the detection of two positive ions at m/z 219 ([M+Na]$^+$) and 237 ([M+Na]$^+$) (Fig. 9b) suggested the formation of the dimer or the cross dimer of 2,2′-oxybis (methylene) difuran and its hydration products (Scheme 2a). Indeed, these results were also consistent with literature data [27,28], which indicated that the self-condensation of furfuryl alcohol occurred under acidic conditions. It was also assumed that the relative stability of the ether bearing three or four oxygen atoms as crown ether generates the peaks at m/z 379 ([M+Na]$^+$), 397 ([M+Na]$^+$), and 415 ([M+Na]$^+$) (Fig. 9c) under the acidic conditions. Moreover, the peaks at m/z 211

([M+H]$^+$) and 229 ([M+H]$^+$) (Figs. 8b and 9b) were attributed to the Diels-Alder reaction [29,30] of two furan-2-carbaldehydes and the corresponding hydration products, which also proved the self-condensation of furfural under acidic conditions (Scheme 2b). Based on the ESI-MS analysis, it was also suggested that acetal products can be easily formed under these conditions. For example, the positive ion at 297 ([M+Na]$^+$) (Fig. 8b) suggested the generation of an acetal product by the reaction between furan-2-carbaldehyde and furan-2-ylmethanol, implying the effective reaction between furfural and furfuryl alcohol under acidic conditions. In addition, the formation of 5-acetylfuran-2-carbaldehyde by the acetylation of a furfural monomer was revealed by the positive ion at m/z 217 ([M+H]$^+$, while the subsequent aldol/dehydration reaction with furan-2-carbaldehyde afforded 5-(3-(furan-2-yl)acryloyl) furan-2-carbaldehyde (Scheme 2c) that was assigned to the positive ions at m/z 217 ([M+H]$^+$) and 239 ([M+Na]$^+$) (Figs. 8b and 9b). Furthermore, the formation of a glucose from the hydrolysis of starch protected by a furfural monomer was assumed by the positive ion at m/z 281 ([M+Na]$^+$) (Figs. 8b and 9b), while the positive ion at m/z 283 [M+Na]$^+$ suggested the generation of a glucose glycoside with a furfuryl alcohol monomer by the Cannizzaro reaction of furan-2-carbaldehyde (Fig. 9b). Moreover, the reaction of glucose with two equivalents of furan-2-carbaldehyde was proven by the peak at m/z 359 ([M+Na]$^+$), which can further react with water to give the positive ions at m/z 377 ([M+Na]$^+$) and 395 ([M+Na]$^+$) (Figs. 8c and 9c). In addition, the etherification reaction of glucose with two equivalents of furan-2-ylmethanol afforded a positive ion at m/z 363 ([M+Na]$^+$). Likewise, the reaction of sucrose with furan-2-carbaldehyde generated a positive ion at m/z 421 ([M+H]) (Fig. 8c), which does not present in Fig. 9. The etherification and esterification reactions among sucrose, furfural, and furfuryl alcohol was suggested by the positive ions at m/z 517 ([M+H]$^+$) and 539 ([M+Na]$^+$), while the obtained products could further react with water to generate the positive ions at m/z 557 ([M+Na]$^+$) and 575 ([M+Na]$^+$) (Fig. 9d). The formation of a trisaccharide protected by furan-2-carbaldehyde was also assumed by the positive ion at m/z 605 ([M+Na]$^+$). Its subsequent reaction with water could afford a positive ion at m/z 623 ([M+Na]$^+$) (Fig. 9d). All the ^{13}C NMR and ESI-MS results confirm that successful reactions between starch, furfural, and furfuryl alcohol took place.

In terms of plywood performance, the water resistance of panel prepared with the adhesive SFF+9% EPR was better than that of SFF and PF adhesive-bonded panels. Thus, the possible establishment of a cross-linking among starch, furfural, and furfuryl alcohol contributed to the formation of oligomers (Table 2; 517 and 539). These oligomers could easily crosslink with EPR under acidic conditions during the curing process (Scheme 3). In particular, the EPR could react with the hydroxyl groups of starch, while the formed three-dimensional network structure of the SFF + EPR adhesive was responsible for improving the water resistance.

4. Conclusions

Starch-furfural-furfuryl alcohol (SFF) can condense together under acidic conditions to yield good wood adhesive in a multi-step reaction. The ESI-MS and ^{13}C -NMR analysis results revealed that furfural and furfuryl alcohol could react with starch to generate ether groups [–CH$_2$–O–]. The gel time of the SFF adhesive with respect to SF adhesive signifies a more complicated network structure with sufficient flexibility, which could also contribute to a better wet shear strength of the SFF based plywood in comparison to that of SF based plywood. A tiny portion around 9% EPR can be added as co-condenser to the starch-based adhesive in order to further enhance the water resistance of the SFF-based plywood as compared to that of the PF-based plywood, highlighting the potential of the enhanced SFF adhesive for industrial applications as wood adhesive.

Declaration of competing interest

The authors declare no conflict of interest.

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References

[1] Pizzi A, Vosloo R, Cameron FA, Orovan E. Self-neutralizing acid-set PF wood adhesives. Holz Roh-Werkst 1986;44:229–34.

[2] Raknes E. Durability of structural wood adhesives after 30 years ageing. Holz Roh-Werkst 199; 55: 83-90.

[3] Huang X, Chen SB, Wan SH, Niu B, He XR, Zhang R. Effect of phenolic resin oligomer motion ability on energy dissipation of poly (butyl methacrylate)/phenolic resins composites. Polymers 2020;12:490.

[4] Zhang YH, Ding LL, Gu JY, Tan HY, Zhu LB. Preparation and properties of a starch-based wood adhesive with high bonding strength and water resistance. Carbohydr Polym 2015;115:32–7.

[5] Chen L, Wang YJ, Din Z, Fei P, Jin WS, Xiong HG, Wang ZJ. Enhancing the performance of starch-based wood adhesive by silane coupling agent (KH570). Int J Biol Macromol 2017;5:182.

[6] Din Z, Xiong HG, Wang ZJ, Chen L, Ikram U, Fei P, Naveed A. Effects of different emulsifiers on the bonding performance, freeze-thaw stability and retrogradation behavior of the resulting high amylose starch-based wood adhesive. Colloid Surface Physicochem Eng Aspect 2017;11. 002.

[7] Zheng XY, Cheng L, Gu ZB, Yan H, Li ZF, Li CM. Effects of heat pretreatment of starch on graft copolymerization reaction and performance of resulting starch-based wood adhesive. Int J Biol Macromol 2017;96:11–8.

[8] Zhang JY, Zhang Y, Li JZ, Gao Q. Development of a high-performance adhesive with a microphase, separation crosslinking structure using wheat flour and a hydroxymethyl melamine prepolymer. Polymers 2019;11:893.

[9] Tongdeesoontorn W, Mauer LJ, Wongruong S, Sriburi P, Rachtanapun P. Physical and antioxidant properties of cassava starch–carboxymethyl cellulose incorporated with quercetin and TBHQ as active food packaging. Polymers 2020;12:366.

[10] Bruyn HD, Sprong E, Gaborieau M, Rober JA, Gilbert RG. Starch-graft-(synthetic copolymer) latexes initiated with Ce4$^+$and stabilized by stabilized by amylopectin. *J Polym Sci*: Polym Chem 2007;45(18):4185–92.

[11] Gong Q, Wang LQ, Tu K. In situ polymerization of starch with lacticacid in aqueous solution and the microstructure characterization. Carbohydr Polym 2006;64(4):501–9.

[12] Tanrattanakul V, Chumeka W. Effect of potassium persulfate on graft copolymerization and mechanical properties of cassava starch/natural rubberfoams. J Appl Polym Sci 2010;116(1):93–105.

[13] Sun SL, Cao XF, Li HL, Zhu YB, Li YJ, Jiang W, Wang Y, Sun SN. Simultaneous and efficient production of furfural and subsequent glucose in MTHF/H$_2$O biphasic system via parameter regulation. Polymers 2020;12:557.

[14] Sweygers N, Harrer J, Dewil R, Appels LA. microwave-assisted process for the in-situ production of 5-hydroxymethyl furfural and furfural from lignocellulosic polysaccharides in a biphasic reaction system. J Clean Prod 2018;187:1014–24.

[15] Wu C, Chen W, Zhong L, Peng X, Sun R, Fang J, Zheng S. Conversion of xylose into furfural using lignosulfonic acid as catalyst in ionic liquid. J Agric Food Chem 2014;62:7430–5.

[16] Yaghmur A, Aserin A, Garti N. Furfural−cysteine model reaction in food grade nonionic oil/water microemulsions for selective flavor formation. J Agric Food Chem 2002;50:2878–83.

[17] Chun JA, Lee JW, Yi YB, Hong SS, Chung CH. Direct conversion of starch to hydroxymethylfurfural in the presence of an ionic liquid with metal chloride. Starch/Starke 2010;62:326–30.

[18] Li X, Nicollin A, Pizzi A, et al. Natural tannin-furanic thermosetting moulding plastics. RSC Adv 2013;3:17732–40.

[19] Zhou XJ, Li B, Xu Y, Essawy H, Wu ZG, Du GB. Tannin-furanic resin foam reinforced with cellulose nanofibers (CNF). Ind Crop Prod 2019;34:107–12.

[20] Celzard A, Zhao W, Pizzi A, et al. Mechanical properties of tannin-based rigid foams undergoing compression. Mater Sci Eng 2010;16–17:4438–46.

[21] Lacoste C, Pizzi A, Laborie MP, Celzard A. Pinuspinaster tannin/furanic foams: Part II. Physical properties. Ind Crop Prod 2014;61:531–6.

[22] Lacoste C, Basso MC, Pizzi A, Laborie MP, Garcia D, Celzard A. Bioresourced pinetannin/furanic foams with glyoxal and glutaraldehyde. Ind Crop Prod 2013;45:401–5.

[23] Abdullah UHB, Pizzi A. Tannin-furfuryl alcohol wood panel adhesives without formaldehyde. Eur J Wood Wood Prod 2013;71(1):131–2.

[24] Zhang J, Xi XD, Liang JK, Pizzi A, Du GB, Deng SD. Tannin-based adhesive cross-linked by furfuryl alcohol –glyoxal and epoxy resins. Int J Adhesion Adhes 2019; 94:47–52.

[25] Zhang J, Wang WL, Zhou XJ, Liang JK, Du GB, Wu ZG. Lignin-based adhesive crosslinked by furfuryl alcohol–glyoxal and epoxy resins. Nord Pulp Pap Res J 2019;34:228–38.

[26] Kennedy HM. Starch and dextrin-based adhesives. Adhesives from renewable resources. Am Chem Soc 1989;385:326–36.

[27] Pasch H, Pizzi A, Rode K. MALDI-TOF mass spectrometry of polyflavonoid tannins. Polymer 2001;42(18):7531–9.

[28] Guigo N, Mija A, Vincent L, Sbirrazzuoli N. Chemorheological analysis and model-free kinetics of acid catalysed furfuryl alcohol polymerization. Phys Chem Chem Phys Pccp 2007;9(39):5359–66.

[29] Borisova KK, Nikitina EV, Novikov RA, Khrustalev VN, Dorovatovskii PV, et al. Diels–Alder reactions between hexafluoro-2-butyne and bis-furyl dienes: kinetic versus thermodynamic control. Chem Commun 2018;54:2850–3.

[30] Zhang J, Xiong LH, Zhou XJ, Liang JK, Du GB, Xi XD. Development of mimosa tannin-based adhesive cross-linked by furfuryl alcohol, formaldehyde and epoxy resins. Wood Res 2019;64(5):847–58.