ENVIRONMENTALLY FRIENDLY SOY-BASED BIO-ADHESIVE: PREPARATION, CHARACTERIZATION, AND ITS APPLICATION TO PLYWOOD

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Defatted soy-based flour (DSF) modified with a combination of acid, salt, dicyandiamide, and alkali for preparing soy-based bio-adhesives (SBA) was investigated in this study. The resulting modified products from different reaction stages were characterized by FTIR, XPS, and TG. The results from FTIR and XPS indicated that the hydrolysis of the amide link and decarboxylation had occurred after the reaction by acid and salt; these reactions resulted in an increase of active groups, such as primary amine, carboxyl, and hydroxyl groups. The active groups were further increased by treatment with dicyandiamide and alkali. Curing the SBA resulted in the condensation and cross-linkage between active functional groups. Moreover, TG analysis proved that the active functional groups were increased during the modification process of the DSF, which was consistent with the results presented in FTIR and XPS. Finally, SBA was applied to plywood made from four wood species (basswood, *Pinus massoniana, Triplochiton scleroxylon*, and poplar) to test its water resistance performance. The average bonding strength between wood species was close to 0.91 MPa, which demonstrated that the SBA can be regarded as an alternative to petro-based adhesives.

Key words: Soy-based bio-adhesive; FTIR; XPS; TG; Plywood

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INTRODUCTION

In the 1930s defatted soy flour (DSF) was primarily used as an adhesive and was used by U.S. plywood manufacturers; however, it had poor water and decay resistance (Huang and Sun 2000; Johnson *et al.* 1984). To compensate for these deficiencies, the soy-based adhesive was substituted with petro-based adhesives (*e.g.* aldehyde adhesive). However, most petro-based adhesives contain many harmful substances (*e.g.* formaldehyde, phenol, *etc*.), which are not good for workers' and consumers' health if they are exposed to it for long periods of time. With increasing demands for minimal environmental impact and increased quality of life, the development of renewable and eco-friendly high-performance adhesives for furniture production will help to solve this problem.

Soybean is a renewable resource with features such as its abundance, ease of processing, and low cost. Its derivatives, including soy protein isolate (SPI), defatted soy flour (DSF), and soy flour (SF) are ideal materials for adhesive production with minimum health impact. However, despite the fact that SPI contains 90% crude protein (Hojilla-Evangelista 2010) and is easy to modify as the wood adhesives with higher adhesion and water-resistance (Huang and Sun 2000; Khosravi *et al.* 2010; Wang *et al.* 2005, 2007), its industrialization has been significantly limited due to its high cost. For this reason, recent research related to soy-based adhesives has been mainly directed toward the modification of DSF and SF.

In recent years, improved results had been obtained with DSF and synthetic resin blends, and with DSF modification. After blending DSF with phenolic resin (PF), Gao *et al.* (2010) applied this mixture to plywood type I. It was found that the bonding strength of plywood could be significantly improved. Moreover, due to similar properties to PF, polyethylenimine (Gu and Li 2011; Huang and Li 2008), isocyanate (Tong *et al.* 2008), and melamine-urea-formaldehyde resin (Fan *et al.* 2011) were also used to partially replace DSF and SF. The results indicated that they could improve the water-resistance of DSF-based adhesive, but it was less than PF alone. Other approaches were also used to improve the water-resistance of DSF-based adhesives, such as increasing the protein content (Kim and Netravali 2010), protein modification (Mo *et al.* 2011), adding nano-composite (Zhang *et al.*, 2007), and cross-linking with glutaraldehyde (Li *et al.* 2010). These approaches can be used for plywood (Fan *et al.* 2011; Huang and Li 2008; Huang and Sun, 2000; Tong *et al.* 2008), particleboard (Gu and Li 2011; Schwarzkopf *et al.* 2009), and medium density fiberboard (Gao *et al.* 2009; Li *et al.* 2009). Unfortunately, these methods are complex for preparation of soy-based adhesives.

To characterize the variation of material properties, there are many useful methods such as Fourier transform infra-red spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TG), water-resistance, and adhesion performance. Therefore, this work will use a novel method to modify the DSF to produce a soy-based bio-adhesive using acid, salt, dicyandiamide, and alkali as a combined modification. FTIR, XPS, and TG were employed to characterize the structure change of DSF during the process of modification. Finally, the modified soy-based bio-adhesive was applied to wood veneers to make plywood in order to check its water-resistance and adhesion performance.

EXPERIMENTAL

Materials

DSF was purchased from Shandong Longfeng Soybean Co. Ltd (China), and it contained 53.00% crude protein (dry basis), 8.56% water, 0.97% crude fat, and 6.20% ash. The DSF was sifted through a 100-mesh screen to obtain a uniform particle size. *Pinus massoniana* veneer was generously donated by Jianyang Luban Wood Industry Co. Ltd (China). Poplar, basswood, and *Triplochiton scleroxylon* veneers were purchased from Vicwood Industry (Suzhou) Co. Ltd (China). The moisture content of these veneers ranged from 10 to 12%. Veneers were approximately 300 mm × 300 mm × 1.2 mm in size. Except for potassium bromide, all chemicals used in this study were of analytical grade; potassium bromide was spectrally pure and used as received. All chemicals were purchased from Sinopharm Chemical Reagent Beijing Co. Ltd., (China).

Methods

SBA modification

A combination of acid, salt, dicyandiamide, and alkali was used to modify the soy-based bio-adhesive. Distilled water (800 g) was added to 200 g of DSF in a three-neck flask. This was stirred at a speed of 100 rpm at 35°C for 60 min (labeled as DSFA). Then, 25 g hydrochloric acid (37%) solution containing 0.01% (w/w) ferric chloride was added to the flask and stirred at 120 rpm for 30 min (labeled as DSF II). Afterwards, 8 g of dicyandiamide was added into the flask and stirred for another 60 min (labeled as DSF III). Finally, 80 g of sodium hydroxide solution (28% wt.) was added to the above mixture and stirred for 10 min. The resulting product can be regarded as modified soy-based bio-adhesive and labeled as SBA.

SBA characterization

The DSF, DSF II, DSF III, and SBA were freeze-dried at -47°C and 4.75 Pa for 24 hours. The SBAC was SBA dried in an air oven at 140°C for 2 hours. After drying, all of the above samples were ground into powder.

The powder of DSF, DSF II, DSF III, SBA, and SBAC were mixed with potassium bromide, pressed at 20 MPa for 3 min, then scanned in a Nicolet 380 FTIR (U.S.) over the 500 to 4000 cm^{-1} wave number range.

The surfaces of DSF, DSF II, DSF III, SBA, and SBAC were tested with an X–ray photoelectron spectrometer (Thermo Fisher Scientific, ESCALAB250, UK). The percentages of the elements presented in the surface of the samples were derived from a high-resolution spectra run with a pass energy of 20 eV at increments of 0.1 eV. The data were analyzed with software of Thermo Advantage and Origin 7.0.

Thermal stability of DSF, DSFII, DSFIII, and SBA were tested by heating them from 25 to 300°C at a rate of 20°C/min under a nitrogen atmosphere with a Netzsch TG209 (German) thermogravimetric analyzer.

SBA application

The veneers of four wood species mentioned above are often used in the Chinese wood industry. DSFII and DSFIII were not used to make plywood due to their low pH value (pH < 2.0). Therefore, SBA and DSFA were used in the preparation of three-layer plywood by coating 140 g/m^2 of the SBA on each veneer layer. The assembling time, pressing temperature, pressure, and time were set as 10 min, 140°C, 1.0MPa, and 5.4 min, respectively. The preparation of plywood for each wood species was repeated three times.

The size and performance of specimen were determined according to the China National Standards GB/T 9846-2004, with minor modification. A piece of plywood can be cut into ten specimens. The size of the specimen was 100 mm × 25 mm × 3 mm. To test the water resistance performance of SBA and DSFA, the obtained specimens for each wood species were soaked into a water bath at 63°C for 3 hours and then cooled at room temperature (20°C) for 10 min. The bonding strength of these specimens was determined on a tensile testing machine (MTS, USA) at a crosshead speed of 10 mm/min. The final bonding strength presented in the paper was the average value of 30 replicates.

RESULTS AND DISCUSSION

FTIR Characterization of SBA

The products from different stages of the DSF modification process were sampled, including the defatted soy flour (DSF), acid and salt (DSF II), and dicyandiamide (DSF III) modified, soy-based bio-adhesive (SBA), and cured soy-based bio-adhesive (SBAC). The FTIR spectra of all these samples are shown in Fig. 1. It was found that the absorption peaks of protein amide-bands I (C=O stretching vibration in amide groups) at 1650 cm^{-1}, amide-bands II (N-H in-plane bending vibration in amide groups) at 1570cm^{-1}, and amide-bands III (C-N stretching vibration and N-H deformation vibration in amide groups) at 1242 cm^{-1} appeared in the DSF and all other samples, which indicated that the backbone structure of the DSF had not changed during the modification. The absorption peaks at 3303 cm^{-1} were stretching vibrations of O-H and N-H. The stretching vibration of C-N and the out-of-plane bending vibration of N-H could be found at 1000 and 720 cm^{-1}, respectively. The bonds of O–H and N–H in the functional groups of -OH, -NH-CO-, and -NH_2 indicate a great potential of hydrogen bonding; however, hydrogen bonding offers weak water-resistance (Nakanishi 1977; Silverstein *et al.* 2005).

Compared to DSF, an absorption peak of the C=O in -COOH groups at 1725 cm^{-1} appeared in the spectra of DSF II, indicating that the carboxyl group was formed from the DSF after acid and salt treatment. This arises from the amido-bond hydrolysis in DSF. Furthermore, electrophilic functional group (H^+) bonding with the secondary amine and protonation resulted in the disappearance of amido-bands II (N-H in-plane bending vibration in amide groups) at 1570 cm^{-1}, but the appearance of a wide-strength absorption peak at 1537 cm^{-1}.

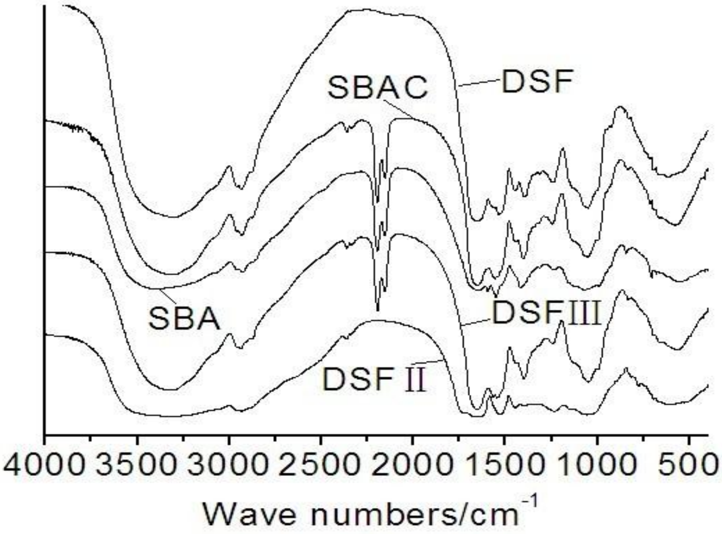

Fig. 1. FTIR spectra of DSF, DSF II, DSF III, SBA, and SBAC

As shown in Fig. 1, for the spectrum of DSF III, the absorption peak of C=O in -COOH at 1725 cm^{-1} was shifted after adding dicyandiamide. This may be explained by the reaction of carboxyl with protonated $–NH_2$ in dicyandiamide. Meanwhile, a number of functional groups and status were also changed. The spectrum of SBA showed the absorption peaks of O-H and N-H at 3400 cm^{-1}, and the dissymmetric bending vibration of $-H_3N^+$ at 1596 cm^{-1} (Wade 2003), which indicated that some amido-bonds in DSF III could be further hydrolyzed by alkali, increasing the hydrophilic groups such as $-COO^-$ and $-H_3N^+$. In the spectrum of SBAC, it was found that the stretching vibration frequency of functional groups O-H and N-H were decreased, and the dissymmetric bending vibration of functional group $-H_3N^+$ disappeared. This illustrated that the curing process caused the removal of protonation, and the occurrence of chemical reaction such as amidation, which would be helpful in improvement of bonding strength and water-resistance of SBA based materials.

XPS Characterization of SBA

Element O analysis

The survey spectra of all samples at different modification stages are shown in Fig. 2, indicating that all the samples mainly contain three kinds of elements: carbon, nitrogen, and oxygen; relative content is listed in Table 1. Figure 3 (i) shows the scanning result for the element O in the five samples. To illustrate the forms of element O, the deconvoluted spectra curves are shown in Figs. 3 (ii) to 3 (vi). After peaks area computation and factors analysis, it was shown that element O existed in samples as: O1(C=O), O2(NaOH), O3(C-OH), and O4($-COO^-$) (Crist 1999; Pretsch *et al.* 2000; Wagner *et al.* 1992).

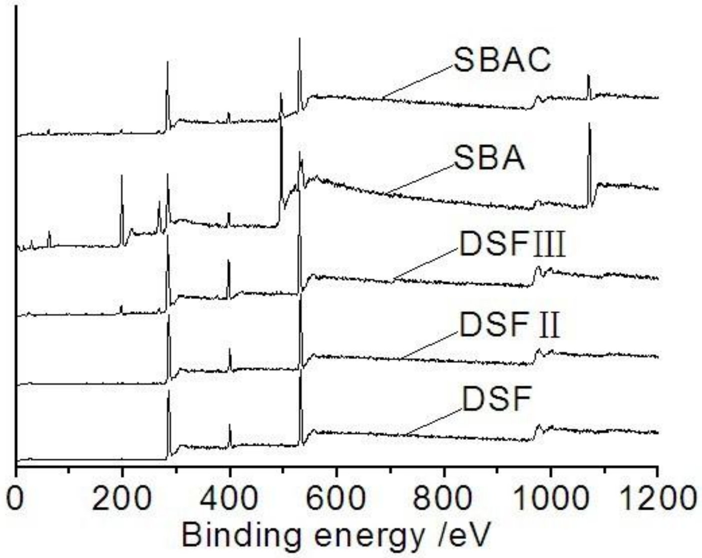

Fig. 2. XPS survey spectra of DSF, DSFII, DSF III, SBA, and SBAC

Compared to DSF, it was found that the relative content of elements C, N, and O in DSF II varied from 2.50:1:3.59 to 2.35:1:3.33 (Table 1); the O1 decreased from 53.76 to 33.33%, while the O3 and the O4 increased from 29.57 to 43.29% and 16.67 to 23.38%, respectively. These results were in agreement with the FTIR results, and they indicated that the peptide chains had been hydrolyzed during the acid and salt treatment. Ferric chloride can be regarded as Lewis acid (or catalyst) and facilitated the hydrolysis reaction (Han 2003).

Table 1. Ratios of Element C, N, and O and Relative Percentages of Element O's Functional Groups in the Samples

Samples	C:N:O	C=O (%)	NaOH (%)	C-OH (%)	-COO¯ (%)
DSF	2.50:1:3.59	53.76	0	29.57	16.67
DSF II	2.35:1:3.33	33.33	0	43.29	23.38
DSF III	1.61:1:2.61 /1:0.62:1.62	28.71	0	47.85	23.44
SBA	1:0.28:1.26	22.82	4.37	48.54	24.27
SBAC	1:0.12:1.12	54.64	0	28.42	16.94

It was also found that the relative percentage of C, N, and O in DSF III continued to change (Table 1). This was caused by reactions and also by dicyandiamide itself, which contains N. The decrease of O1 and increase of O3 indicated that amido-bands were also hydrolyzed during the reaction with dicyandiamide. In SBA, the relative ratio of N and O1 decreased, but O3 and O4 increased, indicating that amido-bands could be further hydrolyzed during alkali treatment. Furthermore, Fig. 3 (vi) shows the reduction of O3 and O4 while O1 increases, which indicates that the curing process could involve the cross-linking between functional groups of $–NH_2$ and -COOH or –OH. This cross-linking could improve the water-resistance performance of SBAC.

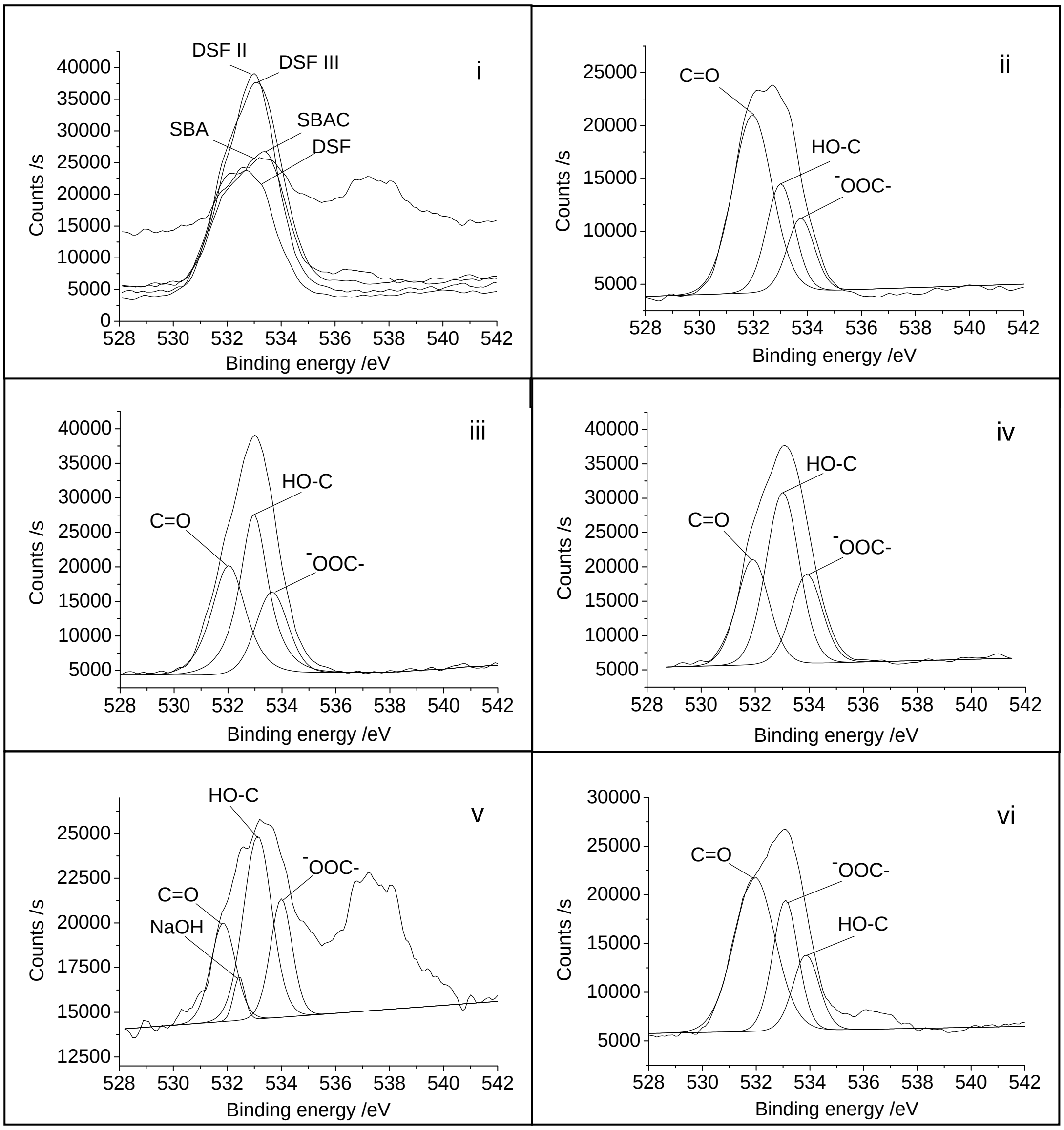

Fig. 3. XPS spectra of various materials: (i) Element O's XPS spectra of DSF, DSFII SBA and SBAC; (ii) XPS spectra of DSF, (iii) XPS spectra of DSF II, (iv) XPS spectra of DSFIII, (v) XPS spectra of SBA and (vi) XPS spectra of SBAC deconvoluted into multiple sub-peaks of element O into contained in different functional groups using Gaussian-Lorentzian fit

Element N analysis

The XPS spectrum of element N is given in Fig. 4 (i). The form of N in the spectrum curve for each samples is further deconvoluted, namely N1(-CN), N2 (-CH-NH-CH$_2$-), N3 (C-NH$_2$/-NH-CO-/-CH=NH), N4 (-H$_3$N$^+$), and N5 (-NH$_3$OH) (Crist 1999; Pretsch *et al.* 2000; Wagner *et al.* 1992). The relative percentages for each of these forms of N are shown in Table 2.

The highest percentage of N3 and N5 were found in the DSF, which could be attributed to the proteins. After the acid and salt treatment of the DSF, it was observed that the relative contents of N3 and N5 in DSF II decreased to 87.72% and 0.00%, respectively, indicating significant hydrolysis of amido-bands in the DSF. For DSF III, N1 was firstly presented and N3 was increased to 91.74%. It is probably caused by dicyandiamide, since it contains the functional groups of -CH=NH and -NH$_2$, which is also consistent with the ratio change of C:N:O shown in Table 1. The reductions of N1 and N3 indicated that the –CN functional group in DSF III started to hydrolyze during the reaction with alkali.

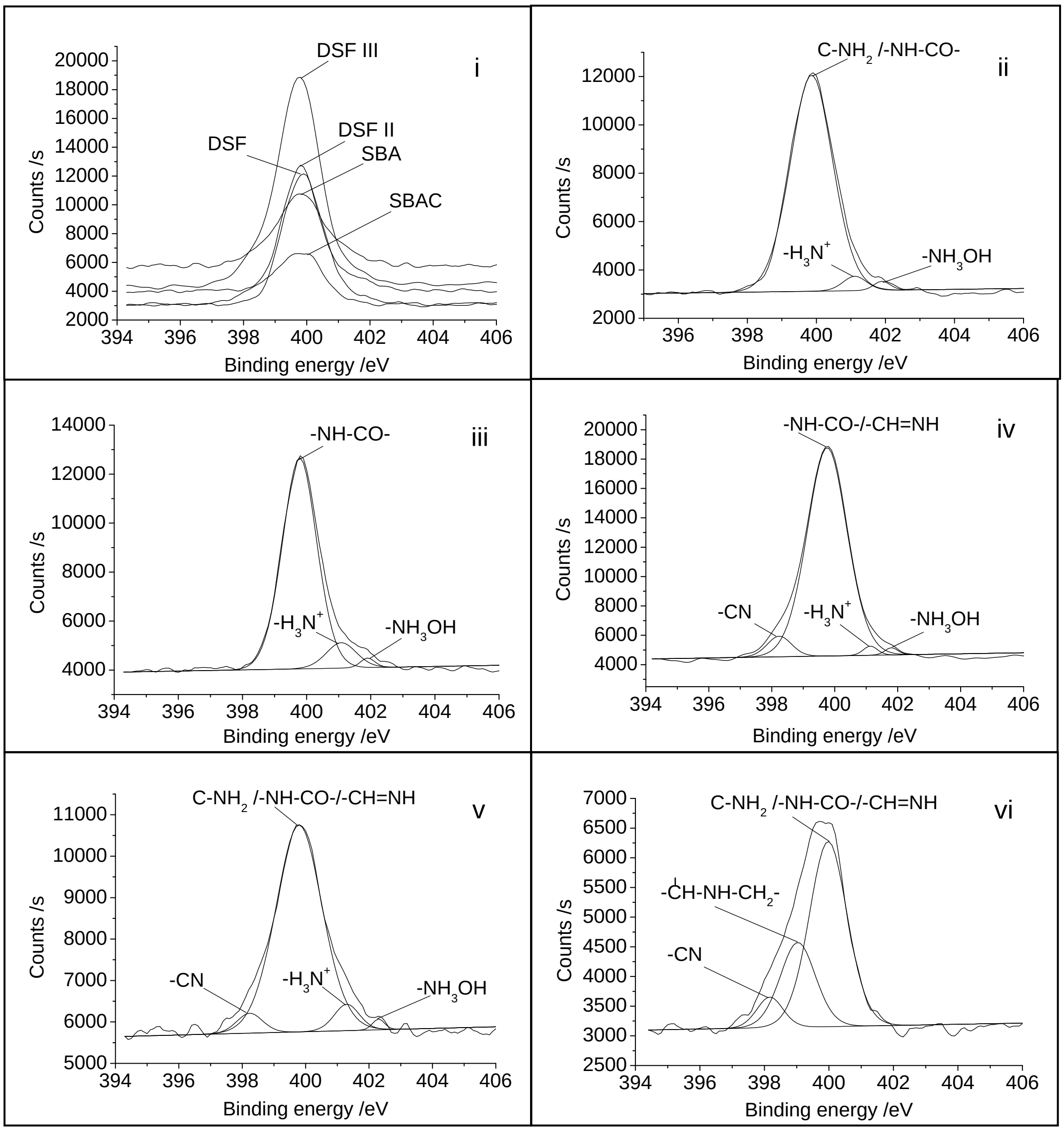

Fig. 4. XPS spectra of various materials: (i) Element N's XPS spectra of DSF, DSFIISBA and SBAC; (ii) XPS spectra of DSF, (iii) XPS spectra of DSF II, (iv) XPS spectra of DSFIII, (v) XPS spectra of SBA and (vi) XPS spectra of SBAC deconvoluted into multiple sub-peaks of element N into contained in different functional groups using Gaussian-Lorentzian fit

For SBAC, the relative percentage of N1 decreased to 2.70%, which could be caused by the reaction of –CN with other functional groups. Moreover, when comparing SBAC to SBA, the N3 in SBAC decreased to 89.29% and the N2 sharply increased to 29.73%, indicating that ammonization reaction occurred between $–NH_2$ and –OH during curing. The disappearance of N4 in SBAC was mainly caused by the volatilization of the acid after drying and the condensation reaction between N4 and O4. The formation of amido-bands and the reduction of hydrophilic groups are favorable to improving the water-resistance of SBAC. Hence good water-resistance performance would be achieved when SBA was used as adhesive for making plywood.

A schematic diagram of chemical reactions such as hydrolyzation and ammonization occurring during the SBA's preparation and curing process are shown in Fig. 5.

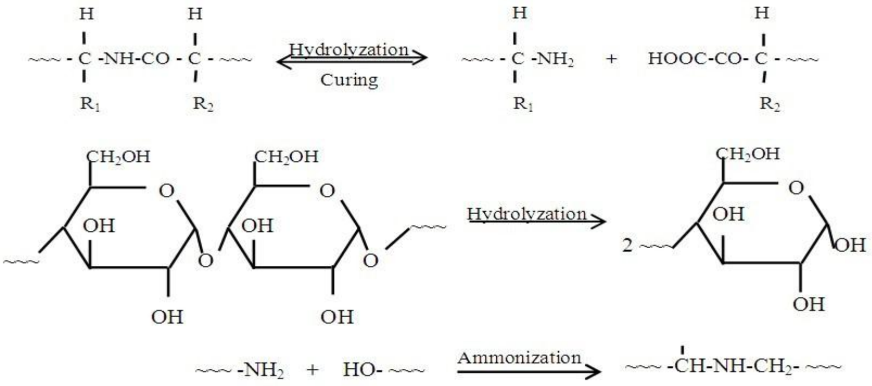

Fig. 5. Chemical reaction schema in XPS analysis described

Table 2. Relative Percentages of Elements N's Five Functional Groups in the Samples

Samples	-CN (%)	$-\overset{\mid}{C}H-NH-CH_2-$ (%)	$C-NH_2$/ -NH-CO-/-CH=NH[a] (%)	$-H_3N^+$ (%)	$-NH_3OH$ (%)
DSF	0.00	0.00	94.34	3.77	1.89
DSF II	0.00	0.00	87.72	12.28	0.00
DSF III	5.50	0.00	91.74	2.75	0.00
SBA	4.46	0.00	89.29	6.25	0.00
SBAC	2.70	29.73	67.57	0.00	0.00

[a] Binding energy of the three kinds of functional groups are close to each other and overlap in Fig. 4ii to 4vi, hence ascribed to be a kind of status.

TG Analysis

Thermogravimetric analysis was performed on DSF, DSFII, DSFIII, and SBA samples; the results are shown in Fig. 6. The mass of these four samples decreased significantly due to the evaporation of hydroscopic water or absorbed water (Long 1982) when heated from 25 to 100°C. Then, as temperature increased above 100°C, the mass remained unchanged until the temperature passed beyond the decomposition temperature. The range of equilibrium temperature for DSF, DSF II, DSF III, and SBA were 141°C to 156°C, 132°C to 149°C, 130°C to 135°C, and 136°C to 157°C, respectively.

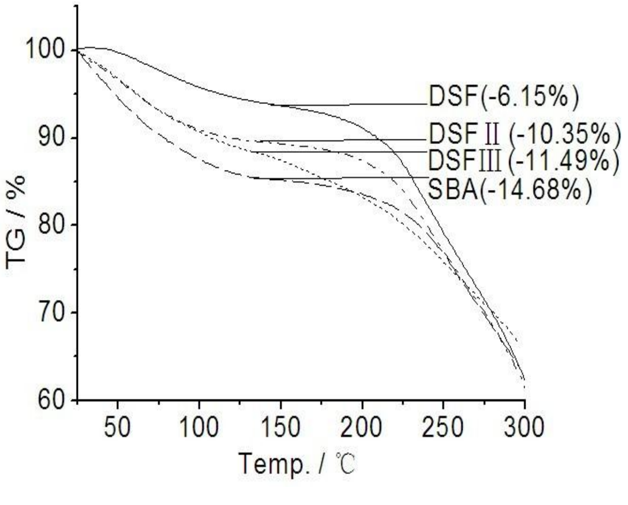

Fig. 6. TG spectra of samples

Finally, it could be calculated that the total loss of mass before TG decomposition for DSF, DSF II, DSF III, and SBA were 6.15%, 10.35%, 11.49%, and 14.68%, respectively, which indicated that the active functional groups increased during the DSF modification process. As we know, more condensation reaction occurred between active groups, which will generate more water or micromolecule. This result was also verified by the FTIR and XPS analyses. Equilibrium temperature of SBA also suggests that the curing and using temperature lower than 157°C is better; otherwise, the decomposition of SBAC would reduce the strength of final products such as plywood. Up to 230°C, the weight loss of these four samples accelerated significantly. This suggests that the decomposition of the protein backbone occurred, and final products would be damaged completely.

The Application of SBA in Plywood

The performance of DSFA and SBA when used in the plywood made from veneers of the four wood species is summarized in Table 3. The bonding strength of plywood made by DSFA was 0.00 MPa, indicating that DSF-bonded plywood panels are not water-resistant. The average bonding strength of plywood made by SBA was approximately 0.91 MPa, which will meet the requirement of the China National Standard --- the plywood type II for interior (the required bonding strength of plywood prepared from poplar, basswood, and *Triplochiton scleroxylon* ≥ 0.70MPa, from *Pinus massoniana* ≥ 0.80MPa). The order of bonding strength for four kinds of plywood were basswood > *Pinus massoniana* >*Triplochiton scleroxylon* > poplar, due to different extractives in the four wood species. To our knowledge, wood extractives could influence adhesive's properties such as curing process, and further affect the performance of plywood. Plywood that is prepared from urea-formaldehyde resin also may be used as plywood type II for interior applications. Therefore, chemical modified DSF (*i.e.* SBA) can be regarded as an alternative for petro-based adhesives application for interior plywood, making it possible to avoid the use of some harmful additives (*e.g.* formaldehyde, *etc.*).

Table 3. Bonding Strength of Plywood made with DSFA and SBA

Species of wood	Bonding strength ± SD (MPa)	
	DSFA	SBA
Triplochiton scleroxylon	0.00	0.89±0.03
Pinus massoniana	0.00	0.91±0.06
Basswood	0.00	0.97±0.07
Poplar	0.00	0.87±0.02

SD represents standard deviation.

CONCLUSIONS

1. The FTIR and XPS analysis indicated that when DSF was treated with acid and salt, the reactions resulted in an increase of carbonyl groups (–COOH). Ammonization could occur with dicyandiamide and alkali. The amide link was reformed, but protonation of $-NH_2$ decreased during the SBA curing process.
2. The TG analysis indicated that the total loss of mass before thermal decomposition for DSF, DSF II, DSF III, and SBA increased from 6.15 to 14.68%, indicating that combination treatment could increase the reactivity of functional groups in DSF.
3. The application of SBA for plywood made from veneers of four different wood species was found to have an average bonding strength of *ca.* 0.91 MPa, which can meet the requirement of application for interior plywood type II. Therefore, SBA can be an alternative for petro-based adhesive.

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REFERENCES CITED

Crist, B. V. (1999). *XPS Handbook: Elements & Native Oxides*. XPS International, LCC., USA, 171-174, 192-195.

Fan, D. B., Qin, T. F., and Chu, F. X. (2011). "A soy flour-based adhesive reinforced by low addition of MUF resin," *J. Adhes. Sci. Technol*. 25(1-3), 323-333.

Gao, Q., Dang, R., Sang, Z. T., Zhang, S. F., and Li, J. Z. (2010). "Investigation of soybean/PF resin based adhesive applying on plywood," *Advanced Materials Research*, Vol. 113-114, 2007-2011.

Gu, K., and Li, K. (2011). "Preparation and evaluation of particleboard with a soy flour-polyethylenimine-maleic anhydride adhesive," *J. Am. Oil Chem. Soc*. 88(5), 1-7.

Han, W. (2003). *Catalytic Chemistry Introduction*, Science Press, China, 186-189.

Hojilla-Evangelista, M. P. (2010). "Adhesion Properties of plywood glue containing soybean meal as an extender," *J. Am. Oil Chem. Soc*. 87(9), 1047-1052.

Huang, J., and Li, K. (2008). "A new soy flour-based adhesive for making interior type II plywood," *J. Am. Oil Chem. Soc*. 85(1), 63-70.

Huang, W., and Sun, X. (2000). "Adhesive properties of soy proteins modified by sodium dodecyl sulfate and sodium dodecylbenzene sulfonate," *J. Am. Oil Chem. Soc*. 77(7), 705-708.

Johnson, L. A., Myers, D. J., and Burden, D. J. (1984). "Early uses of soy protein in far east," *Inform* 3, 282-284.

Khosravi, S., Khabbaz, F., Nordqvist, P., and Johansson, M. (2010). "Protein-based adhesives for particleboards," *Ind. Crops Prod*. 32(3), 275-283.

Kim, J. T., and Netravali, A. N. (2010). "Mechanical, thermal, and interfacial properties of green composites with ramie fiber and soy resins," *J. Agric. Food. Chem*. 58(9), 5400-5407.

Li, F., Li, X. P., Weng, X. L., and Wang, W. H. (2010). "Study on Preparing wood adhesive from defatted soy flour," *China Forest Products Industry* 37(1), 22-25.

Long, K. P. (1982). *Thermoanalysis*, Chemical Industry Press, China, 119-129.

Mo, X., Wang, D., and Sun, X. S. (2011). "Physicochemical properties of β and $\alpha'\alpha$ subunits isolated from soybean β-conglycinin," *J. Agric. Food. Chem.* 59(4), 1217-1222.

Nakanishi, K. (1977). *Infrared Absorption Spectroscopy*, Holden-Day, Inc., USA. 8-45.

Pretsch, E., Bühlmann, P., and Affolter, C. (2000). *Structure Determination of Organic Compounds Tables of Spectral Data*. Springer-Verlag GmbH & Co. KG, Germany. 245-312.

Silverstein, R., Webster, F., and Kiemle, D. (2005). *Spectrometric Identification of Organic Compounds*, John Wiley & Sons, Inc., USA. 90-100.

Tong, L., Lin, Q. J., Weng, X. Y., and Chen, N. R. (2008). "Environment-friendly wood adhesive preparation from soy," *Chinese Journal of Eco-Agriculture* 16(4), 957-962.

Wade, L. G. (2003). *Organic Chemistry*, Pearson Education, New York, pp. 850-853, 889, 986.

Wagner, C. D., Riggs, W. M., and Davis, L. E. (1992). *Handbook of X-ray*

Photoelectron Spectroscopy, Perkin Elmer Corporation, USA. 5-7.

Wang, Y., Mo, X., Sun, X. S., and Wang, D. (2007). "Soy protein adhesion enhanced by glutaraldehyde crosslink," *J. Appl. Polym. Sci.* 104(1), 130-136.

Wang, Y., Wang, D., and Sun, X. S. (2005). "Thermal properties and adhesiveness of soy protein modified with cationic detergent," *J. Am. Oil Chem. Soc*. 82(5), 357-363.

Zhang, X., Huang, W., Kim, Y., and Zou, Q. (2007). "Adhesive properties of 7S and 11S globulins of soybean treated by nano-particle SiO_2 and urea modification," *China Oils and Fats* 32(12), 24-28.

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