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Storage stability of polyamidoamine-epichlorohydrin resin and its effect on the properties of defatted soybean flour-based adhesives

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ABSTRACT

A polyamidoamine (PA) without introducing epichlorohydrin, and two epichlorohydrin-modified polyamidoamine (PAE) samples with solid contents of 12% (PAE-12) and 25% (PAE-25) were synthesized, and their short-term storage stabilities, evaluated at intervals of at least 3 months were assessed for chemical structure, viscosity, pH, thermal degradation behavior, crystalline degree and wet bond strength. The results showed that PA was stable during storage for 98 days, while PAE-12 had better storage stability than PAE-25. PAE was active due to complex side reactions, as the number of azetidinium groups within PAE significantly decreased resulting from the ring open reaction after storage for 42–56 days, leading to decreased crosslinking degree and thermal stability, and increased crystalline content of defatted soy flour (DSF)-PAE adhesives. Thus, the wet bond strength of the corresponding plywood decreased with the increasing storage time of PAE-12 and PAE-25, and finally decreased to 1.05 MPa and 0.66 MPa after storage for 98 days, respectively. In order to ensure the water resistance of DSF-PAE adhesives, the preferable application time at room temperature is 3 months for PAE-12 and 4 weeks for PAE-25.

1. Introduction

Formaldehyde-based adhesives including urea-formaldehyde, phenol-formaldehyde, and melamine formaldehyde resins are still dominant in timber industry, due to their advantages like fast curing speed, high bonding strength, acceptable water resistance, long storage time and good technological applicability [1,2]. However, these adhesives are mainly derived from nonrenewable petroleum resources, and have serious formaldehyde emission issues, as formaldehyde has been classified as a potential human carcinogen [3–5]. Therefore, there is great interest in developing formaldehyde-free adhesives from sustainable and renewable resources such as protein, polysaccharide, lignin, and vegetable oil [6–8]. Among them, soybean protein is considered to be a promising candidate for the development of wood adhesives for wood composites, including plywood, chipboard, particleboard and fiberboard [9,10].

Soybean protein-based adhesives have been widely used in the plywood industry, which dates back to the 1920s because it easily-handled, environmentally friendly, abundant and inexpensive [11]. But after the 1960s, soybean protein-based adhesives have been replaced by petroleum-based adhesives due to the former exhibiting disadvantages including poor water resistance, low bonding strength, and relatively high cost [12–15]. Recently, driven by decreasing reserves of non-renewable fossil fuels and growing environmental concerns, soybean protein based adhesives have attracted renewed interest [8]. More than 15000 tons of commercial soybean adhesives have been consumed annually since 2016 in China for manufacturing plywood, chipboard and laminated wood composites.

Native soybean protein has a globular structure with hydrophilic groups exposed on the outside and hydrophobic groups buried inside, and such a globular structure prevents protein from achieving sufficient interaction with wood. Moreover, weak interactions, including hydrogen bonds, electrostatic bonds, van der Waals forces, disulfide bonds, and hydrophobic interactions, are not sufficient to withstand hot water attack, leading to low bond strength and poor water resistance. Therefore, many attempts have been made to improve the water resistance of soybean protein-based adhesives, and a variety of combined modification methods have been reported [16]. First, attempts have been made to unfold the ordered globular structure of soybean protein employing alkalis, acids, urea, and sodium dodecyl sulfate, which would expose its hydrophobic groups and increase the crystallinity degree to prevent water intrusion [14,17]. But plywood fabricated with

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Abbreviations: PA, polyamidoamine; PAE, epichlorohydrin-modified polyamidoamine; DSF, defatted soybean flour

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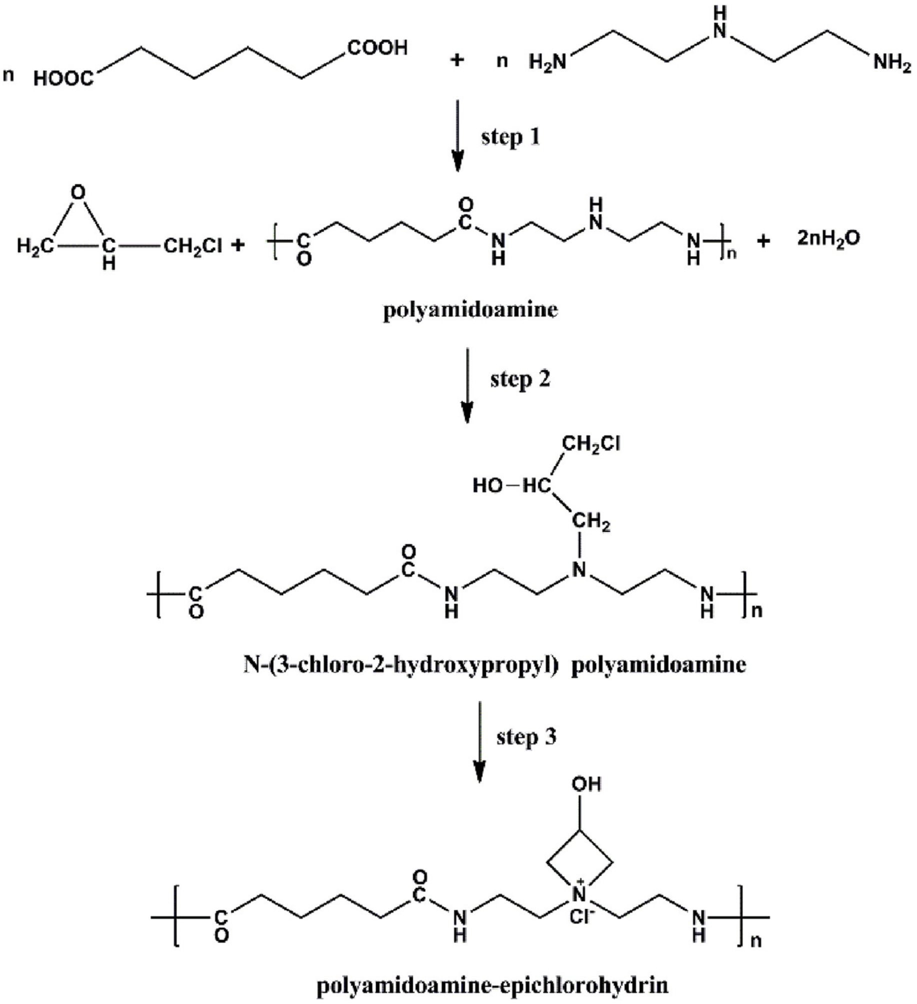

Fig. 1. Schematic for the synthesis of PAE resin.

such adhesives would not be able meet the requirements for structural use due to soybean protein being insufficiently modified to result in a water-insoluble crosslinked structure [18,19]. A second approach which has been considered involves modification via crosslinking or grafting using active crosslinkers, such as formaldehyde-based resins, maleic anhydride, latex-based resins and epoxy resins [20–24]. After crosslinking modification, the water resistance of soybean protein based adhesives were significantly improved due to the soybean protein molecules being crosslinked into insoluble three-dimensional network structures.

However, the utilization of soybean protein leads to much higher cost adhesives in comparison to commercially employed formaldehyde-based adhesives, thus greatly restricting the industrialization of soybean protein based adhesives. Soybean protein with more than 90% of protein content is generally extracted from defatted soy flour (DSF) with about 50% of protein content, and the cost of DSF is 3–5 times lower than that of soybean protein [19]. Therefore, the prevailing commercial soybean adhesive is a two-component system which consists of fine DSF powder and a crosslinker solution (such as commonly used 12 wt% PAE solution); with the DSF dispersed in crosslinker solution before use by mechanical blending for about 5 min at room temperature.

PAE is a water soluble polymeric resin that is widely used as a wet strength additive to paper sheets [25,26]. In recent years, PAE has been shown to be one of the most effective and practical crosslinkers for improving the water resistance of protein based adhesives [13,22,27,28]. However, PAE has active azetidinium groups, which can react with active hydrogen containing groups, such as amine, hydroxyl and carboxyl groups, which can cause a gradual deterioration in properties during storage [29,30]. Moreover, commercial PAE is usually accompanied with byproducts such as N-(3-chloro-2-hydroxypropyl) polyamidoamine and unreacted free epichlorohydrin that may also affect the storage stability of PAE resin. Therefore, it is of great significance to study the storage stability of PAE aqueous solutions and its effects on the bond properties of soybean adhesives. Obokata and Isogai investigated the structural changes of a PAE solution during storage for 9 years at 4 °C by ^{1}H NMR [31]. However, a storage temperature of 4 °C would not be considered suitable for practical industrial conditions (generally at room temperature from 20 to 30 °C). Moreover, the monitoring time interval of PAE is 0.8, 5.3 and 8.9 years, which is too long to meet the modern industry practical production requirement. The preferred storage time for the plywood industry is generally considered to be approximately 2–3 months, as the life cycle (the time from production, transport and storage to utilization) of fresh PAE resin is no more than 3 months. To the best of our knowledge, this is the first time that the short-term storage stability of a PAE solution has been thoroughly investigated together with the influence of storage time on the properties of a resultant DSF based adhesive that is a novel bio-based adhesive just commercialized in the plywood industry since 2016 in China.

In this work, PA, PAE-12 and PAE-25 were synthesized and their short-term storage stabilities were evaluated by means of Fourier transform infrared spectroscopy (FT-IR), ^{1}H nuclear magnetic resonance spectroscopy (^{1}H NMR), thermogravimetric analysis (TGA), X-

Table 1
Test parameters of synthesized PA, PAE-12 and PAE-25.

Samples	Solid content (%)	pH	Viscosity (mPa.s, 25 °C)	Free epichlorohydrin (ppb)
PA	45.0	10.98	690.6	–
PAE-12	12.0	2.63	56.2	63.89
PAE-25	25.3	2.51	96.5	52.66

ray diffraction (XRD), and plywood evaluation. This work has great significance to the plywood industry using DSF-PAE adhesives, providing theoretical support for the practical production.

2. Materials and methods

2.1. Materials

DSF with a 53.4% protein content was provided by Harbin High Tech Soybean Food Co. Ltd., China. Birch veneers with 1.8 mm thickness were obtained from Harbin Plywood Factory, Heilongjiang, China. Epichlorohydrin was purchased from Tianjin Bodi Chemical Co. Ltd. Both diethylenetriamine and adipic acid were supplied by the Xinquan Papermaking Additives Plant, Shandong, China. All other chemicals were analytical grade and were used without further purification.

2.2. Synthesis of PA, PAE-25 and PAE-12

PAE was synthesized by a three-step reaction as shown in Fig. 1. The molar ratio of diethylenetriamine/adipic acid/epichlorohydrin was maintained at 1.05/1/1. At the first step, adipic acid and diethylenetriamine were mixed in a three-necked flask equipped with a stirrer, a thermometer, and a condenser, then the mixture was heated at 170–195 °C for about 5 h to obtain PA, and the solid content was adjusted to about 45% by water. At the second step, N-(3-chloro-2-hydroxypropyl) polyamidoamine was prepared by reaction of PA solution and epichlorohydrin at 30 °C for 0.5 h, and then PAE-12 and PAE-25 were obtained after further heating at 60–70 °C for 6 h to the target viscosity (50–100 mPa s at 25 °C), the pH was adjusted to 2.4–2.6 using sulfuric acid before stopping the reaction [30]. The solid content, initial pH, viscosity, and unreacted free epichlorohydrin of samples measured by liquid chromatogram are list in Table 1.

2.3. Viscosity and pH value tracing

The viscosity and pH values of PAE-12 and PAE-25 were measured every two weeks at 25 °C using a pH meter (Sartorius PB-10, Shanghai) and a viscometer (Brookfield, USA), respectively.

2.4. ^{1}H NMR analysis

The ^{1}H NMR spectra of PA, PAE-12 and PAE-25 were measured using a 500 M ^{1}H nuclear magnetic resonance spectrometer (Bruker

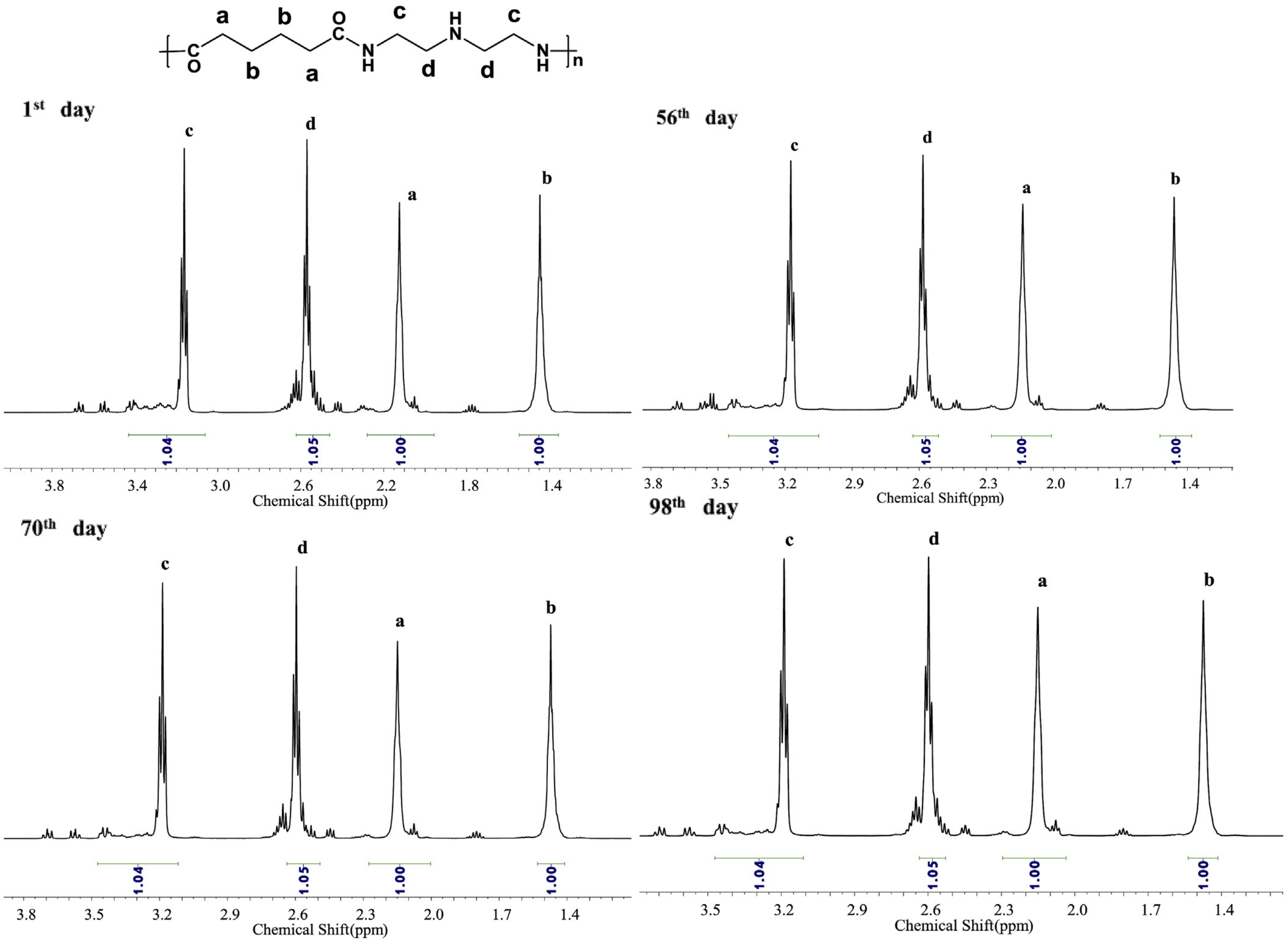

Fig. 2. ^{1}H NMR spectrum of PA solution after storage for 1 and 98 days.

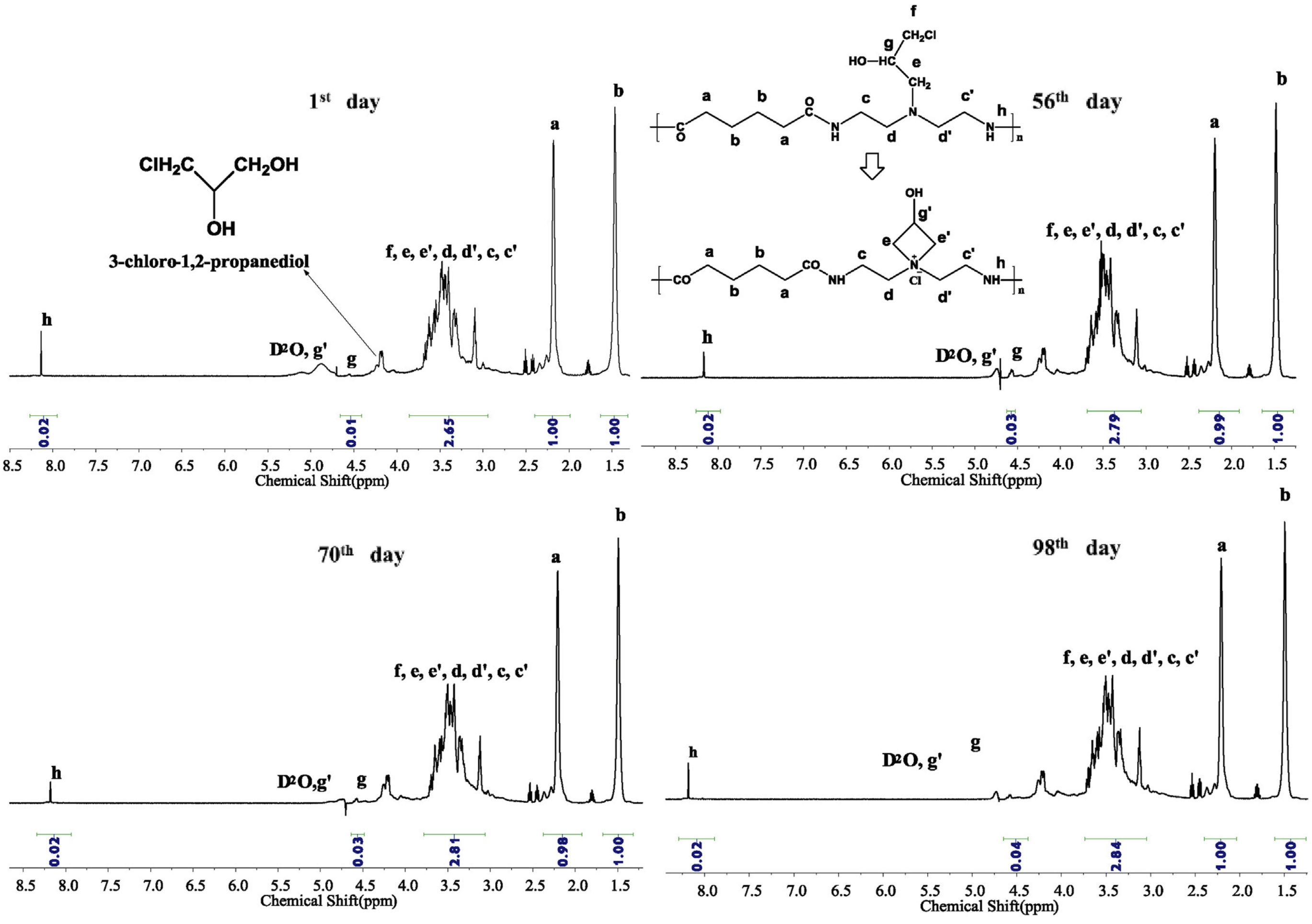

Fig. 3. ^{1}H NMR spectrum of PAE-25 solution after storage for 1, 56, 70 and 98 days.

AVANCE-III, Germany) every two weeks until the storage time reached 98 days at room temperature. The samples were dissolved in D_2O to obtain a 5% solids content. The water peak was suppressed during the test in order to get a high signal to noise ratio.

2.5. FT-IR analysis of PAE-12 and PAE-25

FT-IR spectra of PAE-12 and PAE-25 were obtained on a Spectrum One FT-IR spectrophotometer (Nicolet Co., USA) with a wavenumber range from 4000 to 400 cm^{-1}. Test time intervals investigated were 0 day, 56 days and 98 days.

2.6. FT-IR, TGA and XRD analysis of PAE modified DSF-based adhesives

Following storage for 0, 56, and 98 days at room temperature, 100 g of PAE-12 or PAE-25 was then blended with 30 g of DSF homogeneously to form a viscous slurry. The prepared adhesives were labeled DSF-PAE-12, and DSF-PAE-25 according to the crosslinkers employed.

The adhesives DSF-PAE-12 and DSF-PAE-25, with different PAE storage times, were cured at 120 °C for 2 h and then ground into a fine powder and passed through a 120-mesh sieve before undergoing FT-IR, TGA and XRD tests. The FT-IR tests were performed in the wavelength range from 4000 to 400 cm^{-1} on a Spectrum One FT-IR spectrophotometer (Nicolet Co., USA). Thermal stability was recorded on a TGA instrument (Netzsch 209 F3, German). Fine ground powders (5 ± 0.1 mg) were weighed in a platinum cup and scanned from 25 to 600 °C at a heating rate of 10 °C/min under an argon atmosphere. The XRD tests were performed on a D/max-2200 diffractometer (Rigaku International Corporation, Tokyo, Japan) equipped with a Cu-Kα (λ = 0.154 nm) radiation source at an accelerating voltage of 40 kV, and a current of 30 mA. The diffraction data was gathered from 5 to 60° with a step size of 2°/min.

2.7. Fabrication of plywood and its water resistance evaluation

Three-layer plywood panels were fabricated by spreading adhesive uniformly on both sides of birch veneers with an adhesive loading of 190 g/m^2 (single bondline). The adhesive-coated veneers were stacked between two uncoated veneers while the grain directions of adjacent veneers were perpendicular to each other. The glued veneers were cold pressed at 0.80 MPa for 1 h and then hot pressed at 1.3 MPa and 120 °C for 4.5 min. The prepared plywood panels were then stored in an ambient environment for 24 h before evaluation. A total of 20 specimens with a bond area of 25 mm × 25 mm were cut from each panel according to commercial standard JIS K6806-2003 to determine the water resistance (or wet bond strength) using a tensile testing machine with a crosshead speed of 5 mm/min. The specimens underwent water soaking at 63 °C for 3 h before determination of the shear tensile strength under the wet state at room temperature.

3. Results and discussion

3.1. The storage stability of PA, and PAE solution

In order to assess the storage stability of PAE solution, the storage stability of PA solution was investigated because it is an intermediate for the PAE resin and is generated from a condensation reaction

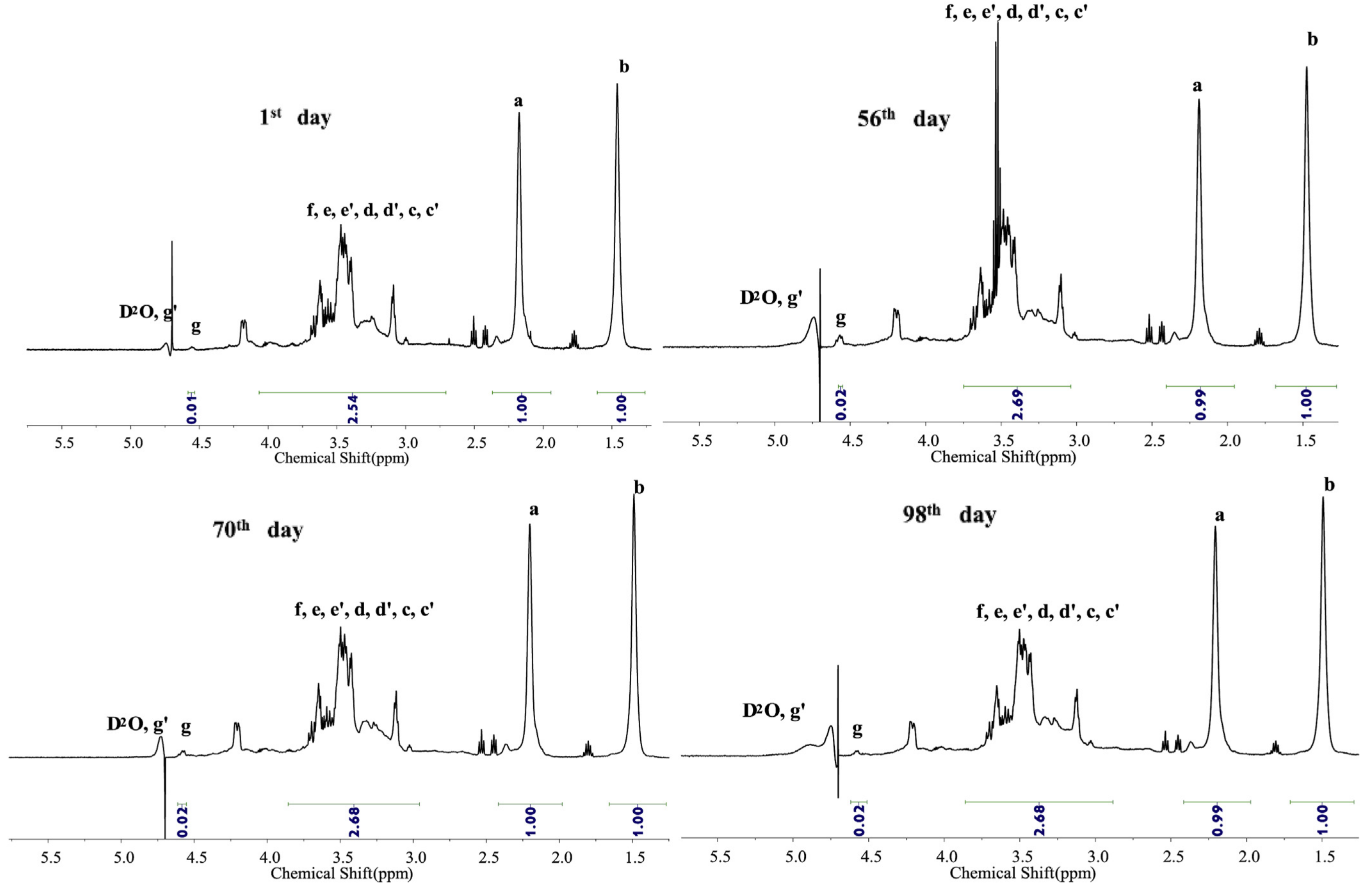

Fig. 4. ^{1}H NMR spectrum of PAE-12 solution after storage for 1, 56, 70 and 98 days.

Table 2
^{1}H integral area of PAE-25 resin during storage for different time.

Storage time (days)		A_a	A_b	$A_{c+c'+d+d'}$	A_e	$A_{e'+f}$	$A_f = A_{2g}$	$A_{e'}$	Introduction degree of epichlorohydrin (%)	Ring closing reaction ratio (%)
1		1.00	1.00	2.00	0.325	0.325	0.02	0.305	65.0	93.8
14		1.00	1.00	2.00	0.325	0.325	0.02	0.305	65.0	93.8
28		1.00	1.00	2.00	0.330	0.330	0.02	0.310	66.0	93.9
42		1.00	1.00	2.00	0.335	0.335	0.04	0.295	67.0	88.1
56		0.99	1.00	1.99	0.400	0.400	0.06	0.340	80.0	85.0
70		0.98	1.00	1.98	0.415	0.415	0.06	0.355	83.0	85.4
84	1.00	1.00	2.00	0.425	0.425	0.08	0.345	85.0	81.2	
98	1.00	1.00	2.00	0.420	0.420	0.08	0.435	84.0	81.0	

Note: A represents the integral area of the related ^{1}H.

between adipic acid and diethylenetriamine.

^{1}H NMR spectra of PA with various storage times are shown in Fig. 2. The peaks at $\delta = 1.4$ and 2.1 ppm can be assigned to the proton peak of methylene from adipic acid [31]. The signals at $\delta = 2.6$ and 3.2 ppm correspond to the proton of methylene from diethylenetriamine. All integral areas of the above peaks were observed almost unchanged during storage for 98 days, confirming that the chemical structure of PA was stable during storage for 98 days, and this result was in according with the previous reports by Obokata and Isogai [30].

The chemical structure changes of PAE-25 and PAE-12 during storage for 1, 56, 70, and 98 days are shown in Fig. 3 and Fig. 4. It has been reported that PAE solution contains some unreacted free epichlorohydrin and N-(3-chloro-2-hydroxypropyl) polyamidoamine thus not contributing to azetidinium ring formation [29,31]. The peak *b* at $\delta = 1.4$ ppm ascribes to the proton peak of methylene from adipic acid which was employed as an internal standard, and the integral area was set as 1.00. The signal at $\delta = 4.2$ ppm ascribes to the protons of methylene from 3-chloro-1,2-propanediol, which is a byproduct resulting from an addition reaction of acid to the epoxide ring of free epichlorohydrin [30], as shown in Eq.(1) of Fig. 3. The peak *g* at $\delta = 4.5$ ppm is the proton peak of methine from N-(3-chloro-2-hydroxypropyl) groups, and the signal *g'* at $\delta = 4.8$ ppm represents the methine proton of azetidinium rings in PAE-25, overlapped by the peak of D_2O [22].

Thus, the degree of introduction of epichlorohydrin can be quantitatively estimated by $A_e/0.5$, where A_e is the actual integral area of the peak *e* related to both N-(3-chloro-2-hydroxypropyl) groups and azetidinium groups, and 0.5 represents the theoretical value of the introduction of epichlorohydrin. The ring closing reaction ratio related to N-(3-chloro-2-hydroxypropyl) groups turned to azetidinium groups can be quantitatively estimated by the equation of $A_{e'}/A_e$, where $A_{e'}$ is the integral area of the peak related to azetidinium rings [31,32]. According to material balances during reaction equation shown in Fig. 3, $A_{c+c'+d+d'} = A_a + A_b$, $A_e = A_{e'+f}$, and $A_f = A_{2g}$. Therefore, A_e and $A_{e'}$

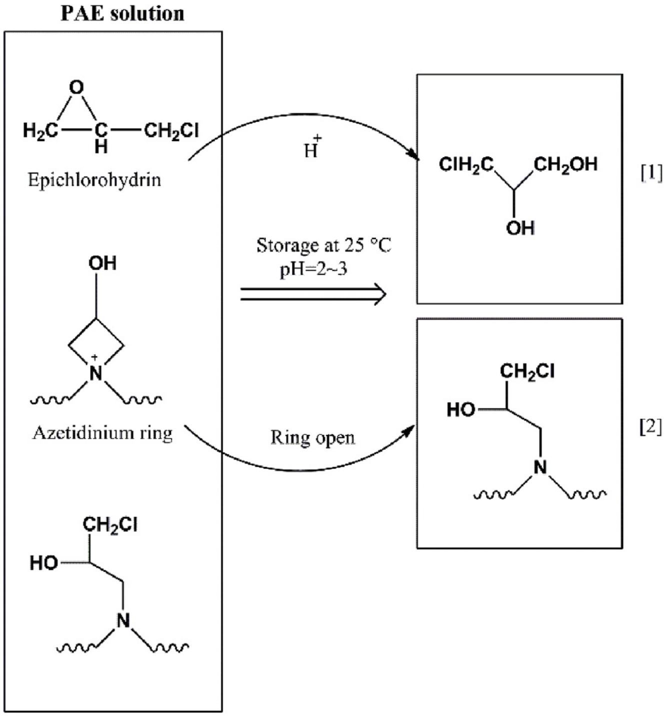

Fig. 5. Schematic for side reactions of PAE solution during storage.

can be calculated, and the results are shown in Table 2.

The introduction degree of epichlorohydrin for the fresh PAE-25 resin is 65.0%, which increases to 80.0% after storage for 56 days and continues to increase to 84.0% until 98 days. Accordingly, the azetidinium ring decreases from 93.8% to 81.0% after storage of PAE-25 for 98 days, leading to a 13.6% loss of azetidinium groups. These facts indicate that PAE-25 solution is unstable during storage due to: (i) some free epichlorohydrin molecules change to 3-chloro-1,2-propanediol (Eq (1) in Fig. 5), and (ii). some azetidinium rings open and form more N-(3-chloro-2-hydroxypropyl) polyamidoamine (Eq(2) in Fig. 5). via the self-crosslinking reaction of azetidinium groups with the unreacted secondary amines, terminal carboxyls and primary amines.

Compared to the ^{1}H NMR spectra of PAE-25, PAE-12 exhibits similar behavior with the introduction degree of epichlorohydrin increased and the closing reaction ratio of azetidinium ring decreased with the increase of PAE-12 storage time (Table 3). After storage for 56 days, the introduction degree of epichlorohydrin for PAE-12 is 70% which is lower than that of PAE-25 (80%). Moreover, the ring closing reaction ratio of PAE-12 decreases to 4.2% after storage for 98 days while that of PAE-25 is 12.8%, indicating that PAE-12 had less side reactions than PAE-25 during storage. Therefore, PAE with a low solid content had better storage stability than that with a high solid content after storage for 3 months, which can be attributed to the less effective collisions of low-solid-content PAE for sufficiently completing the side reactions during storage according to the Collision Theory [33].

Table 4
The pH value and viscosity of PAE-25 and PAE-12 during storage.

Storage time (days)	PAE-25		PAE-12	
	pH	Viscosity (mPa.s, 25 °C)	pH	Viscosity (mPa.s, 25 °C)
1	2.51	96.5	2.63	56.2
14	2.63	101.7	2.72	57.3
28	2.88	114.3	2.84	57.8
42	3.12	133.4	2.97	59.4
56	3.46	167.1	3.19	62.8
70	3.53	209.0	3.22	65.9
84	3.60	230.5	3.20	67.2
98	3.64	268.3	3.30	73.5

Moreover, the pH of PAE-12 and PAE-25 resin increased from 2.63 to 3.30 and from 2.51 to 3.64, respectively, with the storage time increasing from 1 to 98 days (Table 4). And the viscosity of PAE-12 and PAE-25 resin increased from 56.2 to 73.5 mPa s and from 96.5 to 268.3 mPa s, respectively. These facts also confirm the occurrence of self-crosslinking reactions during storage.

FT-IR was performed to further confirm the chemical structure changes of the PAE resin during 98-day storage. The FT-IR absorption band at approximate 1090 cm^{-1} shown in Fig. 6 A and Fig. 6 B is ascribed to the hydroxyl groups within the azetidinium ring of the uncured PAE-25 and PAE-12. The decreases of peak intensity at 1090 cm^{-1} with the increasing storage time of PAE-12 and PAE-25 confirms the loss of azetidinium rings, which accord with the ^{1}H NMR results in Fig. 2.

In the FT-IR spectra of the DSF based adhesives (Fig. 6C and 6 D), the absorption band at 3296 cm^{-1} is attributed to the vibrations of O—H and N—H of DSF [16,34]. The peaks at 2937 and 2864 cm^{-1} corresponding to the symmetric and asymmetric stretching vibrations of the $-CH_2$ group of DSF adhesives are selected as internal standards [35]. The band observed at 1627, 1542 and 1268 cm^{-1} ascribe to the typical characteristic peaks of amide I (C=O stretching), amide II (N—H bending) and amide III (C—N and N—H stretching), respectively [2,36].

As shown in Fig. 6C, the peak of the DSF-PAE-25 adhesives at 1268 cm^{-1} shifts to 1245 cm^{-1} after storage of PAE-25 for 3 months, and the absorption bands at 1245 (assigned to C—N—C) and 1130 cm^{-1} (assigned to C—O—C) become broader and smaller with increasing PAE-25 storage time, indicating that crosslinking reactions between the PAE and DSF adhesive systems decreased. The cured DSF-PAE-12 adhesive also exhibits similar behavior to that of DSF-PAE-25 (Fig. 6 D).

3.2. *Thermal degradation behavior and crystallinity of the resultant adhesives*

The thermal stabilities of cured DSF-PAE-12 and DSF-PAE-25 adhesives are shown in Fig. 7 A and 7 B. With the storage time of PAE-12 and PAE-25 resin increasing from 0 to 98 days, the char residues values (550 °C) of DSF-PAE-25 and DSF-PAE-12 adhesives decrease gradually, indicating that the thermal stabilities of the two adhesives decrease

Table 3
^{1}H-integral area of PAE-12 resin during storage for different time.

Storage time (days)	A_a	A_b	$A_{c+c'+d+d'}$	A_e	$A_{e'+f}$	$A_f = A_{2g}$	$A_{e'}$	Introduction degree of epichlorohydrin (%)	Ring closing reaction ratio (%)
1	1.00	1.00	2.00	0.270	0.270	0.02	0.250	54	92.6
14	1.00	1.00	2.00	0.270	0.270	0.02	0.250	54	92.6
28	1.00	1.00	2.00	0.280	0.280	0.02	0.260	56	92.8
42	1.00	1.00	2.00	0.275	0.275	0.02	0.255	55	92.7
56	0.99	1.00	1.99	0.35	0.35	0.04	0.310	70	88.6
70	1.00	1.00	2.00	0.34	0.34	0.04	0.300	68	88.2
84	1.00	1.00	2.00	0.34	0.34	0.04	0.300	68	88.2
98	0.99	1.00	1.99	0.345	0.345	0.04	0.305	69	88.4

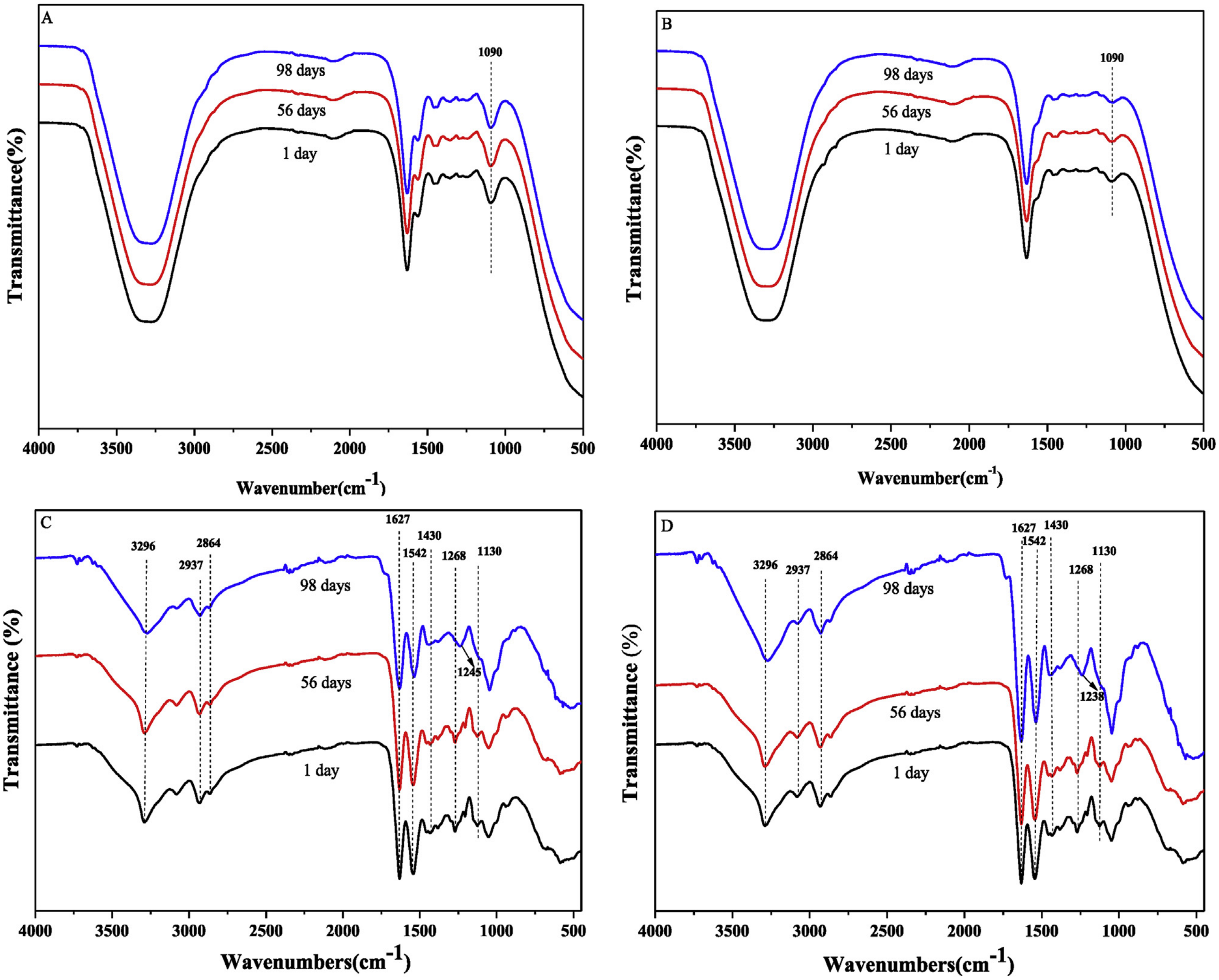

Fig. 6. FT-IR spectra of uncured PAE-25 (A) and PAE-12 resin (B), and cured DSF-PAE-25 adhesives (C) and DSF-PAE-12 adhesives (D) with various storage times.

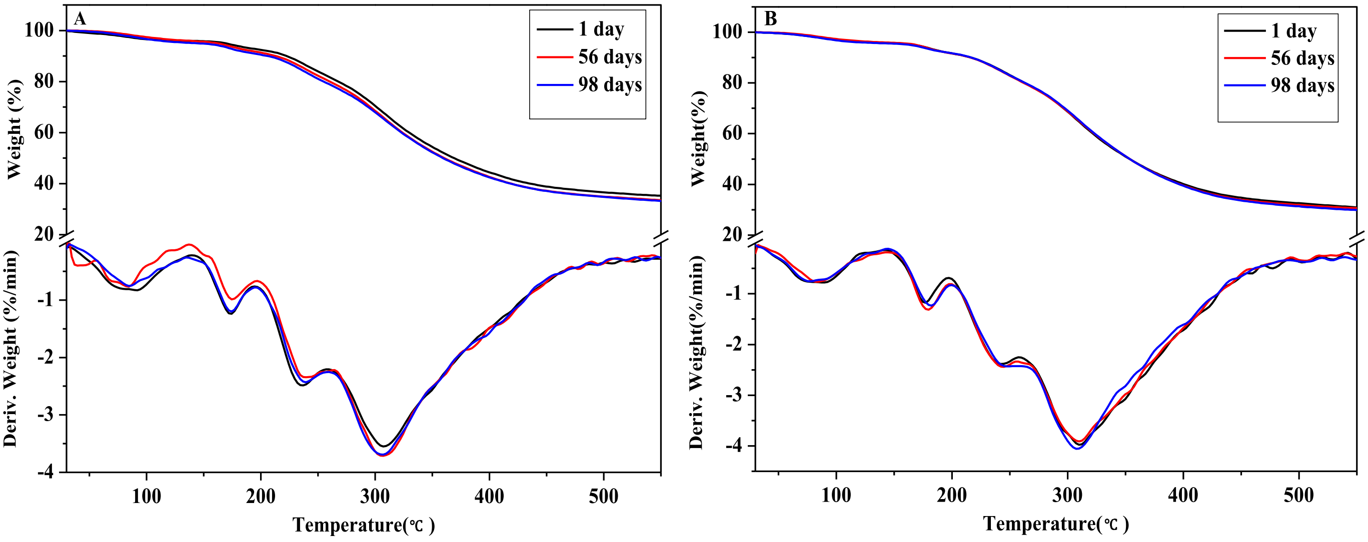

Fig. 7. TG and DTG curves of DSF-PAE-25 adhesives (A) and DSF-PAE-12 adhesives (B) with various storage times.

with increased PAE storage time due to the loss of azetidinium groups in the PAE resin (^{1}H NMR results in Tables 2 and 3) that leads to a decrease in the crosslinking degree of the DSF-PAE adhesives.

XRD analyses of cured DSF based adhesives prepared with PAE-25 and PAE-12 with various storage times indicated that all samples had strong characteristic peaks at 2θ near 21.4° (Fig. 8 A and 8 B), which belong to the ordered β-sheet structure of a protein molecule [2,6,12]. As exhibited in Fig. 8 A, the crystalline degree of the cured DSF-PAE-25

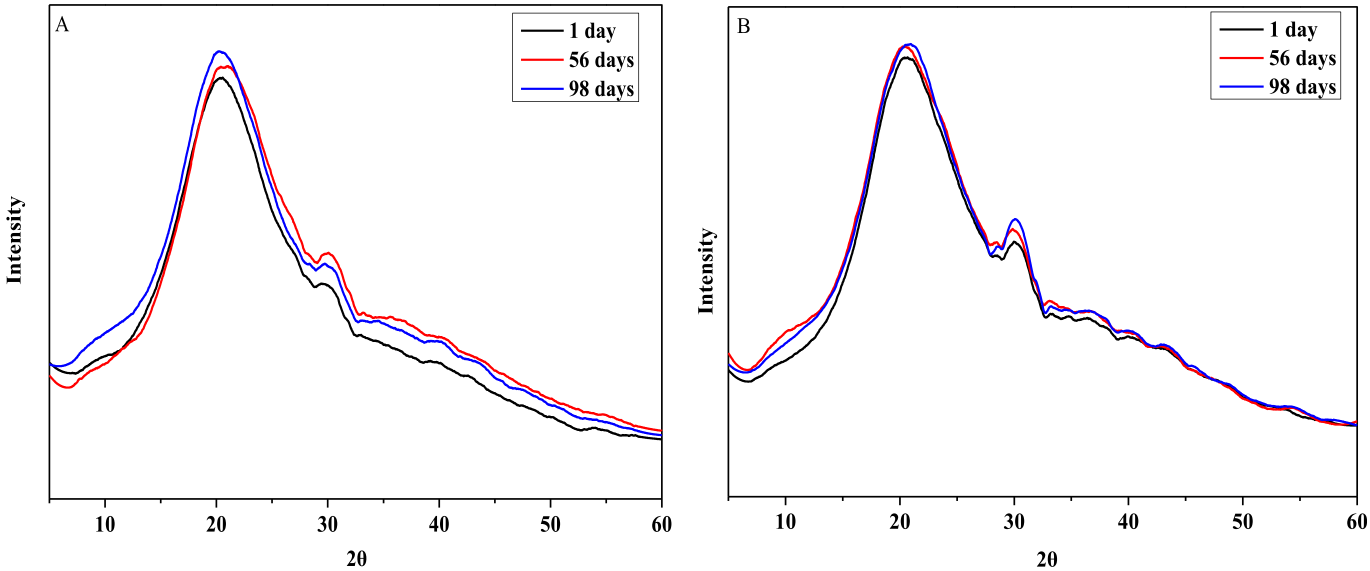

Fig. 8. XRD patterns of DSF-PAE-25 adhesives (A) and DSF-PAE-12 adhesives (B) with various storage times.

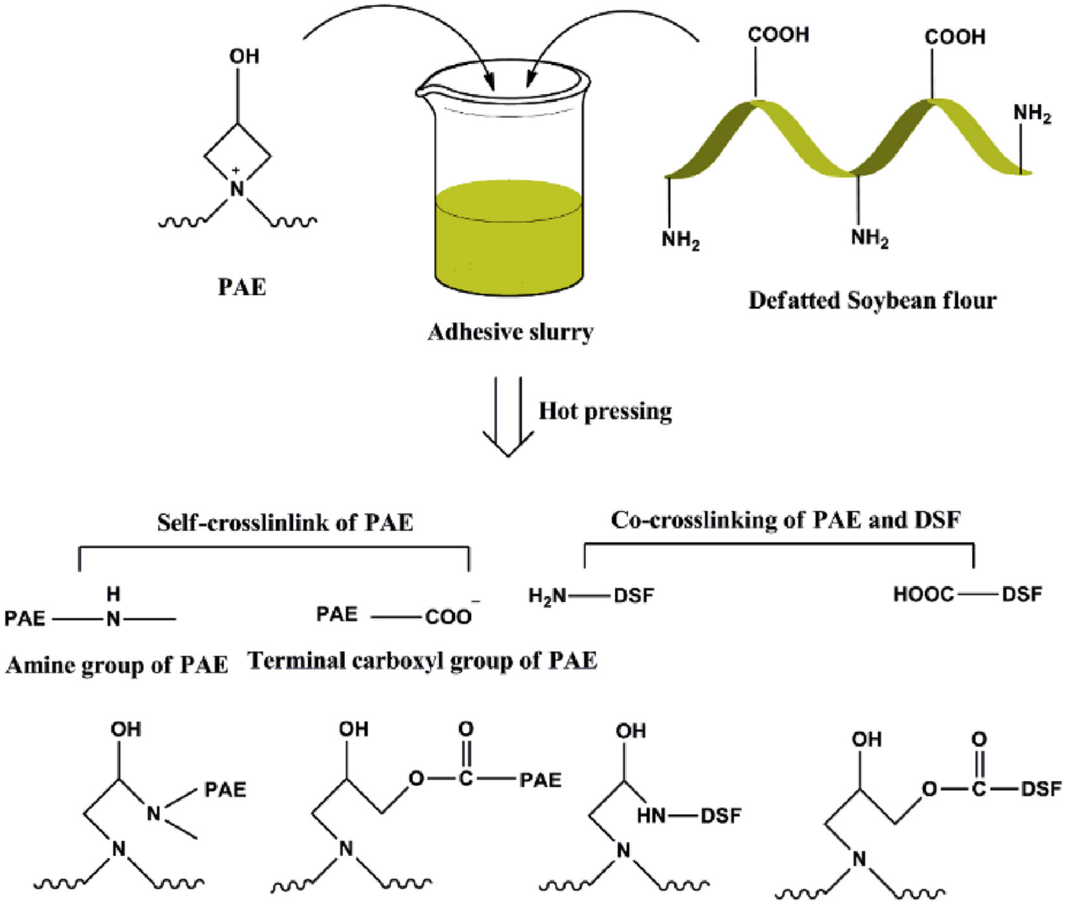

Fig. 9. Schematic illustration of the crosslinking reaction in PAE crosslinked DSF based adhesives.

adhesives increase with the storage time of PAE-25 increasing from 0 to 98 days due to a significant consumption of reactive azetidinium groups after storage for 56 days. Thus, the crosslinking reactions between PAE and DSF decrease because of the loss of reactive azetidinium groups during storage, which increases the chance for DSF adhesive to form ordered crystalline structures [4,28]. The crystalline degree of the cured DSF-PAE-12 adhesive also exhibits a similar tendency (in Fig. 8 B). However, the crystalline degree of DSF-PAE-25 adhesives after storage for 98 days is more than that of DSF-PAE-12, further implying that PAE-25 has an inferior storage stability than the PAE-12 resin because PAE-25 resin, with a high solid content, has more chances to undergo self-crosslinking or other side reactions that consume azetidinium groups during storage. Consequently, commercial PAE products should preferably have a solid content of approximately 12.5% [23, 35].

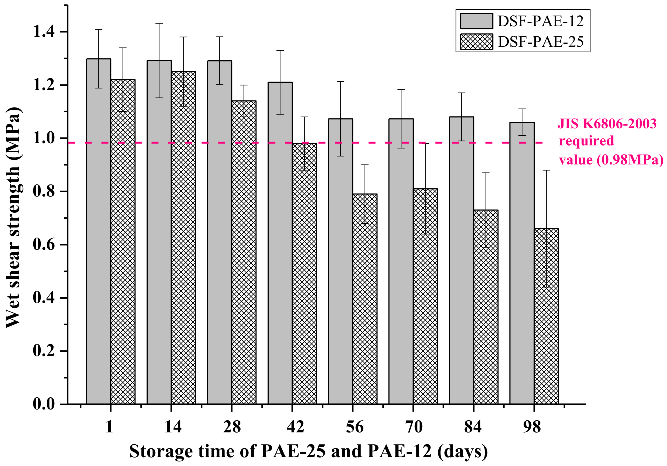

Fig. 10. Wet shear strength of plywood bonded by DSF-PAE-12 adhesives and DSF-PAE-25 with different PAE-12 and PAE-25 storage time.

3.3. Wet shear strength of the plywood

The crosslinking reactions of PAE-modified DSF adhesives are illustrated in Fig. 9, which indicates that the azetidinium groups of PAE can effectively crosslink with primary and secondary amines, and carboxyl groups within DSF to form three-dimensional crosslinking networks that improve the water resistance of the DSF based adhesives. The water resistance of DSF based adhesives prepared with PAE at various storage times are investigated every two weeks by plywood evaluation in terms of wet shear strength (Fig. 10). The plywood panels bonded by DSF adhesive with fresh PAE-12 and PAE-25 have wet shear strengths of 1.30 MPa and 1.22 MPa, respectively. After storage for 56 days, the wet shear strength of plywood bonded with adhesive DSF-PAE-12 decreases by 17.69% to 1.07 MPa, and that of plywood with adhesive DSF-PAE-25 decreases by 35.25% to 0.79 MPa. This indicates that PAE-12 has a better storage stability than PAE-25. Based on the H NMR analysis and XRD analysis, the decreased water resistances of DSF-based adhesives with storage times shown in Fig. 10 are mainly attributed to the loss of azetidinium groups in the PAE solution that leads to decreased crosslinking of the cured DSF-based adhesive.

A further increase in storage time from 56 to 98 days, results in a reduction in the rate of decline of wet shear strength (with both PAE-12 and PAE-25). Following storage for 98 days, the wet bond strength of plywood fabricated with DSF-PAE-12 adhesive decreases to 1.06 MPa, which is close to the requirements of the JIS K6806-2003 commercial standard (0.98 MPa). As for PAE-25 which was stored for 6 weeks (42 days), the wet bond strength of plywood fabricated with the DSF-PAE-25 adhesive decreased to 0.97 MPa, which is slightly lower than the required value (0.98 MPa). These results imply that the most allowable storage times of PAE-12 and PAE-25 at room temperature (20–30 °C) are 3 months and 4 weeks, respectively, for ensuring the water resistance of plywood panels; and that PAE-12 is more preferable than PAE-25 because of its much longer storage time.

The water resistance of adhesive composed of DSF and PA was also evaluated by plywood evaluation under the same conditions, however, all the resultant plywood specimens did not withstand water soaking at 63 °C because of the absence of crosslinkable azetidinium groups.

4. Conclusions

The short-term storage stabilities of PA, PAE-25 and PAE-12 are evaluated in this work. PA is stable during storage for 3 month, while PAE undergoes complex side reactions during storage, and PAE-12 with a low solid content has better storage stability than that of PAE-25 with a high solid content. The DSF based adhesives show decreased water resistance with increasing PAE storage time due to the reactive azetidinium group loss of PAE solution and the decreased crosslinking degree of cured adhesive. The most allowable storage times of PAE-12 and PAE-25 at room temperature (20–30 °C) are 3 months and 4 weeks, respectively, which makes the DSF-based adhesive still having a wet bond strength more than the required value (0.98 MPa) according to JIS K6806-2003 commercial standard.

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