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Synthesis of a bio-based polyamidoamine-epichlorohydrin resin and its application for soy-based adhesives

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ABSTRACT

In view of sustainable development and environmental protection, renewable itaconic acid was used to synthesize a bio-based curing agent for soy-based adhesives. The bio-based curing agent, i.e., itaconic acid-based polyamidoamine-epichlorohydrin resin (IA-PAE), was characterized by RSV and ^{1}H-NMR. Results showed that IA-PADA and IA-PAE had much lower molecular weights than commercial PAE (C-PAE). Both N-(3-chloro-2-hydroxypropyl) groups and azetidinium rings of IA-PAE could perform as functional groups in IA-PAE modified soy flour adhesive (IA-PAE-SF). The pH values affected the viscosities of IA-PAE-SF adhesives significantly but had little effect on the wet strengths. Wet strength of IA-PAE-SF on plywood (0.95 MPa) was comparable to that of C-PAE-SF and met the requirements of Chinese National Standards for type-II applications. Cross-linking networks were formed during hot-pressing process and thus, improved water resistance of IA-PAE-SF on plywood. Measurement of water-insoluble solid content of cured adhesives and observation of SEM confirmed the formation of cross-linking networks in cured IA-PAE-SF.

1. Introduction

Formaldehyde-based resins are the predominant adhesives applied in wood product industry [1]. However, there are two challenges for formaldehyde-based adhesives. On one hand, formaldehyde-based adhesives are derived from non-renewable fossil resources whose reserves are limited [2]. On the other hand, wood products bonded with formaldehyde-based adhesives have the drawback of formaldehyde emission [3]. In recent years, many concerns about the depletion of non-renewable resources have been aroused [4]. Besides, strict regulations Refs. [5,6] have been carried out to limit the emission of formaldehyde which is carcinogenic to both humans and animals [4]. Therefore, great efforts were made to explore formaldehyde-free adhesives from renewable bioresources [1,7–9]. Soy-based adhesive was one of the research focuses because soybean is an abundant and inexpensive raw material [1,7,8].

The fatal weakness of soy-based adhesives is poor water resistance [1]. Much work has been carried out to improve water resistance of soy-based adhesives. Alkali, urea, guanidine hydrochloride, sodium dodecyl sulfate and dopamine were used to modify soy protein [10–13]. Polyamines are the most commonly used modifying (curing) agents for soy-based wood adhesives [14–18]. For example, soy flour (SF)–polyethylenimine (PEI)–maleic anhydride (MA) adhesive was developed to bond type-II plywood [15]; a commercial soy-based adhesive was prepared by curing soy protein with polyamidoamine-epichlorohydrin resin (PAE) [14]. However, polyamines mentioned above are currently derived from petrochemicals.

In view of sustainability and environmental protection it is desirable to develop bio-based polyamines to improve water resistance of soy flour-based adhesives. Jang et al. [3] synthesized a bio-based polyamine by the reaction of ammonia with epichlorohydrin which can be made from bio-based glycerol. PAE (synthesized from the reaction of epichlorohydrin with polyamidoamine resin, which was formed by the reaction of diethylenetriamine and adipic acid) can also be synthesized from renewable materials since adipic acid can now be derived from renewable materials [19]. But bio-based adipic acid is not readily available worldwide yet. Using other types of renewable raw materials, such as citric acid, to replace adipic acid is an effective way to produce bio-based PAE resins [20,21]. In this paper, readily available renewable itaconic acid was chosen to synthesize bio-based PAE due to its similar structure compared to adipic acid except that itaconic acid has a double bond. In addition, itaconic acid is a non-toxic compound which is considered as one of the top value added building block chemicals that can be produced from sugars [22]. The objective of this study was to synthesize a bio-based PAE using itaconic acid as a raw material and to characterize adhesion performance of itaconic acid-based PAE (IA-PAE) modified SF adhesives. If IA-PAE can improve water resistance of soy

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flour-based adhesives as well as commercial PAE (C-PAE), it will bring a sustainable development to wood product industry.

2. Experiments

2.1. Materials

NaOH, HCl (37.5%), diethylenetriamine (DETA), itaconic acid (IA), and epichlorohydrin (ECH) were purchased from Aladdin Reagent Co., Ltd., Shanghai. Commercial PAE (C-PAE, 12.5 wt%) was purchased from Aoyida Chemical Co., Ltd, Zibo. Soy flour with about 50% protein content was purchased from Hisoya Biological Science & Technology Co., Ltd., Guangzhou. Poplar veneers with the size of 1000 mm × 500 mm × 1.6 mm were supplied by Zhongke Zhaolu New Materials Co., Ltd., Ningbo and the veneers were cut into 200 mm × 200 mm × 1.6 mm for experiments.

2.2. Synthesis of itaconic acid-based PAE

PAE is well-known as a wet strength additive in paper making process. The synthesis of C-PAE is typically a two-step process [20]. A polyamidoamine is first prepared by polycondensation of DETA and adipic acid. The resultant polyamidoamine is then dissolved in water and is reacted in aqueous solution with ECH to form PAE solution.

The two-step process was also employed to synthesize IA-PAE. The molar ratio of DETA/IA/ECH was 1/1/1. At the first step, 31 g DETA and 39 g IA were added to a three-neck flask equipped with a stirrer, a thermometer, and a condenser. Twenty grams of water was also added to the flask to form a homogeneous solution. The aim of adding water was to dissipate the large amount of heat released by the exothermic reaction. Itaconic acid-based polyamidoamine (IA-PADA) molten was obtained after the reaction occured under 170 °C for 1.5 h. Then 100 g water was added to dissolve IA-PADA resin. At the second step, 27.8 g ECH was added to the three-neck flask, stirred at room temperature for 2 h. Then IA-PADA was reacted with ECH in aqueous solution under 70 °C for 1 h. The solid content of IA-PAE solution was about 50 wt%, and the apparent viscosity was 144 cp measured with a Brookfield HBDV-II+PRO viscometer using #2 spindle at 100 rpm.

2.3. Characterization of itaconic acid-based PAE

A small amount of D_2O was added to the solution of IA-PAE for obtaining an NMR-lock signal. Solid content in the solution for NMR measurement was about 5% [23]. The reduced specific viscosity (RSV) of a polymer solution correlates directly to its molecular weight. Flow times of PADA and PAE solutions were measured at 2% concentration using a capillary viscometer and 1 M NH_4Cl as the solvent at 25 °C. RSVs were calculated from the flow times [20].

2.4. Preparation of soy flour-based adhesives

Preparation of IA-PAE modified soy flour adhesives followed the process described by Sun et al. [24]. The difference compared with Sun et al. was that the protein derivative used in this paper was soy flour while the one they used was soy protein isolate. One hundred grams of H_2O, 40 g soy flour, 8 g IA-PAE solution were added to a 500 mL three-neck flask to form viscous slurry. To study the effect of pH on adhesive properties, pH of resultant adhesives was adjusted by 2 M HCl and 2 M NaOH solutions. Previous study [24] showed that the weight ratio of PAE/SF should be more than 1/20 to significantly improve water resistance of plywood. But high PAE content might interfere with interactions between soy proteins and wood substrate, so the adhesion properties had no more increasing. Therefore, the weight ratio of IA-PAE/SF was chosen at 1/10 in this study.

Sodium hydroxide (NaOH) was an effective modifier to improve water resistance of soy-based wood adhesives [10,25]. In this study, we used NaOH modified SF for comparative analysis, and we prepared the adhesive by adding 0.3 g NaOH and 40 g soy flour to100 g H_2O, followed by stirring for 30 min [25]. C-PAE modified SF adhesive was also prepared for comparison. The weight ratio of C-PAE/SF was 1/10 [24].

2.5. Preparation of three-layer plywood panels bonded by soy flour-based adhesives

The method described by Gui et al. [18] was used for preparing three-layer plywood panels. Poplar veneers with a dimension of 1.6 mm × 200 mm × 200 mm were used to prepare plywood panels. Moisture content of wood veneers was about 8%. Adhesives were coated onto two sides of the core veneer by a brush. The amount of adhesive was kept at 400 g/m^2, i.e., about 8 g adhesive was applied to each side of the core veneer. Two uncoated veneers were assembled to the core veneer with grain directions perpendicular to the core veneer. The stacked veneers were cold-pressed at 0.5 MPa for 30 min at room temperature and then hot-pressed at the parameters of 140 °C, 1.0 MPa and 100 s/mm [18]. After hot-pressing, the panel was stored at ambient environment for at least 24 h before it was cut into specimens for evaluating its strength.

2.6. Evaluation of water resistance of plywood bonded by soy flour-based adhesives

The samples were cut into A type specimens (Fig. 1) according to Chinese National Standard GB/T 9846.7–2004 [26]. Chinese National Standard GB/T 17657–1999 [27] was followed for the bonding strength test. Wet strength was used to characterize the water resistance of soy flour-based adhesives on plywood. At least 7 specimens were first immersed in water at 63 °C for 3 h. The soaked specimens were cooled at room temperature for 10 min and then tested. The crosshead speed was 1.0 mm/min. According to these standards, plywood can be used for type-II application while its wet strength passes 0.7 MPa. Wet strengths were analyzed by single-factor ANOVA and LSD tests using Origin8 software (OriginLab Corporation, Northampton, MA, USA). All comparisons were based on a 95% confidence interval.

2.7. Other tests

The fractured surface of tested specimens was used to examine the interface of failed adhesion through Scanning Electron

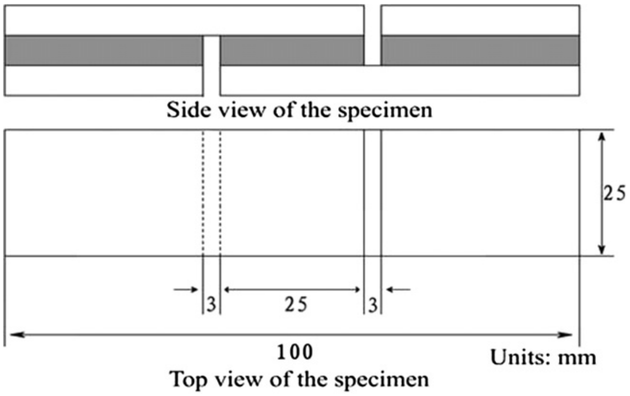

Fig. 1. The diagram of A type specimen.

Microscopy (SEM) after gold plating [28]. The viscosities of adhesives were measured with a Brookfield HBDV-II+PRO viscometer using a #5 spindle at 50 rpm. The pH of adhesives and IA-PAE solution was measured with an OHAUS STARTER2C pH meter. Water-insoluble solid content of cured adhesives was measured to show the cross-linking network formed by the reactions occurred between IA-PAE and SF. Soy flour-based adhesives were cured at 140 °C in an oven for 3 h. Five grams of cured adhesive was extracted with water in the Soxhlet Extractor for 24 h. The residue was oven-dried at 120 °C for 3 h and recorded as the water insoluble solid content [29]. Results of water-insoluble solid contents were analyzed by single-factor ANOVA and LSD tests using Origin8 software (OriginLab Corporation, Northampton, MA, USA). All comparisons were based on a 95% confidence interval.

3. Results and discussion

3.1. Synthesis and characterization of itaconic acid-based PAE

The synthesis process and possible structures of IA-PAE are shown in Fig. 2. Morello [30] and Asif et al. [31] had reported that pyrrolidone structure was easily formed by the reaction of C=C of itaconic acid and primary amines. The functional groups of IA-PAE were characterized by ^{1}H-NMR spectrum which was commonly used to characterize the functional groups of PAE products. Results (Fig. 3) showed that the resultant IA-PAE contained both N-(3-chloro-2-hydroxypropyl) groups and azetidinium rings, corresponding to a complex structure (Fig. 2). The signals at 4.44 ppm and 3.98 ppm were assigned to the methine proton *a* of azetidinium rings and the methine proton *b* of N-(3-chloro-2-hydroxypropyl) groups, respectively. The molar ratio of N-(3-chloro-2-hydroxypropyl) groups and azetidinium rings was about 1/1. It has been reported that both N-(3-chloro-2-hydroxypropyl) groups and azetidinium rings could effectively react with amino groups, carboxylic acid groups, and other nucleophilic groups in soy protein, thus effectively cross-linking soy proteins [3,14,32].

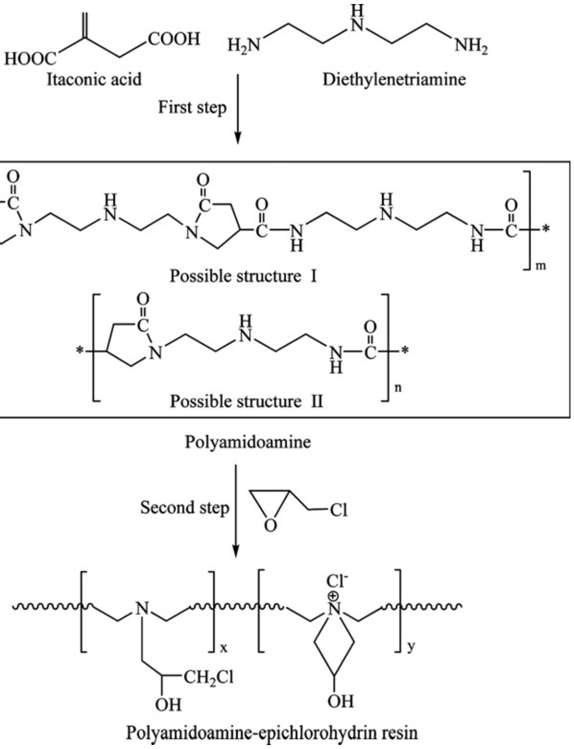

Fig. 2. Synthesis process of itaconic acid-based polyamidoamine-epichlorohydrin resin.

The measurement of RSVs indicated that IA-PADA and IA-PAE had much lower molecular weights than C-PAE. The RSVs of IA-PADA and IA-PAE were only 0.0470 and 0.0386 dL/g while the RSV of C-PAE was 0.1597 dL/g. When preparing C-PAE, cross-linking among polyamidoamine chains usually occurred during the second step. Molecular weight of C-PAE and viscosity of the solution increased with an increase in the reaction time. Higher molecular weight is known to give greater strength characteristics in paper [21]. Solid content of such a C-PAE solution is always below 20% due to its high viscosity. In addition, four-membered azetidinium rings are formed by the reaction of polyamidoamine with ECH. The C-PAE solutions obtained are not stable because the azetidinium rings are active to nucleophiles under alkaline conditions. Thus, pH of the final C-PAE solution is always adjusted to 3~5 by adding extra mineral acid [20]. Unlike the PAE used in papermaking process, high molecular weight of PAE is not necessary for modifying soy-based adhesives. Some studies were carried out to obtain PAE solutions with high solid contents and low viscosities [20,21]. When preparing IA-PAE, the main focus of the second step was to functionalize IA-PADA with ECH without incurring a great increase in molecular weight, which would limit the solid content of the final solution. Therefore, the resultant IA-PAE solution had a high solid content of 50 wt% and low apparent viscosity of 144 cP. The IA-PAE solution was stable as its pH was about 4.6.

3.2. Water resistance of plywood bonded by soy flour-based adhesives

Table 1 showed that pH affected the viscosities of IA-PAE–SF adhesives significantly but had little effect on the wet strengths.

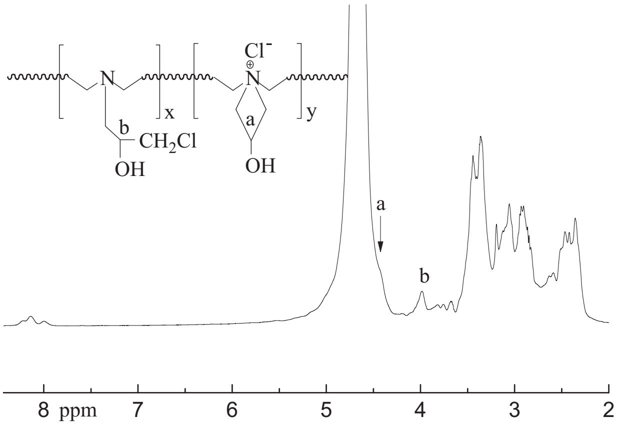

Fig. 3. 1H-NMR spectrum of IA-PAE solution.

Table 1
Effect of pH on properties of IA-PAE–SF adhesives.

pH of IA-PAE–SF adhesives	Solid content (%)	Viscosity (cP)	Wet strength of plywood (MPa)
3.5	28.1	9,450	0.94 ± 0.04 (a)
4.6	28.0	7,250	0.89 ± 0.13 (a)
5.6	28.2	4,160	0.92 ± 0.10 (a)
6.4	27.1	4,340	0.95 ± 0.06 (a)
7.5	27.3	8,930	0.87 ± 0.11 (a)
8.6	27.0	14,720	0.94 ± 0.05 (a)

Values are means ± standard deviations of 7 replicates. Means within a column followed by different letters are significantly different at $p < 0.05$.

Soy protein is pH sensitive and has a typical isoelectric point of 4.5 [33]. It was thoroughly studied that the viscosity of PAE–SF adhesive was dependent on the solubility of proteins [34,35]. Insoluble protein aggregates were formed by protein–protein interactions while protein–solvent interactions were the weakest at pH=4.5, where the protein electrostatic repulsions are the minimum [34]. Therefore, soy protein had the minimum solubility in a range of pH from 4.5 to 6.5 [33–35]. IA-PAE–SF adhesive had the minimum viscosity of 4160 cP at pH=5.6. This was consistent with the reported results [33–35]. At a pH lower than 4.6 or greater than 7.5, the solubility of proteins increased due to the electrostatic repulsions of proteins. The viscosity of IA-PAE–SF adhesive increased to 9450 cP (14,720 cP) with the pH reduced to 3.5 (increased to 8.6). Wet strength of plywood bonded by IA-PAE–SF adhesives with various pH values had no significant difference and all passed 0.7 MPa. This indicated that IA-PAE–SF adhesives could be used for type-II applications under various pH conditions. IA-PAE–SF at pH 6.4 was chosen for further comparison.

Wet strength of plywood bonded by NaOH–SF adhesive was only 0.47 MPa (Table 2), which could not meet the requirement for type-II applications. But the wet strength of plywood bonded by IA-PAE–SF adhesive was 0.95 MPa which was equivalent to the one of that bonded by C-PAE–SF adhesive and met the requirement for type-II applications. This result demonstrated the feasibility of using itaconic acid to synthesize bio-based PAE.

3.3. Mechanism for improvement of water resistance

IA-PAE performed as the cross-linking agent in IA-PAE–SF adhesives. During the hot-pressing process, N-(3-chloro-2-hydroxypropyl) groups and azetidinium rings reacted with functional groups of soy protein, such as $-NH_2$ and $-COOH$, to form cross-linking networks (Fig. 4). Plywood bonded by IA-PAE–SF had higher water resistance than that bonded by NaOH–SF because water-soluble components of the bond line became less while cross-linking network was formed and movement of protein chains was restricted by the cross-linking network.

Table 2
Water-insoluble solid content of cured soy flour-based adhesives and related wet strength.

Adhesives	Water-insoluble solid content (%)	Wet strength (MPa)
C-PAE–SF	68 ± 1 (*a*)	0.99 ± 1.10 (*a*)
IA-PAE–SF	68 ± 2 (*a*)	0.95 ± 0.06 (*a*)
NaOH–SF	58 ± 3 (*b*)	0.47 ± 0.07 (*b*)

Values are means ± standard deviations of 7 replicates. Means within a column followed by different letters are significantly different at $p < 0.05$.

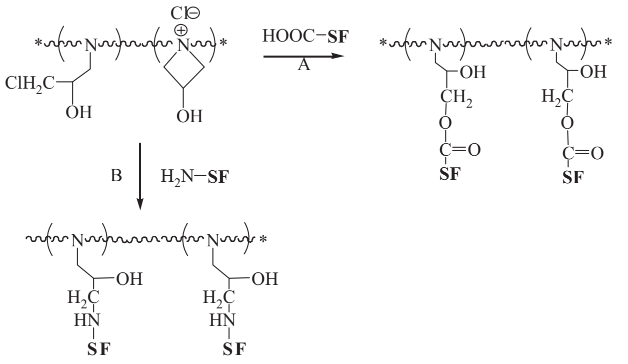

Fig. 4. Curing reactions between IA-PAE and soy proteins.

The formation of cross-linking network was proved by measuring water-insoluble solid contents of cured adhesives (Table 2). Cured NaOH–SF had 58% water-insoluble solid content. There were 42% of water-soluble solids in cured NaOH–SF adhesive. These water-soluble solids were reported to be mainly water-soluble carbohydrates and low molecular peptides [36]. Cured IA-PAE–SF adhesive had a water-insoluble solid content of 68%, which was 10% greater than the one of cured NaOH–SF adhesive. Ten percent was higher than the calculated value even if IA-PAE became an entirely water-insoluble network. This meant that some water-soluble components also reacted with IA-PAE and became water-insoluble cross-linking network. There were more residues left in the bond line of cured IA-PAE–SF than cured NaOH–SF adhesive, which meant that the structure of cured IA-PAE–SF was maintained better than cured NaOH–SF after immersing the specimens in water at 63 °C for 3 h. More residues also resulted in stronger interactions with wood surface. Therefore, water resistance of IA-PAE–SF on plywood was significantly better than NaOH–SF. Wet strength of plywood bonded by IA-PAE–SF adhesive was greater than 0.7 MPa, which meant that the plywood obtained could be used for type-II applications.

Observation of the state of residues of cured adhesives after Soxhlet extraction confirmed the cross-linking network formed by reactions between IA-PAE and soy protein. After Soxhlet extraction, the residues of cured IA-PAE-SF adhesive were small particles after drying while the residues of NaOH-SF adhesive became aggregated by movement of protein chains (Fig. 5). This indicated that cured IA-PAE–SF adhesive was cross-linked by IA-PAE. So the soy proteins could not move because they were apparently restricted by the network of cross-linking. However, there was no such network in cured NaOH–SF adhesive. So in cured NaOH–SF adhesive the soy proteins which were not restricted by cross-linking network could still move to aggregate after Soxhlet extraction. The movement of soy protein broke the interactions between adhesive and wood surface. Thus, water resistance of NaOH–SF adhesive on plywood was poorer than restricted IA-PAE–SF adhesive.

SEM observation confirmed the statements discussed above. Wood surface without adhesives showed a regular oriented structure (Fig. 6a). Fractured adhesion interface of immersed specimens bonded by IA-PAE–SF adhesive was entirely coated with adhesive (Fig. 6b). This indicated that IA-PAE–SF adhesive could wet the wood surface very well and formed a cross-linked glue line during the hot-pressing process. Most components in such a cross-linked glue line were restricted by the cross-linking network. Only a small part of water-soluble substance was lost

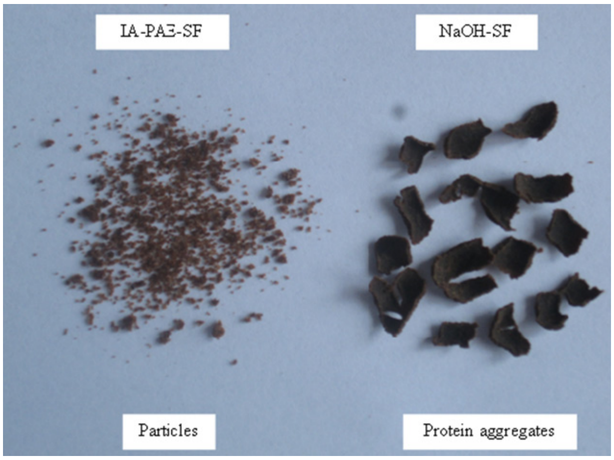

Fig. 5. Pictures of the residues of cured adhesives after Soxhlet Extraction (Oven-dried).

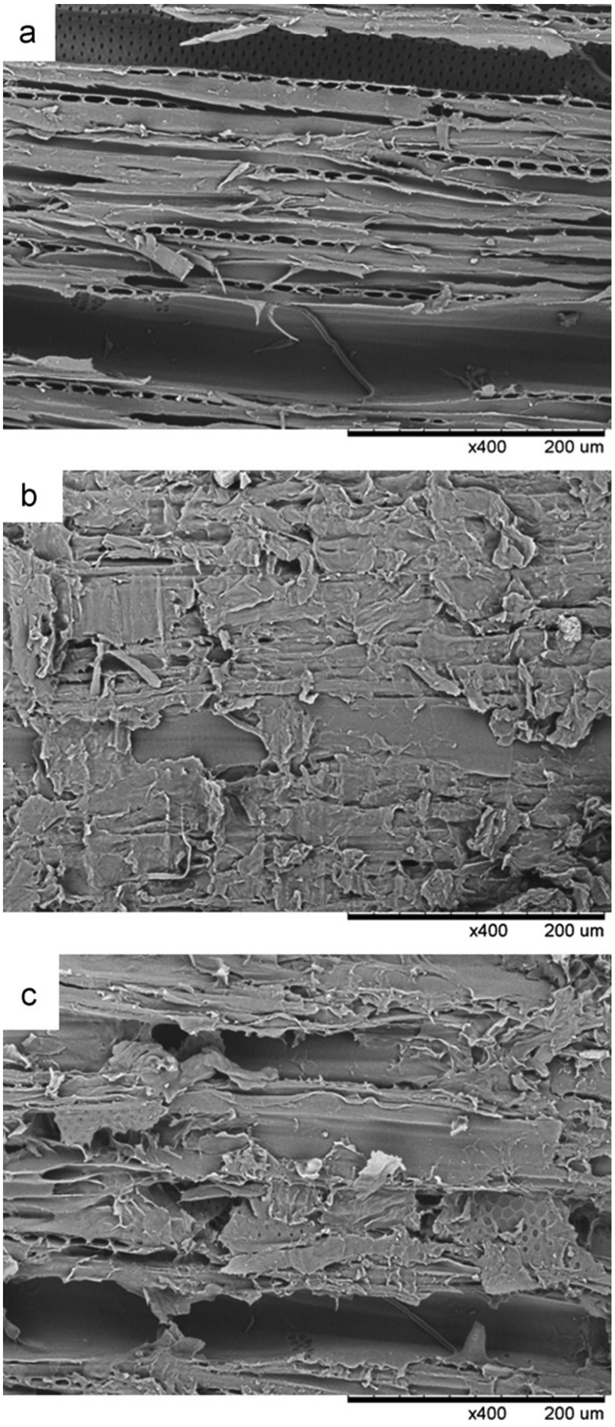

Fig. 6. SEM images of the fractured adhesion interfaces for immersed specimens. (a) Wood surface without adhesives, (b) IA-PAE-SF adhesive, and (c) NaOH–SF adhesive.

into water during the immersion in water at 63 °C. Therefore, the interaction between the adhesive and the wood surface was maintained very well, and the wet strength of such specimens could pass 0.7 MPa. However, there was no such strong cross-linking network in the glue line of NaOH–SF adhesive. And there were more components of the glue line lost into water during the immersion in water at 63 °C. Therefore, the fractured adhesion interface of immersed specimens bonded by NaOH–SF adhesive (Fig. 6c) was different from the one bonded by IA-PAE–SF adhesive in two aspects. On one hand, interaction between such a glue line and wood surface was weakened due to the loss of adherent components. On the other hand, the glue line was easily destroyed during the shear strength test because of the movement of soy proteins. As a result, there were many cracks and gaps on wood surface bonded by NaOH–SF adhesive (Fig. 6c).

Epichlorohydrin is widely used in the production of numerous synthetic materials, including epoxy resins, polyamide resins, plasticizers, and adhesives. As epichlorohydrin can severely damage the skin and eyes, safety protection equipments have to be used in experiments and industries [37]. After reacted with IA-PADA to form IA-PAE, epichlorohydrin was unlikely emitted from the resultant IA-PAE solutions, IA-PAE–SF adhesives and plywood bonded with such adhesives. However, further measurements have to be done to make sure there is no residual epichlorohydrin before IA-PAE–SF adhesives can be commercialized to bond plywood [3].

4. Conclusions

An itaconic acid-based PAE was synthesized and characterized. N-(3-chloro-2-hydroxypropyl) groups and azetidinium rings performed as functional groups of IA-PAE to improve water resistance of plywood bonded by IA-PAE–SF adhesive. Water resistance of IA-PAE–SF on plywood was comparable to that of C-PAE–SF. Formation of cross-linking network was demonstrated to account for improving water resistance of plywood bonded by IA-PAE–SF adhesive. All results showed that it is feasible to synthesize bio-based PAE using itaconic acid. Bio-based IA-PAE is expected to bring a sustainable development to soy-based adhesives.

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