Research Progress on Formaldehyde-Free Wood Adhesive Derived from Soy Flour

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Abstract

Soy-based adhesives have been regarded as the most suitable candidates for wood industry. For a widespread use of soy-based adhesives, new technologies need to be developed to improve the water resistance. An overview on the methods to improve water resistance of soy-based adhesives is presented. Denaturants were once considered necessary to modify soy protein. However, water-resistant soy adhesives could be prepared by simply removing water-soluble carbohydrates and low molecular peptides from soy flour. In addition, proper grafting and cross-linking agents help to prepare water-resistant soy-based adhesives, which are used widely to bond interior wood composites. In particular, a new type of polyamidoamine (PADA) resin and an itaconic acid-based polyamidoamine-epichlorohydrin (IA-PAE) resin were synthesized to perform as cross-linking agents for soy-based adhesives. This review concludes that soy-based adhesives have great potential for use in numerous applications. However, future work is still needed to make soy-based adhesives more competitive with synthetic adhesives.

Keywords: soy adhesive, formaldehyde-free adhesive, denaturation, cross-linking agent

1. Introduction

Soy-based adhesives were once the dominant glue for manufacturing plywood in the 20th century [1]. The soy flour (SF) adhesives used at that time were made under highly alkaline conditions. They were also modified by casein, blood, borax, sodium silicates or carbon disulfide to give better water resistance. Such soy adhesive typically had a characteristic of high viscosity, low-solid content, and short usable pot life [1]. Plywood bonded by such soy flour-based adhesives (SAs) was adequate for interior applications. However, fossil fuel–based adhesives, such as urea-formaldehyde (UF), replaced soy-based adhesives for interior applications because UF adhesives were cheaper, easier to use, and more water resistant.

Formaldehyde-based polymers are currently dominated in the adhesive systems to bond wood composites, including plywood, blockboard, particleboard, fiberboard etc. The cured adhesives are easily decomposed to emit formaldehyde, especially under elevated temperature and high humidity conditions. Many events were reported that human health was threatened by the toxicity of exposure to formaldehyde. The harm of formaldehyde to humans was proved by a large quantity of research. In 2004, formaldehyde was classified by WHO as a carcinogen to both human and animals [2]. Many countries carried out strict regulations to limit the emission of formaldehyde from wood composites. For example, Japan implemented F★★★★ standards in 2003. California implemented CARB standards in 2007. And the "Formaldehyde Standards for Composite Wood Product Act" was carried out in America since 2011. Besides the hazardous issues associated with formaldehyde-based adhesives, finite fossil reserves generate a commercial interest in bio-based technology. Therefore, many bioresources were considered as the feedstock to prepare wood adhesives. Research focused on dextrin, starch, tannin, lignin, and soy [3–7]. Among them, soy protein-based adhesives have been regarded as the most suitable candidates for wood industry [7].

Older soy adhesive formulations, made under alkaline conditions and using calcium compounds [8], were good adhesives for wood under dry conditions, but their water resistance was typically poor. None of these formulations made products that could fully meet current performance standards, such as ANSI/HPVA HP1-2009 4.6 three-cycle soak test for decorative plywood. Thus, for a widespread use of soy adhesives, new technologies need to be developed to improve the water-resistance.

2. Modification of soy-based adhesives

Based on their protein contents, soybean products are mainly divided into soy flour (SF), soy protein concentrate (SPC), and soy protein isolate (SPI) [9]. SF, which is produced by extracting the oil from soybeans, contains about 50% protein and 35% carbohydrates (water-soluble carbohydrates [WSCs] and water-insoluble carbohydrates [WISCs]). SPC containing 70% protein is produced by simply removing soluble carbohydrates from SF using ethanol extraction. SPI containing 90% protein is further purified product where all carbohydrates have been removed. Apparently, SPI is much more expensive than SPC and SF due to the increased processing costs and lower yield as a result of removal of carbohydrates.

2.1. Technologies to modify soy proteins

Proteins are the main adhesion components in soy flour. With over 90% protein content, SPI is the commercial soy product used in many soy reaction studies. A large number of published research focused on the method to modify soy protein isolate to improve its water resistance. SPIs have been altered using a variety of denaturants, including surfactants, amino-containing agents, alkali, and enzymes, in efforts to improve adhesive properties.

Native soy proteins have a secondary structure of α-helices and β-sheets, and a three-dimensional tertiary structure where α-helices and β-sheets fold into compact globules that interact with the surfaces of other globules forming a quaternary structure [10]. The physical and chemical properties of proteins are influenced by this complex structure.

To use soy proteins as wood adhesives, denaturation was once considered to be necessary to expose more polar groups for solubilization and bonding via hydrogen bonds [11]. Denaturation is a process that changes the multilevel structure of the protein molecule without breaking covalent bonds (**Figure 1**). The hydrophilic groups of soy proteins are uncoiled and exposed after denaturation. Proteins can be denatured by exposure to heat, acid/alkali, organic solvents, surfactants, or urea. Dispersion of soy proteins to denaturants' solution can break apart the native quaternary state into individual polypeptides folded into their native tertiary structure. This tertiary structure can be further opened into short-range and then long-range expansion, leaving the secondary structure intact. Further disruption of α-helices and ß-sheets provides a normal polymer chain [12].

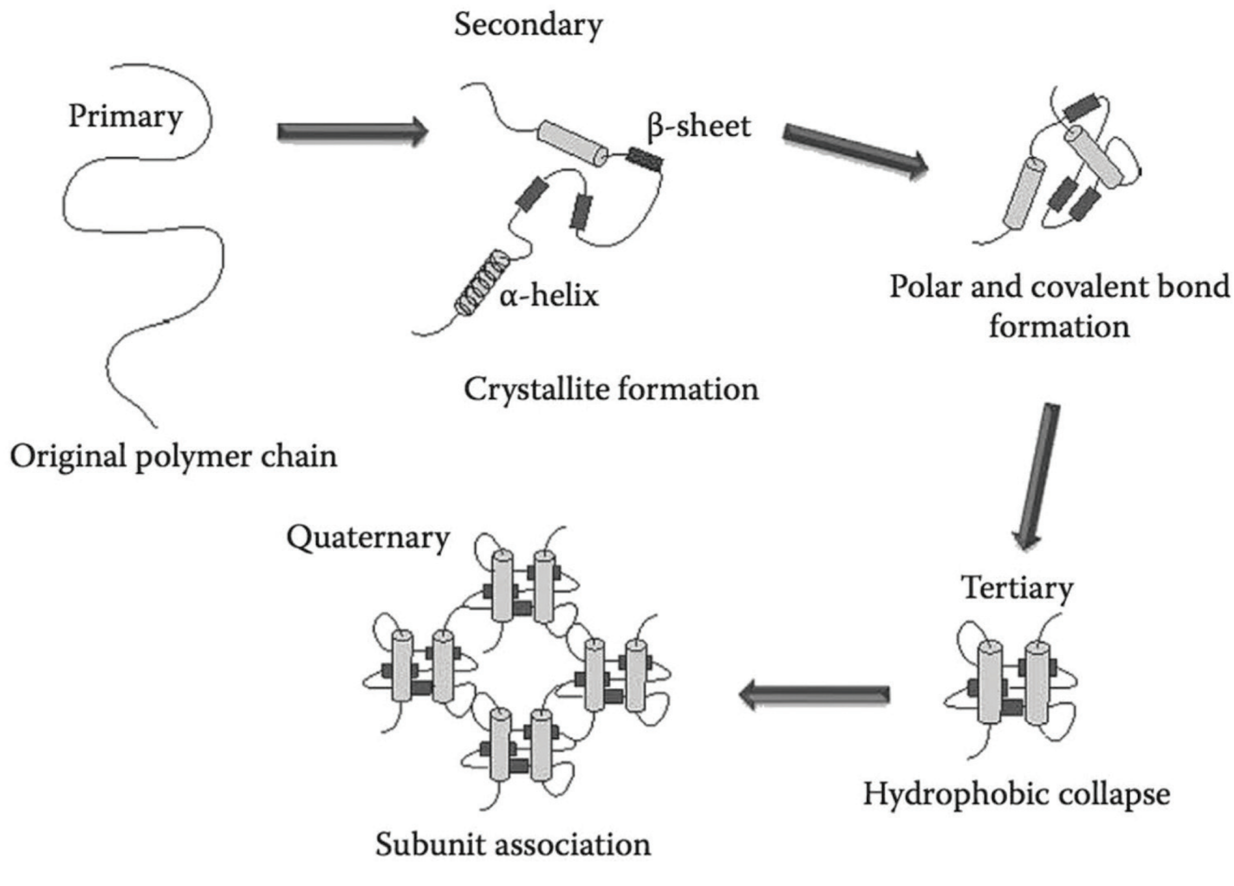

Figure 1. Multilevel structure of soy proteins [12].

Research on soy protein isolates had shown that both the pH value and the surfactant concentration have significant effects on the adhesive strength of modified soy protein isolate. Hettiarachchy et al. [13] used moderate alkali (pH=10) at 50°C to unfold soy protein isolate. Results showed that the adhesion strength and water resistance of modified SPI were dramatically improved. It is also possible to unfold protein complexes with urea, as its oxygen and hydrogen atoms interact with hydroxyl groups of the proteins and break down the hydrogen bonding in the protein body [14]. Too high a concentration of urea also breaks the secondary structure of the protein, and this can have a negative effect on the adhesive properties of the protein. The best adhesion has been found when the tertiary structure is disrupted, but disruption of the secondary structure is limited. Soy proteins can also be treated with sodium dodecyl sulfonate (SDS), sodium dodecyl benzene sulfonate (SDBS), and bioenzyme to break apart the quaternary protein structure while still retaining some secondary structure [15].

However, recent studies [16–18] showed that strong water-resistant soy protein-based adhesives could be prepared by adjusting the pH value to the protein's isoelectric point and they were much more stable than the traditional denatured soy adhesives when stored at room temperature.

Hunt et al.'s results also showed that SPI itself has a good water resistance even without any modification [19]. The results of our investigation also revealed that lab-prepared SPI could be used as adhesive directly and had a good wet strength without further modification. The wet strength of SPI was 1.09 MPa. The wet strength requirement for type II plywood (indoor application) was only >0.7 MPa according to Chinese National Standard [20]. We further found that the water-soluble carbohydrates and low molecular peptides (WSCs-LMPs) were the main causes of poor water resistance within soy flour, removing these fractions results in adhesives having less water attracting, less swelling (which can lead to the wet debonding of the adhesives). But the water-insoluble carbohydrates (WISCs) did not influence the water resistance of soy protein adhesive [21]. Based on these recent findings, we obtained water-resistant soy flour-based adhesives (SAs) by simply removing WSC-LMP from soy flour (**Table 1**, unpublished results) leaving the multilevel structure of soy protein retained.

	Protein content (%)	Wet strength (MPa)	Water uptake	Viscosities of adhesives (cP)	Water-insoluble content of cured adhesive (%)
SF	56.3	0.43 ± 0.07 (c)	70%	12,500	64.5 ± 0.9 (d)
SA	69.8	1.02 ± 0.08 (a)	80%	10,200	86.2 ± 1.2 (b)
SPI	93	1.09 ± 0.05 (a)	72%	13,500	90.3 ± 0.5 (a)

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

Table 1. Relationship between wet strength and adhesive properties.

2.2. Soy adhesives modified with grafting and cross-linking agents

Traditional methods of preparing soy adhesives have not provided as much water resistance as their competing synthetic adhesives. Uncross-linked soy proteins are good adhesives for wood under dry conditions, but their water resistance is typically poor. In recent years, more emphasis has been placed upon covalent cross-linking.

A number of grafting agents were also applied to improve water resistance of soy proteins. OSA, dopamine, undecylenic acid, and $POCl_3$ were used to graft soy proteins [22–25]. After grafting, the attached groups acted as cross-linking agents, either via covalent esterification with hydroxyl groups on wood chips or via ionic and hydrogen-bonding interactions with functional groups in wood chips.

Epoxy resins were studied as effective cross-linking agents to modify soy adhesives [26–28]. Gao et al. [26] used DETA and EGDE as the modifiers to cross-link soy protein. The results showed that DETA reacted with EGDE to form a long-chain structure with epoxy groups, which cross-linked the soy protein molecules to form a denser cured adhesive layer to improve the water resistance of the resultant adhesive (**Figure 2**). Incorporating EGDE/DETA, the wet shear strength of the plywood bonded by the resultant adhesive was improved by 30.7% to 1.15 MPa, which met the requirement of Chinese National Standard for interior use.

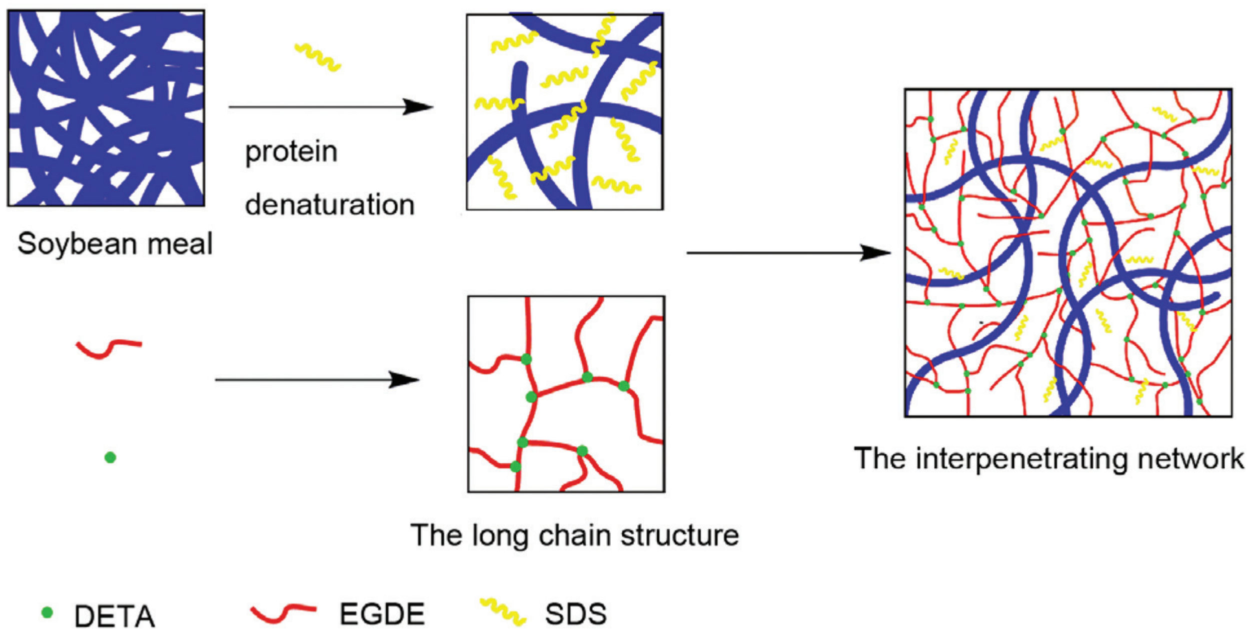

Figure 2. The diagram of DETA reacted with EGDE to form a long-chain structure [26].

However, epoxy-modified soy adhesives have the problem of low dry bond strength. Luo et al. [29] introduced polyisocyanate (pMDI) into epoxy-resin-modified soy-based adhesive to address the issue of low dry bond strength. By adding 2% pMDI, the dry and wet strength of the plywood was improved 29.5% and 39.7%, respectively. The pot life of resultant adhesive reached in 4 h which could meet the processing requirements of most manufacturers. The reactions between epoxy group and carbonyl as well as isocyano and amino were the main reasons for forming the cross-linking network of cured adhesive, thus, improved the dry and wet strength of the resultant plywood.

Soy flour adhesives using a polyamidoamine-epichlorohydrin (PAE) resin as a cross-linking agent are used increasingly as wood adhesives for interior products in North America [30]. The soy adhesive systems, SOYAD® [31], are easy to prepare in the panel mills and do not require harsh reaction conditions (**Figure 3**).

However, low-solid content and/or high viscosity are the main characteristics of most commonly used commercial PAE (C-PAE) [32]. For the purpose to improve the solid content of

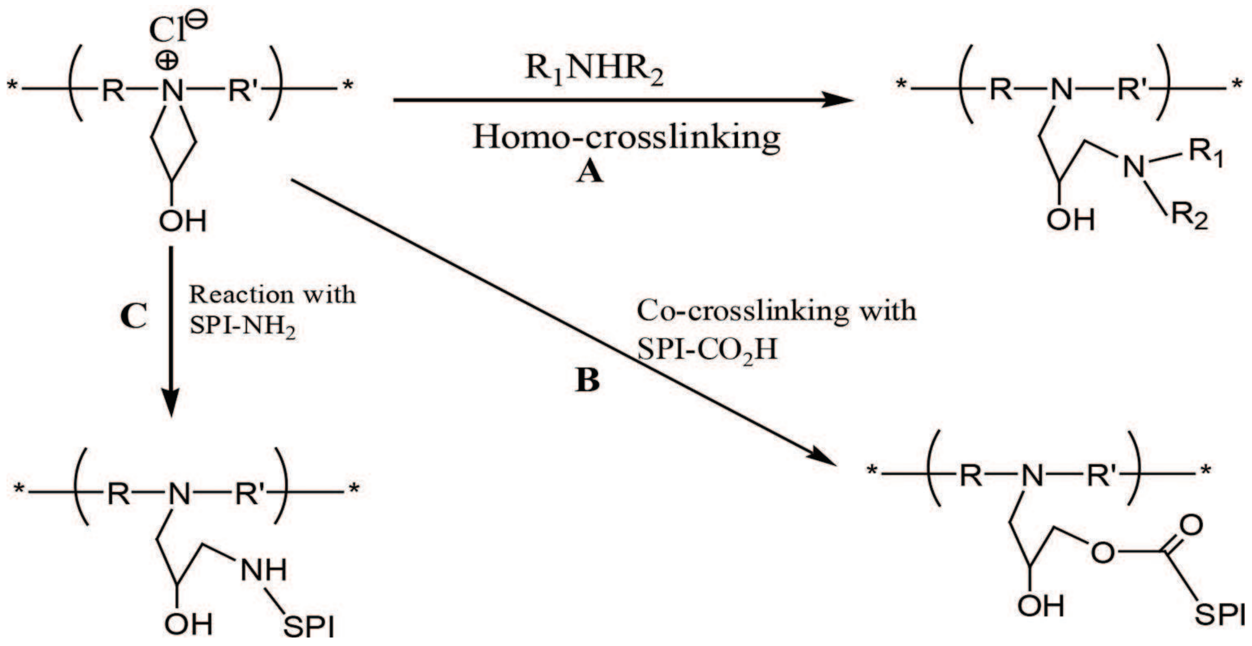

Figure 3. Proposed reactions of soy protein-PAE adhesives [30].

soy-based adhesives, curing agents which have a high-solid content and low viscosity are desired [32, 33]. Therefore, many studies had been done to prepare the curing agents for soy-based adhesives with a high-solid content and low viscosity. The results showed that a polyamine solution which had a solid content of 40–60% and a viscosity of less than 600 cP was preferable to prepare soy-based adhesives [32]. To solve the problems of low-solid content and high viscosity of curing agents, our group synthesized a new type of polyamidoamine (PADA) resin [34] for producing soy flour-based adhesives (**Figure 4**). The obtained PADA solution had high-solid content of 50 wt% and low viscosity of 270 cP. This PADA combined with maleic anhydride (MA) was employed as curing agent in SF-PADA-MA adhesive systems. The wet strength of plywood prepared at the optimum weight ratio was 0.82 MPa, which meant that the plywood could be used as type II plywood according to the Chinese National Standard GB/T 9846.7-2004. The cross-linking network formed by the reactions of PADA and MA was discussed as the main reason for improved water resistance (**Figure 5**).

The polyamines talked above are currently derived from fossil resources. In view of sustainability and environmental protection it is desirable to develop bio-based polyamines to perform as the cross-linking agents of soy flour-based adhesives. As epichlorohydrin can now be made from bio-based glycerol, Jang et al. [2] synthesized a bio-based polyamine by the reaction of ammonia with epichlorohydrin. PAE can also be obtained from renewable resources since adipic acid can now be made from bio-based materials [35]. Using other types of renewable raw materials, such as citric acid, to replace adipic acid is also an effective way to produce bio-based PAE resins [32, 33]. In our group, we used readily available renewable itaconic acid to synthesize bio-based PAE. Itaconic acid is a nontoxic compound which is considered as one of the top value-added building block chemicals that can be produced from sugars [36]. The obtained bio-based PAE will bring a sustainable development to wood product industry.

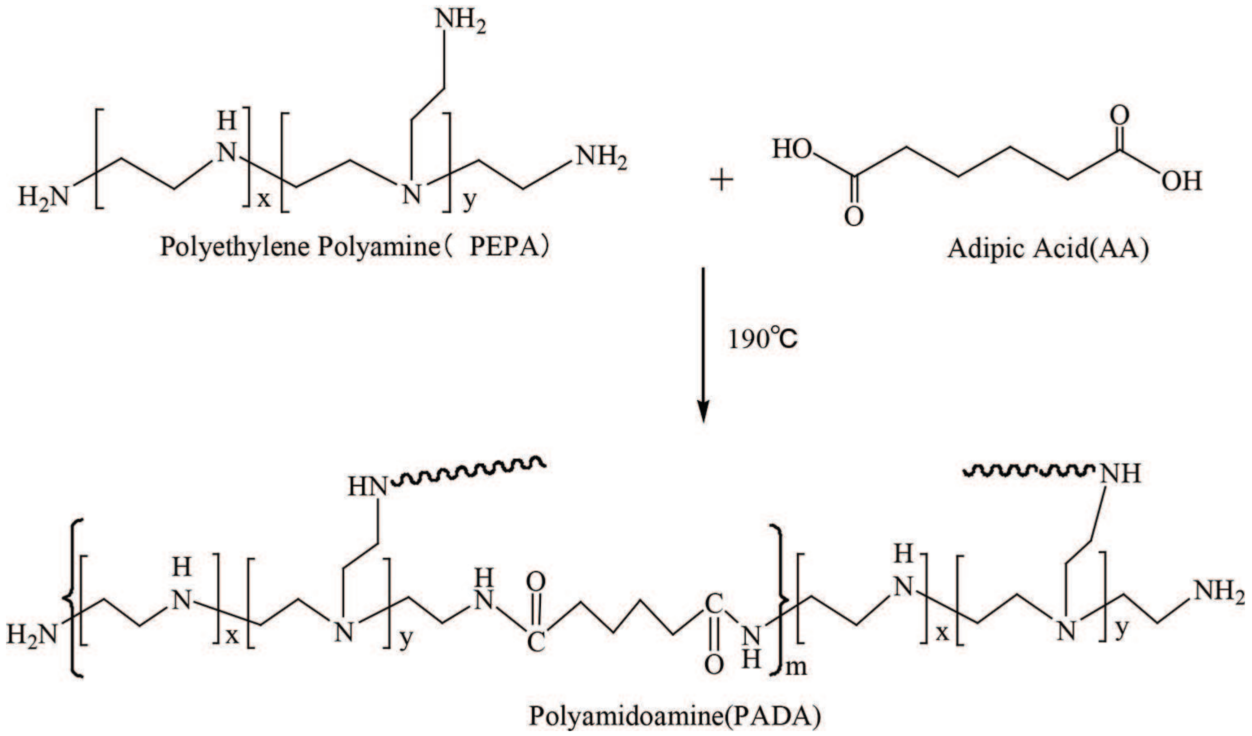

Figure 4. Synthesis of polyamidoamine resin [34].

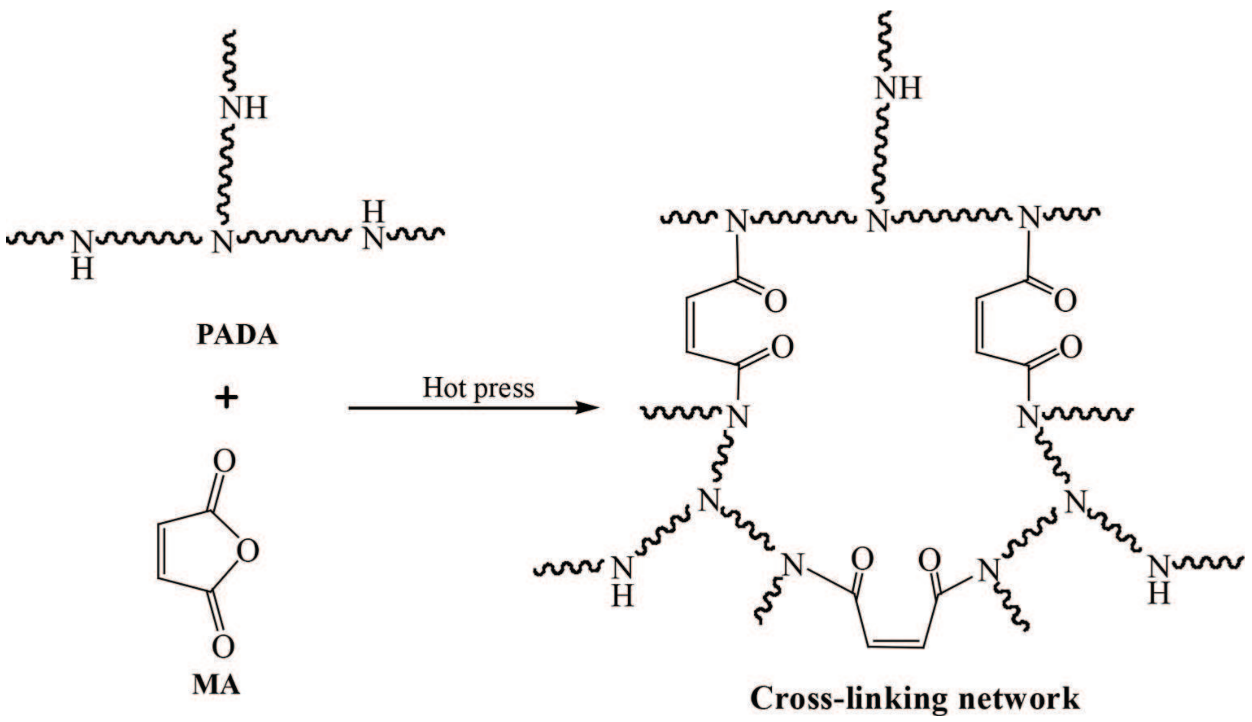

Figure 5. Proposed main curing reactions between polyamidoamine and maleic anhydride [34].

High molecular weight of PAE is not necessary for modifying soy-based adhesives, which is unlike the commercial PAE (C-PAE) used in papermaking process. Some PAE solutions with high-solid contents and low viscosities were synthesized [32, 33]. When preparing IA-PAE

[37], our main focus was to functionalize IA-PADA with ECH without causing much increase in molecular weight, which would limit the solid content of the resultant solution (**Figure 6**). Therefore, the obtained IA-PAE solution had a high-solid content of 50 wt % and low apparent viscosity of 144 cP. Wet strength of IA-PAE-SF on plywood was 0.95 MPa which was comparable to that of C-PAE-SF and met the requirements of Chinese National Standards for interior applications.

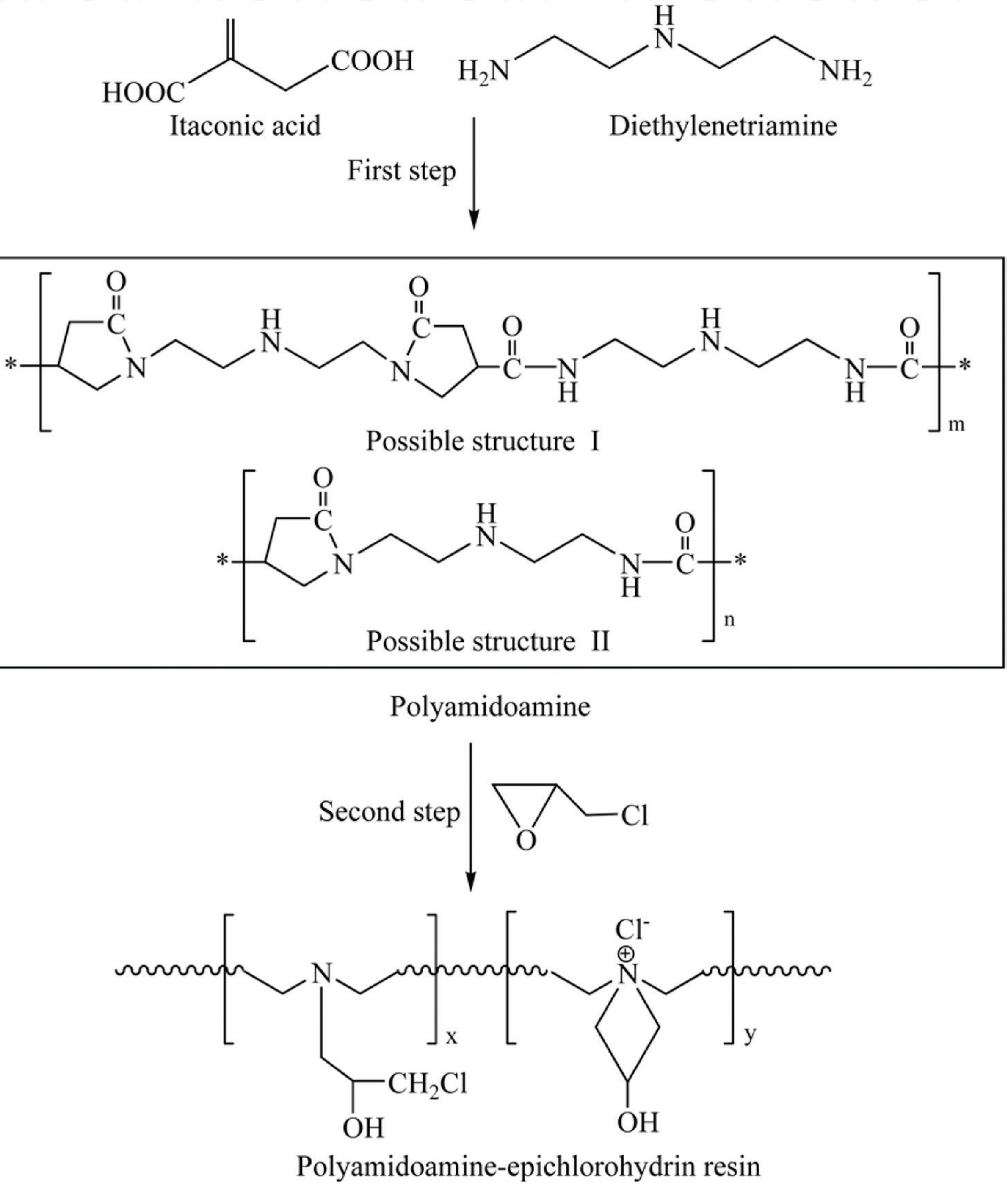

Figure 6. Synthesis process of itaconic acid-based polyamidoamine-epichlorohydrin resin.

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3. Conclusions and perspective

Because of the low cost and wide availability of soy flour, soy adhesives have the greatest potential for widespread use in the wood product industry. At the end of 2006, Columbia Forest Products, the largest manufacturer of hardwood veneer and hardwood plywood in the United States, converted all of its standard hardwood plywood production to produce formaldehyde-free panels called PureBond using SOAYD adhesive. Since 2005, more than 70 million hardwood plywood panels have been produced in North America with SOYAD adhesive technology. In fact, the Hardwood Plywood Veneer Association of North America estimated that more than half of the hardwood plywood panels manufactured in North America during 2010 were made with SOYAD adhesives.

In China, OZERO adhesive is widely used by Nature Flooring, Der Flooring, and Tubaobao Flooring to produce engineered wood flooring. OZERO adhesive is also used by Paterson to produce blockboard and by Furen Group Co. Ltd. to produce particleboard.

Although performance of soy adhesives has vastly improved, there is still a need for better products to make them more competitive with synthetic adhesives.

3.1. Solid content/fluidity

Soy proteins in water have high viscosities and are very shear thinning. The SOYAD®, OZERO®, and SOYBABY® [38–40] used in the wood industry only have a solid content of 28–40%. Making soy adhesives with higher solid contents is an important goal in order to compete more effectively with fossil fuel–based adhesives. This involves understanding how proteins and carbohydrates contribute to the high viscosity and designing methods to reduce the viscosity.

3.2. Carbohydrates

There are about 35% carbohydrates in soy four, including water-soluble carbohydrates and water-insoluble carbohydrates. Understanding the role of these carbohydrates will provide further insight into the use of soy four as a protein-based adhesive. Studies have shown that water-soluble portion is the main cause of poor water resistance. Removing the water-soluble carbohydrates can result in soy adhesives having higher water resistance. On the other way, methods to modify the carbohydrates in the soy flour should be developed so that the carbohydrates also contribute to the strength of the adhesive network.

3.3. Mould

The bondlines of soy-based adhesives are easily affected by mould, including *Rhizopus oryzae* and *Penicillium citrinum*. Sodium diacetate, sodium borate, sodium nitrite etc. were investigated as effective mildew preventives by Zhai et al. [41]. Results from the application of OZERO® adhesive showed that Kathon has an effective mould-proof property for soy adhesives. Caution needs to be drawn that the situation may be different when the wood products are exposed to specific environment conditions.

3.4. Aging properties

As derived from natural resources, bondlines of soy adhesives may be easily decomposed, especially under elevated temperature and high humidity. Zeng et al. [42] employed eight wet-dry cycles of 25°C, 63°C, and 95°C to accelerate the aging of poplar plywood bonded by soy-based adhesives. After eight wet-dry cycles under all three conditions, the strength of soy adhesive decreased. But the loss of strength was not as much as UF adhesive. Thus the aging resistance property was not a big problem of soy adhesive when used for interior applications.

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