Preparation and Properties of Normal Temperature Cured Starch-Based Wood Adhesive

Zhibang Qiao,[a] Jiyou Gu,[a] Shanshan Lv,[a] Jun Cao,[b,*] Haiyan Tan,[a] and Yanhua Zhang [a,b,*]

A normal temperature cured starch-based wood adhesive was prepared using dry method esterification and polyisocyanate prepolymer crosslinking. The effects of esterification and crosslinking on the properties of corn starch adhesive were investigated. The esterified starch and adhesive were characterized using Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), dielectric analysis (DEA), thermogravimetric analysis (TGA), and scanning electron microscopy (SEM). The results showed that maleic anhydride (MAH) esterified starch was obtained using dry method esterification. After esterification, the crystal type of starch did not change, but the crystallinity of starch decreased. The distribution of adhesive at the bonding interface was improved after esterification. The prepolymer improved the thermal stability of the adhesive, and the optimal addition of prepolymer was 10%.

Contact information: a: Materials Science and Engineering College and b: Postdoctoral Station of Mechanical Engineering, Northeast Forestry University, Harbin 150040, China;
* Corresponding authors: zyhnefu@163.com; caojunnefu@163.com

INTRODUCTION

Starch is biodegradable and widely used in paper-making, clothing, food, adhesives, *etc*. (Nachtergaele 1989; Meshram *et al.* 2009; Wang *et al.* 2012; Hong *et al.* 2015; López *et al.* 2015). There are many sources of starch, and its cost is relatively low. Starch is a type of natural polymer with glucose as its basic unit. Hydroxyl groups are present at C_2, C_3, and C_6 in each glucose unit. Hydrogen bonding produced by hydrophilic hydroxyls is the source of starch adhesive bonding forces (Chi *et al.* 2008). However, hydroxyl groups easily combine with water molecules to form hydrogen bonds, resulting in the poor water resistance, poor mobility, and slow drying of starch adhesive. Therefore, starch need modifications, which take three broad forms: physical, chemical, and biological (Kaur *et al.* 2012; van der Maarel and Leemhuis 2013).

Esterification is a useful type of chemical modification for starch. In general, starch esters are prepared under aqueous conditions, with controlled pH or strong polar solvents to control the degree of substitution (DS) (Tessler and Billmers 1996; Neumann *et al.* 2002; Fang *et al.* 2004). New methods for preparing starch esters include reactive extrusion, microwave radiation, and high temperature/pressure reaction (Lewandowicz *et al.* 2000; Miladinov and Hanna 2000; Shogren 2003; Biswas *et al.* 2008).

After esterification, some hydroxyls are transformed into esters, which change the starch structure and its properties (Kaur *et al.* 2012; Zuo *et al.* 2013). The esterification agent greatly influences the properties of the final product. When its chain-length is not

too long, the water absorptivity, water solubility, and thermal stability of the final product decrease as the DS of starch increases (Aburto *et al.* 1999; Stojanović *et al.* 2005; Tupa *et al.* 2013; Zuo *et al.* 2013). However, inorganic or long-chain fatty acid esterification agents produce different results (Staroszczyk *et al.* 2007; Junistia *et al.* 2009).

A portion of hydroxyl groups is substituted after esterification, which improves the hydrophobicity of starch. According to an earlier study (Shi and Wei 2003), simple esterified modification does not completely improve the water resistance of starch; further modification is required. In this study, maleic anhydride-esterified corn starch was prepared using a dry method (Zuo *et al.* 2013), and esterified starch adhesive was obtained. Additionally, a polyisocyanate prepolymer was introduced as the cross-linking agent (Fig. 1) to improve the bonding strength of the adhesive.
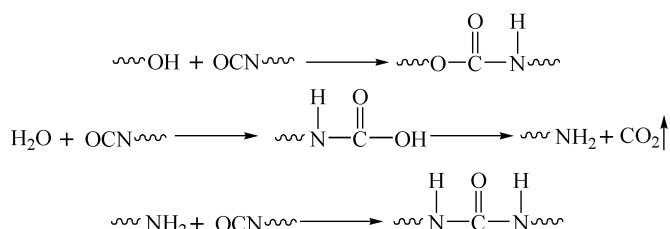
Fig. 1. The mechanism of crosslinking

EXPERIMENTAL

Materials

Corn starch (industrial grade) with moisture content of 10% to 12% was purchased from Dacheng Corn Co., Ltd (Changchun, China) and oven-dried at 50 °C for 48 h to eliminate moisture before use. Maleic anhydride (MAH), potassium bromide, and acetone were bought from Kemiou Chemical Reagent Co., Ltd (Tianjin, China). Distilled water was supplied by Wenjing Distilled Water Company (Harbin, China). Polyisocyanate prepolymer was synthesized as described (Qiao *et al.* 2015). *Betula platyphylla* Suk. blocks (6% moisture content) had dimensions of 30 mm × 25 mm × 10 mm (Jinhai Wood Co., Ltd, Dunhua, China). Unless stated otherwise, the reagents were analytical grade.

Methods

Synthesis of esterified corn starch

One-hundred grams corn starch and 3 g maleic anhydride were mixed thoroughly and transferred to a round-bottomed flask equipped with a mechanical paddle. The flask was incubated at 85 °C in an oil bath for 2 h with a rotation speed of 1 rpm. When the system cooled to ambient temperature, 120 mL acetone was added. The mixture was stirred for several minutes and then filtered. After being washed several times with acetone, the filtered product was dried in an oven at 50 °C until the mass almost remained unchanged.

Preparation of normal cured starch-based wood adhesive

30% (mass fraction) esterified starch slurry was prepared and heated to gelatinization. The gel was cooled to room temperature to obtain esterified starch

adhesive (ESA). Polyisocyanate was added in the required amount to the previously weighed gelatinized starch to prepare polyisocyanate/esterified starch adhesive (PESA). The mass ratio of gel to polyisocyanate was 100:0, 100:5, 100:10, 100:15, and 100:20.

Preparation of shear strength test samples

The birch block was polished using 180-mesh abrasive paper to eliminate the oxidized layer. The single-lap specimen (Fig. 2) was prepared using a coated adhesive between two parallel birch blocks. The adhesive was coated on the birch block at a spread rate of 100 g/m^2. The block was pressed at 1500 N for 24 h (40 to 60% RH). After removing the pressure, the specimens were stored 48 h under 40 to 60% RH.
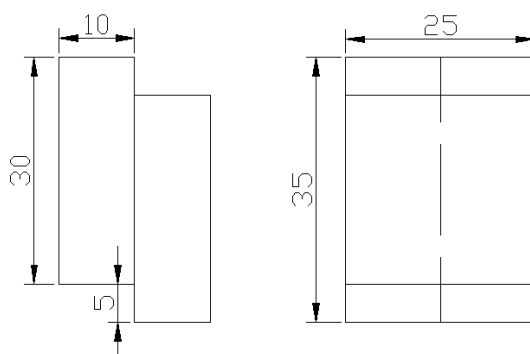
Fig. 2. Specimen dimensions (in mm)

Characterization

Fourier-transform infrared spectroscopy (FT-IR)

FT-IR spectra were obtained using a Magna-IR 560 E.S.P spectrometer with 4 cm^{-1} resolution (Thermo Nicolet Corporation, Waltham, USA). The samples were tested using the transmission method with potassium bromide, with scanning from 4000 to 400 cm^{-1}. The scanning was replicated 32 times.

X-ray diffraction (XRD)

XRD spectra were obtained from dried native starch and esterified starch powder using an X-ray diffractometer (Rigaku D/max 2200, Kyoto, Japan) at 32 kV, 40 mA, with 0.154 nm Cu Kα radiation (Ni filter). The crystallinity was determined as previously described (Xu *et al.* 2012).

Shear strength test

The shear strength was determined according to the National Standard of People's Republic of China HG/T 2727 (2010). The specimens were completely soaked in water at 30 ± 1 °C for 3 h and then at 23 ± 2 °C for 10 min. A CMT 5504 mechanical test machine (Sans, Shenzhen, China) was used to evaluate the wet shear strength. The dry shear strength was measured according to the same standard, and the data was reported as the mean value ± standard deviation (SD).

Dielectric analysis (DEA)

The ion viscosity of adhesive in the curing process was analyzed with a DEA 288 dielectric analyzer (NETZSCH, Selb, Germany). The adhesive was coated on the IDEX 115/60 sensor with a line space of 115 μm, 60-cm leads, and 200 °C maximum

temperature. The sensor was kept at 25 °C for 24 h, and the scanning frequency was 1 mHz. The ion viscosity was plotted as a function of time.

Thermogravimetric analysis (TGA)

TGA was performed on a TG209 F1 Libra thermogravimetric analyzer (NETZSCH, Selb, Germany) to determine the thermal stability of moisture-free samples under nitrogen atmosphere. Each sample was loaded into an aluminum oxide (Al_2O_3) crucible and heated from 30 °C to 600 °C at a rate of 10 °C/min under nitrogen flow rate of 50 mL/min. The residual mass and its first derivative (DTG) were plotted as a function of temperature for all samples.

Scanning electron microscopy (SEM)

An FEI Quanta 200 scanning electron microscopy (FEI, Eindhoven, Dutch) was used at a 20 kV accelerating voltage to characterize the morphology of the interface between wood and adhesive. The magnification was 500×, and the samples were coated with gold under vacuum before test.

Statistical Analysis

The TGA results were analyzed with Proteus Analysis Software 6.1 (NETZSCH, Selb, Germany).

RESULTS AND DISCUSSION

FT-IR

The FTIR spectra of native starch and maleic anhydride esterified starch are shown in Fig. 3. In the native starch spectrum, the 3300 cm^{-1} band was O-H (free hydroxyl, intra-molecular association hydroxyls, and inter-molecular association hydroxyl) stretching vibration, and the band at 2925 cm^{-1} was C-H (methane in a glucose ring), a symmetric stretching vibration.
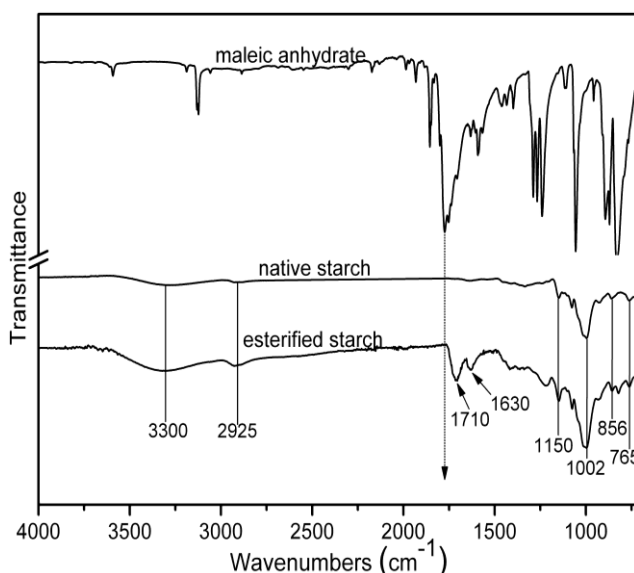
Fig. 3. FT-IR spectra of native starch and esterified starch

The 1630 cm^{-1} peak was due to the H-O bending vibration, and the band at 1150 cm^{-1} belonged to the asymmetric stretching vibration of C-O in the C-O-H. 1002 cm^{-1} was assigned to the anhydroglucose ring C-O vibration peak (Fang *et al.* 2004), and 860 to 700 cm^{-1} was the absorption peak of the C-H swing vibration (Zhuang 2011). The esterified starch not only contained the previously mentioned characteristic absorption peaks, but also a -C=O absorption peak at 1710 cm^{-1}. Because the samples were repeatedly extracted with acetone, the maleic anhydride that did not participate in the reaction had been removed. In accordance with the new characteristic peaks, the carbonyl groups existed in the framework of the starch, which indicated that there was an esterification reaction between the corn starch and the maleic anhydride.
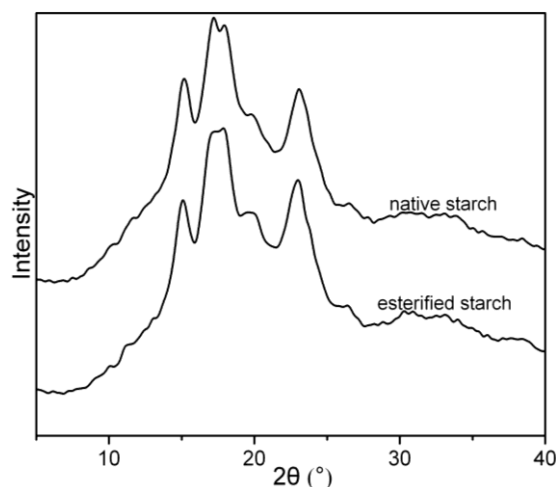

Fig. 4. XRD spectra of native starch and esterified starch particles

XRD

There were significant X-ray diffraction peaks at 2θ = 15.2°, 17.3°, 18.0°, and 22.8° for esterified starch, which was still A-type crystal structure (Yu *et al.* 2009) and basically consistent with native starch (Fig. 4). This result suggested that the esterification reaction between maleic anhydride and starch did not change the crystal type of native corn starch and that the esterification reaction occurred mainly in the amorphous regions. The degree of crystallinity decreased from 26.4% of native starch to 24.7% of esterified starch, which indicated that esterification also destroyed the crystalline structure of starch to some extent.

Shear Strength

Currently, there are not any testing standards regarding normal temperature-cured starch adhesives in the People's Republic of China. Thus, the national standard for polyvinyl acetate wood adhesive (HG/T 2727-2010) was employed to measure the dry and wet shear strength of adhesive (Fig. 5). With an increasing amount of polyisocyanate prepolymer, the dry shear strength increased at first and then decreased. The wet shear strength increased. However, when the added amount of prepolymer was more than 10%, the increasing trend was not obvious. The gel of native starch slurry (NSA) with 30% mass fraction fell apart at room temperature; the specimens cracked before the shear strength test. Thus, the valid shear strength value of native starch adhesive was not obtained, and esterification appeared to improve the mobility of starch adhesive.
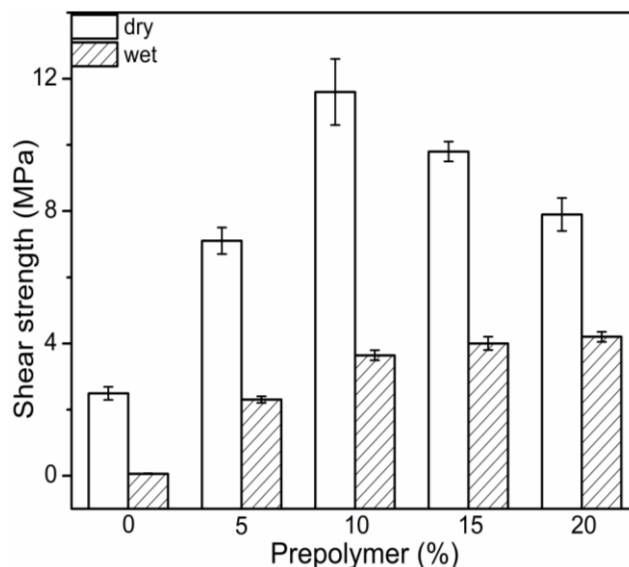
Fig. 5. Dry and wet shear strength of adhesive

With 0% added prepolymer, the dry shear strength of ESA was 2.3 MPa, indicating improved bonding properties. When small amounts of prepolymer were added, the adhesive fluidity was good, and it easily coated the surface of the birch block. At 10% prepolymer, the wet shear strength was approximately 4 MPa, which met the HG/T 2727-2010 criteria (3 MPa). Afterwards, the wet strength was to some extent increased with the increasing addition of prepolymer, while the dry shear strength was decreased. This result revealed that prepolymer addition improved the water resistance of ESA. However, when the addition of prepolymer was too high, the diphenylmethane diisocyanate (MDI) separated out, which resulted in the drifting of the adhesive layer and decreased dry strength (Zhang *et al.* 2013). Given the high cost of the prepolymer, the prepolymer addition should not be too high. The optimal addition of prepolymer was 10:100.
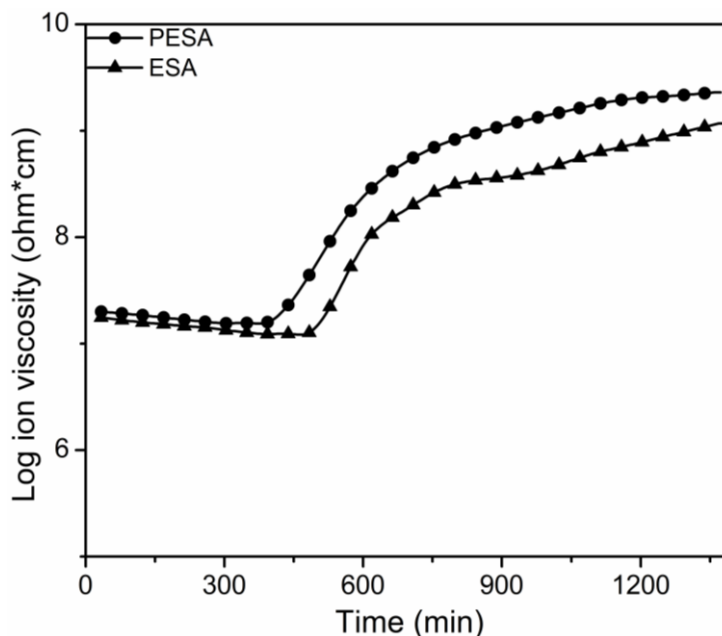
Fig. 6. DEA of ESA and PESA

bioresources.com

DEA

The cure behavior of the adhesive was evaluated by dielectric analysis (Fig. 6). In DEA, a physical property of polar materials (polarization, conductivity, dielectric loss, dielectric constant, *etc.*) is measured as time or frequency is varied (Vassilikou-Dova and Kalogeras 2008). In a continuous electric field, the orientation of dipoles occurs, and changed particles (*e.g.*, ions, electrons, charged atoms or molecules, and impurities) tend to move toward the electrode of opposite charge, resulting in a change in the material properties. In this study, a sinusoidal voltage (excitation, input) was applied to the sample, and the resulting current (output) and phase shift (the phase difference between the input voltage and the detected current) was detected. Using the applied frequency, the exact area of electrodes, and the exact distance between electrodes, the changes in the amplitude and phase changes can be converted into fundamental dielectric properties.

There were three steps in the testing process for ESA and PESA (Fig. 6). The ion viscosity of adhesive decreased first. Over time, the ion viscosity increased. After a sufficient length of time, the ion viscosity remained almost unchanged. When the external heat was first applied, the adhesive did not cure. The decrease in viscosity was attributed to the increase in system temperature (Marcotte *et al.* 2001). When the adhesive started to cure, the viscosity increased. As shown in Fig. 6, the growth rate of ion viscosity became smaller over an extended period of time. When enough time had passed, adhesive curing was completed, and the ion viscosity remained almost unchanged.

Compared with ESA, the initial ion viscosity of PESA was larger, which was attributed to the prepolymer addition. Isocyanate is the main component of the prepolymer. It has high reactivity and reacts with hydrogen-containing substances to form three dimensional structures, resulting in increased viscosity (Gao *et al.* 2011). Meanwhile, the addition of prepolymer was beneficial in curing the adhesive. This result was confirmed by the time ion viscosity began to decrease.
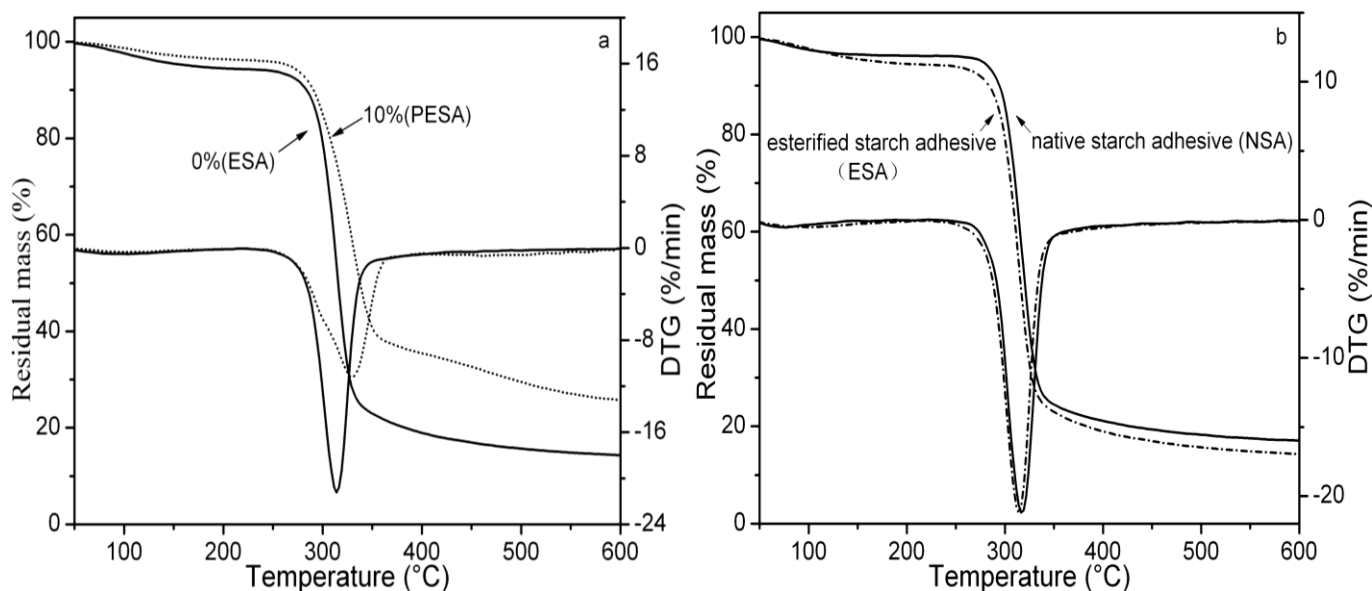

**Fig. 7.** Prepolymer addition on thermal stability of ESA

TGA

As illustrated in Fig. 7a, the effect of prepolymer addition on the thermal stability of ESA was significant. When the prepolymer addition increased from 0% to 10%, the initial decomposition temperature of ESA increased from 297.6 °C to 298.6 °C, the peak temperature increased from 314.6 °C to 328.4 °C, and residual mass increased from 14.35% (599.6 °C) to 25.80% (599.6 °C). Hence, the prepolymer improved the thermal stability of ESA. This effect was due to the reaction between the -NCO groups of prepolymer and the hydrogen-containing substances (water, -OH in starch, *etc*.) in the system (Chattopadhyay and Webster 2009).

As shown in Fig. 7b, the thermal stability of starch adhesive (without prepolymer) decreased after esterification treatment, whereas the thermal stability of PESA increased because of the prepolymer addition. This result illustrated that the enhancement of thermal stability of adhesive *via* prepolymer addition was more significant than the weakening effects of esterification.

According to the DTG curves (Fig. 7a), there was only one weight loss peak, illustrating that the compatibility between esterified starch adhesive and polymer was good. The improvement of shear strength of ESA may be related to this.

SEM

To investigate the increased shear strength and the effect of esterification and prepolymer addition on the distribution of the adhesive at the bonding interface, the morphology of the bonding interface surface was analyzed using SEM (Fig. 8). The distribution of native starch adhesive (NSA) at the interface was basically continuous (Fig. 8a). However, there were visible starch granules. The starch granules completely disappeared after esterification (Fig. 8c), indicating that esterification was beneficial to the uniform distribution of adhesive at the bonding interface.
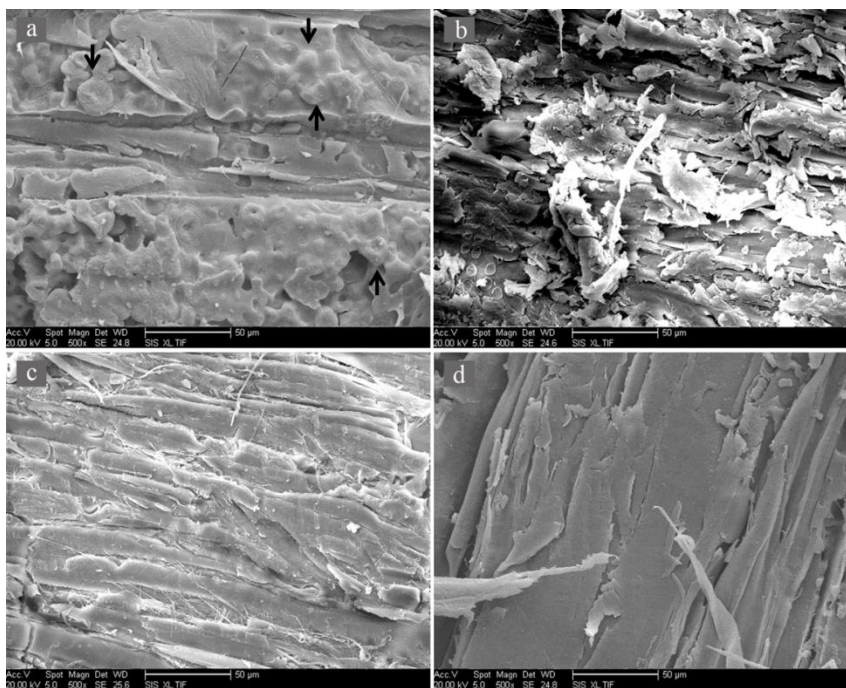
Fig. 8. SEM of bonding interfaces. a, NSA; b, PNSA; c, ESA; d, PESA. Black arrows indicate starch granules.

　　　　With respect to NSA, after adding 10% prepolymer, the adhesive (PNSA) exhibited continuous distribution at the interface (Fig. 8b). However, there were obvious cracks among the different adhesive layers. There were a large number of polar isocyanate groups and benzene rings in the prepolymer. Those groups affected the interfacial compatibility, resulting in poor flexibility of adhesive layers. After esterification, the molecular structure of starch was destroyed (according to the XRD results) to some degree, which changed its properties. When 10% prepolymer was added, the distribution of PESA at the interface was significantly improved (Fig. 8d). The adhesive layers were smooth with no obvious cracks.

CONCLUSIONS

1. Esterification did not change the crystal structure types of native starch, but it did decrease the crystallinity degree, resulting in a decrease in the thermal stability of native starch adhesive (NSA). Esterification improved the uniform distribution of adhesive at the bonding interface.

2. Prepolymer addition was beneficial to the shear strength and thermal stability of starch-based wood adhesive. The prepolymer-based enhancement of thermal stability was greater than the weakening effect of esterification.

3. The optimal prepolymer addition was 10:100. Under this condition, the dry and wet shear strengths were approximately 12 MPa and 4 MPa, respectively, which met the requirements of the Chinese national standard HG/T 2727-2010.

ACKNOWLEDGMENTS

REFERENCES CITED

Aburto, J., Alric, I., Thiebaud, S., Borredon, E., Bikiaris, D., Prinos, J., and Panayiotou, C. (1999). "Synthesis, characterization, and biodegradability of fatty-acid esters of amylose and starch," *J. Appl. Polym. Sci.* 74(6), 1440-1451. DOI: 10.1002/(SICI)1097-4628(19991107)74:6<1440::AID-APP17>3.0.CO;2-V

Biswas, A., Shogren, R. L., Selling, G., Salch, J. L., and Buchanan, C. M. (2008). "Rapid and environmentally friendly preparation of starch esters," *Carbohyd. Polym* 74(1), 137-141. DOI: 10.1016/j.carbpol.2008.01.013

Chattopadhyay, D. K., and Webster, D. C. (2009). "Thermal stability and flame retardancy of polyurethanes," *Prog. Poly. Sci.* 34(10), 1068-1133. DOI: 10.1016/j.progpolymsci.2009.06.002

Chi, H., Xu, K., Wu, X. L., Chen, Q., Xue, D. H., Song, C. L., Zhang, W. D., and Wang, P. X. (2008). "Effect of acetylation on the properties of corn starch," *Food Chem.* 106(3), 923-928. DOI: 10.1016/j.foodchem.2007.07.002

Fang, J. M., Fowler, P. A., Sayers, C., and Williams, P. A. (2004). "The chemical modification of a range of starches under aqueous reaction conditions," *Carbohyd. Polym.* 55(3), 283-289. DOI: 10.1016/j.carbpol.2003.10.003

Gao, Z. H., Wang, W. B., Zhao, Z. Y., and Guo, M. R. (2011). "Novel whey protein-based aqueous polymer-isocyanate adhesive for glulam," *J. Appl. Polym. Sci.* 120(1), 220-225. DOI: 10.1002/app.33025

HG/T 2727. (2010). "Polyvinyl acetate emulsion adhesives for woods," Ministry of Industry and Information Technology of the People's Republic of China, Beijing, China.

Hong, L. F., Cheng, L. H., Lee, C. Y., and Peh, K. K. (2015). "Characterisation of physicochemical properties of propionylated corn starch and its application as stabilizer," *Food Technol. Biotech.* 53(3), 278-285. DOI: 10.17113/ftb.53.03.15.3907

Junistia, L., Sugih, A. K., Manurung, R., Picchioni, F., Janssen, L. P., and Heeres, H. J. (2009). "Experimental and modeling studies on the synthesis and properties of higher fatty esters of corn starch," *Starch-Stärke* 61(2), 69-80. DOI: 10.1002/star.200800076

Kaur, B., Ariffin, F., Bhat, R., and Karim, A. A. (2012). "Progress in starch modification in the last decade," *Food Hydrocolloid.* 26(2), 398-404. DOI: 10.1016/j.foodhyd.2011.02.016

Lewandowicz, G., Fornal, J., Walkowski, A., Mączyński, M., Urbaniak, G., and Szymańska, G. (2000). "Starch esters obtained by microwave radiation-structure and functionality," *Ind. Crop. Prod.* 11(2): 249-257. DOI: 10.1016/S0926-6690(99)00065-5

López, O. V., Castillo, L. A., García, M. A., Villar, M. A., and Barbosa, S. E. (2015). "Food packaging bags based on thermoplastic corn starch reinforced with talc nanoparticles," *Food Hydrocolloid.* 43, 18-24. DOI: 10.1016/j.foodhyd.2014.04.021

Marcotte, M., Hoshahili, A. R. T., and Ramaswamy, H. S. (2001). "Rheological properties of selected hydrocolloids as a function of concentration and temperature," *Food Res. Int.* 34(8), 695-703. DOI: 10.1016/S0963-9969(01)00091-6

Meshram, M. W., Patil, V. V., Mhaske, S. T, and Thorat, B. N. (2009). "Graft copolymers of starch and its application in textiles," *Carbohyd. Polym.* 75(1), 71-78. DOI: 10.1016/j.carbpol.2008.06.012

Miladinov, V. D., and Hanna, M. A. (2000), "Starch esterification by reactive extrusion," *Ind. Crop. Prod.* 11(1), 51-57. DOI: 10.1016/S0926-6690(99)00033-3

Nachtergaele, W. (1989). "The benefits of cationic starches for the paper industry," *Starch-Stärke* 41(1), 27-31. DOI: 10.1002/star.19890410108

Neumann, U., Wiege, B., and Warwel, S. (2002). "Synthesis of hydrophobic starch esters by reaction of starch with various carboxylic acid imidazolides," *Starch-Stärke* 54(10), 449-453. DOI: 10.1002/1521-379X(200210)54:10<449::AID-STAR2222449>3.0.CO;2-R

Qiao, Z. B., Gu, J. Y., Lv, S. S., Cao, J., Tan, H. Y., and Zhang, Y. H. (2015). "Preparation and properties of isocyanate prepolymer/corn starch adhesive," *J. Adhes. Sci. Technol.* 29(13), 1368-1381. DOI: 10.1080/01694243.2015.1030157

Shi, J. Y., and Wei, S.Y. (2003). "Study on modification of esterified corn starch emulsion," *China Forest Products Industry* 30(6), 34-36. DOI: 10.3969/j.issn.1001-5299.2003.06.010

Shogren, R. L. (2003). "Rapid preparation of starch esters by high temperature/pressure reaction," *Carbohyd. Polym.* 52(3), 319-326. DOI: 10.1016/S0144-8617(02)00305-3

Staroszczyk, H., Tomasik, P., Janas, P., Janas, P., and Poreda, A. (2007). "Esterification of starch with sodium selenite and selenite," *Carbohyd. Polym.* 69(2), 299-304. DOI: 10.1016/j.carbpol.2006.10.009

Stojanović, Ž., Katsikas, L., Popović, I., Jovanović, S., and Jeremić, K. (2005). "Thermal stability of starch benzoate," *Polym. Degrad. Stabil.* 87(1), 177-182. DOI: 10.1016/j.polymdegradstab.2004.07.018

Tessler, M. M., and Billmers, R. L. (1996). "Preparation of starch esters," *J. Environ. Polym. Degr.* 4(2), 85-89. DOI: 10.1007/BF02074869

Tupa, M., Maldonado, L., Vázquez, A., and Foresti, M. L. (2013). "Simple organocatalytic route for the synthesis of starch esters," *Carbohyd. Polym.* 98(1), 349-357. DOI: 10.1016/j.carbpol.2013.05.094

Van der Maarel, M. J. E. C., and Leemhuis, H. (2013). "Starch modification with microbial alpha-glucanotransferase enzymes," *Carbohyd. Polym.* 93(1), 116-121. DOI: 10.1016/j.carbpol.2012.01.065

Vassilikou-Dova, A., and Kalogeras, I. M. (2008). "Dielectric analysis (DEA)," in: *Thermal Analysis of Polymers: Fundamentals and Applications*, Menczel, J. D., and Prime, R. B. (eds.), John Wiley & Sons, Hoboken, NJ, USA. DOI: 10.1002/9780470423837.ch6

Wang, Z. J., Li Z. F, Gu, Z. B., Hong, Y., and Cheng, L. (2012). "Preparation, characterization and properties of starch-based wood adhesive," *Carbohyd. Polym.* 88(2), 699-706. DOI: 10.1016/j.carbpol.2012.01.023

Xu, B., Man, J. M., and Wei, C. X. (2012). "Methods for determining relative crystallinity of plant starch X-ray powder diffraction spectra," *Chinese Bulletin of Botany* 47(3), 278-285. DOI: 10.3724/SP.J.1259.2012.00278

Yu, J. L., Wang, S. J., Jin, F. M., Sun, L. Y., and Yu, J. G. (2009). "The structure of C-type rhizoma *Dioscorea* starch granule revealed by acid hydrolysis method," *Food Chem.* 113(2), 585-591. DOI: 10.1016/j.foodchem.2008.08.040

Zhang, Y. H., Gu, J. Y., Tan, H. Y., Jiang, X. K., Shi, J. Y., Zuo, Y. F., and Weng, X. L. (2013). "Fabrication, performances, and reaction mechanism of urea-formaldehyde resin adhesive with isocyanate," *J. Adhes. Sci. and Technol*. 27(20), 2191-2203. DOI: 10.1080/01694243.2013.766833

Zhuang, X. (2011). "Renewable resource-based composites of thermoplastic acorn starch and polycaprolactone: Preparation and FTIR spectrum analysis," *Spectrosc. Spect. Anal.* 31(4), 992-996. DOI: 10.3964/j.issn.1000-0593(2011)04-0992-05

Zuo, Y. F, Gu, J. Y, Yang, L., Qiao, Z. B., Tan, H. Y., and Zhang, Y. H. (2013). "Synthesis and characterization of maleic anhydride esterified corn starch by the dry method," *Int. J. Boil. Macromol.* 62, 241-247. DOI: 10.1016/j.ijbiomac.2013.08.032