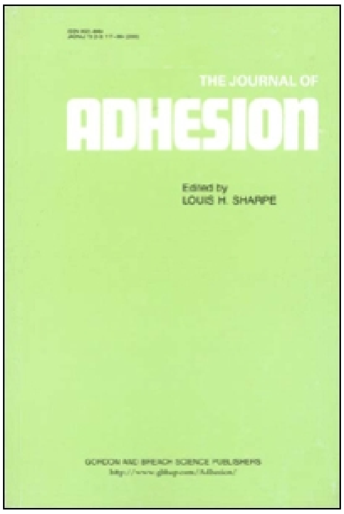

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# Investigation of Adhesion Performance of Aqueous Polymer Latex Modified by Polymeric Methylene Diisocyanate

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*Aqueous polymer isocyanate (API), which has good adhesive properties at ambient temperature and excellent resistance to warm/boiling water, and is friendly to the environment, is widely used in the timber-processing industry. To prepare high performance API, vinyl acetate homopolymer and copolymer emulsion were respectively cross-linked by three types of polymeric methylene diisocyanate (p-MDI). The potlife, curing time, bonding strength, and water resistance of API adhesives were tested with different cross-linkers and varying loadings (5–20%). Also the effect of polyvinyl alcohol (PVOH) content of aqueous vinyl latex on the performance of API was investigated. It was shown that the potlife and curing time of API were obviously influenced by the types of cross-linker and its loading. Correct loadings of p-MDI as crosslinker can remarkably improve the adhesive performance of aqueous polymer emulsion at ambient temperature. Excess cross-linker cannot maintain such an effect of strengthening and may decrease considerably the bond properties of API. The warm- and boiling-water resistance of API improved markedly with increasing cross-linker loading, where emulsifiable*

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*isocyanate gave better cross-linking performance, and p-MDI mixed with organic solvent was the secondbest. With the increase of PVOH content, the curing time of API increased, but no statistically apparent differences in the potlife of API were found. The bonding performance of API was improved as PVOH content increases, but excess PVOH also weakenes the warm- and boiling-water resistance of the joint.*

**Keywords:** Aqueous polymer isocyanate; Percent wood failure; Potlife; Shear strength; Water resistance

## 1. INTRODUCTION

Aqueous polymer isocyanate (API) is formed by blending polyisocyanate in water-based polymers with active hydrogen [1]. API adhesives, which are also called emulsion polymer isocyanates (EPI), were first developed in Japan in 1974. According to JAS 2053-1992 (Japanese Agriculture Standard), API adhesives can be used for structural chipboard production [2]. API adhesives have many distinctive characteristics, as follows:

1) are easily and safely applied and environmentally friendly,
2) high bonding strength,
3) reasonable water resistance and heat resistance,
4) resistant to aging,
5) no potentially harmful formaldehyde and phenol,
6) neutral pH value,
7) fast curing at room temperature, and
8) rapid cross-linking at elevated temperature.

In the past two decades, API adhesives were widely investigated and used for timber processing in developed countries [3–10]. Because of massive demand for solid-wood lamination and finger jointing, API has been used increasingly as a substitute for the traditional urea formaldehyde resin (UF) in China, because the new Chinese national standard regulations for the hazard material limits in adhesives have been enforced since July 1, 2002.

The main component of API is usually an aqueous polymer latex, such as vinyl acetate (PVAc) homopolymer emulsion, vinyl acetate–ethylene (VAE) copolymer emulsion, vinyl acetate/butyl acrylate/hydroxypropyl methacrylate (xPVAc) tri-copolymer emulsion, or carboxylated styrene–butadiene rubber latex (SBR), *etc*. The cross-linker is a polyisocyanate and its prepolymer that contain more than two isocyanate groups (–NCO), such as polymeric methylene diisocyanate (p-MDI), toluene diisocynate (TDI), and its compound with tri-hydroxyl methylpropane (TDI-TMP). Furthermore, p-MDI cross-linkers predominate in two cases: (1) those that require no prior chemical treatment and are directly used as cross-linker; (2) those cross-blended with small amount of hydrophobic organic solvent before compounding with aqueous polymer latex. However, polyisocyanate crosslinkers mixed with organic solvent have the following shortcomings: (1) the ordinary commercial organic solvents (usually ketones and esters) cannot directly act as the masking agent for p-MDI and require drying under vacuum which increases the cost of production; (2) Environment (VOC) pollution; and (3) inconvenience of storage and transportation. The overall performance of aqueous polymer latex cross-linked by the general p-MDI without any chemical treatments is relatively inferior, although it is extensively used in API formulations.

Because it is difficult for general polyisocyanate to disperse in water, Johnson and Wooler [11] proposed a preparation method in 1976 for “aqueous emulsified isocyanate” that utilized a nonionic surfactant without any hydroxyl, amino, or carboxylic group to modify polyisocyanate. Consequently, the dispersion ability of modified isocyanate is improved significantly. Imperial Chemical Industries (ICI) later patented and commercialized this preparation method. It was proved that aqueous emulsifiable isocyanate has a better effect on cross-linking than that of ordinary p-MDI in chipboard application [12, 13]. Therefore, we used this aqueous emulsifiable isocyanate at different loadings to cross-link three kind of typical aqueous vinyl polymer latex to prepare API. This study intends to investigate the potlife, curing time, bonding strength, and water resistance of these API adhesives and to compare them with the cross-linking results of unmodified p-MDI and the polyisocyanate mixed with organic solvent.

## 2. EXPERIMENTAL

### 2.1. Materials

1) Main components of API: (a) poly (vinyl acetate) homopolymer latex (PVAc, GCLOCK606), (b) modified vinyl acetate–ethylene copolymer latex (m-VAE, GCLOCK709), (c) vinyl acetate/butyl acrylate/hydroxypropyl methacrylate tri-copolymer latex (xPVAc, GCLOCK2000). These three latexes contain about 10% (wt.) of poly vinyl alcohol (PVOH), which is a protective colloid and the main provider of hydroxyl groups. To investigate the effect of PVOH content of aqueous vinyl latex on the performance of API, three other similar xPVAc latexes that have the same content of vinyl acetate/butyl acrylate/hydroxypropyl methacrylate tri-copolymer but that differ in the PVOH and inorganic filler content compared

**TABLE 1** Some Properties of Typical Aqueous Vinyl Latex

| Main components | PVOH content (%) | Solid content (%) | Viscosity (Pa · s) | pH | Lowest curing temperature (°C) |
|---|---|---|---|---|---|
| PVAc | 10 | 46–48 | 8–10 | 4–6 | $\leq 10$ |
| m-VAE | 10 | 53–55 | 7–8 | 5–7 | $\leq -3$ |
| xPVAc-10 | 10 | 51–53 | 6–8 | 6–7 | $\leq 0$ |
| xPVAc-6 | 6 | 51–53 | 4–6 | 6–7 | $\leq 0$ |
| xPVAc-8 | 8 | 51–53 | 6–7 | 6–7 | $\leq 0$ |
| xPVAc-12 | 12 | 51–53 | 10–12 | 6–7 | $\leq 0$ |

with GCLOCK2000, were also tested. It is noted that the filler content of xPVAc decreases as the PVOH content increases to maintain the same solid content of the latex. The six aqueous vinyl latexes were supplied by GCLOCK Adhesive Company (Jiangxi province, China). Table 1 shows some properties of these emulsions.

2) Cross-linkers of API: (a) an aqueous emulsifiable p-MDI, cross-linker A (Rubinate 9259, supplied by Huntsman Polyurethanes Company, Salt Lake City, UT, USA); (b) unmodified p-MDI, cross-linker B (MR200, supplied by Nippon Polyurethanes Company, Yokohama, Japan); (c) a p-MDI mixed with xylene, cross-linker C, which was prepared by mixing cross-linker B with xylene in the ratio 100:10 (by weight). The characteristics of three cross-linkers are shown in Table 2.
3) Adherend: rosewood (water content: 10–15%).

## 2.2. Preparation of API Adhesive

First, the raw materials were placed in an environment of constant temperature, 23 ± 2°C, and relative humidity, 45–55%, for 24 h. Second, the aqueous emulsifiable p-MDI, cross-linker A, and unmodified p-MDI, cross-linker B, were, respectively, added into aqueous

**TABLE 2** Characteristics of Three Polymer Isocyanates (p-MDI)

| Crosslinker | Solid content (%) | NCO (%) | Functionality | Modification method |
|---|---|---|---|---|
| A | 100 | 30.6 | 2.7 | Aqueous emulsifiable |
| B | 100 | 30–31.5 | 2.7 | Unmodified p-MDI |
| C | 90 | 27–28.4 | 2.7 | Mixed with organic solvent |

vinyl polymer latexes at the weight ratio of cross-linker 5%, 10%, 15%, and 20%. Meanwhile, cross-linker C was adjusted to a weight ratio of cross-linker 5.6%, 11.1%, 16.7%, and 22.2% to maintain the similar content of isocyanate. Finally, the two components after metering were stirring 10 min by hand, and then the potlife and curing time of API were measured. Meanwhile, the compression shear strength and percent wood failure of bonded rosewood specimens, before and after being aged in warm and boiling water, were tested.

## 2.3. Test Methods

### *2.3.1. Potlife*

The potlife of adhesive refers to the time in which the adhesive remains functional after blending (ASTM D1338). At present, there are three common test methods for the potlife of two-component adhesives viscosity/strength–time curve, double initial viscosity, and physical appearance observation.

1) Viscosity/strength–time curve method: The viscosity of mixed glue is continuously measured, and the bonding specimens are prepared in an interval of time at constant temperature and humidity. According to the curves of measured viscosity and adhesion strength of specimens *versus* time, the times that the slope of the viscosity and bonding strength *versus* time curve abruptly change are obtained, and the smaller value of them is taken as the potlife of the adhesive. The relative standards are ASTM D1338, British BS5350, and Chinese GB7213.
2) Double initial viscosity method: The variations of viscosity of mixed glue against time are continuously measured, and the time at which the viscosity of mixed latex increases to double the initial value is regarded as the potlife of adhesive [14].
3) Physical appearance observation method: The mixed glue is visually observed as soon as blending of two components is stirred uniformly, and the time that the compound achieves a “special state” may be taken as the potlife. The “special state” refers to the phenomena of remarkable viscosity increase, gel state, settling, separating, or color changing of adhesive. This method has been adopted as the Chinese general testing standard for architectural decoration adhesives, GB/T12954, and the Japanese industrial standard, JIS K6833.

Although the potlife is very important for two-component adhesive, the existing test standards for aqueous polymer isocyanate adhesive are not adequate. It is well known that the 'strength–time curve' method is most accurate, but it is very hard to execute for API. Firstly, it is not easy to apportion the time intervals, as the testing will be expensive if the time interval of bonding wood specimens is too small. Conversely, the precise point of the strength *versus* time curve, where the bonding strength decreases markedly, may be inaccurate if the time intervals are too great. Second, the strength of API for bonding wood is easily influenced by the coating operator. According to ASTM D1338, the test results are expressed in terms of average strength of all specimens. If the difference between the strength of each specimen and the average value is larger than 20%, the largest deviations should be eliminated one by one until the difference between the testing strength of each specimen and their average value is less than 20%. However, if more than two bonded wood specimens are removed, then all of experimental samples prepared at this time point are blanked out, and the specimens need to be bonded again for testing. Therefore, ASTM D1338, GB7123, and BS5350 are inefficient for measuring the potlife of API.

Because $-$NCO groups will react with water in emulsions while cross-linkers blend the with main component, shown as Equation (1), the mixed adhesive inevitably foams. Thus, API is a typical non-Newtonian fluid, and it is very difficult to measure the viscosity of API correctly:

$$R-NCO+H_2O \rightarrow (RNHCOOH) \rightarrow R-NH_2+CO_2 \uparrow \qquad (1)$$

*i.e.*, the 'double initial viscosity' method is unfit for API. In addition, the physical appearance observation method is strongly influenced by the operator's experience; thus, this evaluation method has some uncertainties.

Before proposing a new testing method for the potlife of API, we first analyze the chemical changes and physical phenomena of this blended adhesive, which can be divided into three stages, as shown in Figure 1.

SA: Water molecules in polymer emulsion have not yet fully contacted $-$NCO groups. Only small portions of $H_2O$ molecules have penetrated into the tiny droplets of isocyanate. Consequently, little $CO_2$ is released, and the viscosity and volume of API slowly increase.

AB: Emulsion particles start to aglomerate as $-$NCO reactions proceed with water. Liquid adhesive starts to foam rapidly. The

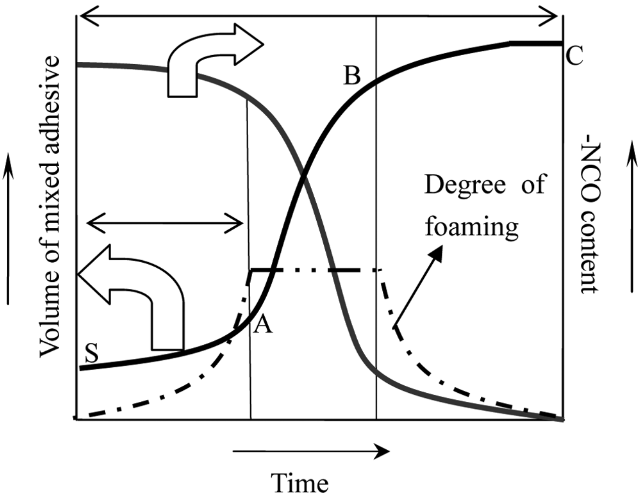


**FIGURE 1** Schematic illustration of volume and foaming of API mixed adhesive *versus* time.

viscosity and volume of API increase quickly, and the temperature of API increases slightly.

BC: The concentration of isocyanate decreases, and its reaction activity goes down remarkably. Viscosity increases and volume expansion of mixed adhesive stabilizes and slows. When all of –NCO are exhausted, the physical parameters (viscosity, volume) in an enclosed system stabilize gradually.

According to these observation and analysis, we may consider that the volume, viscosity, and –NCO contents of API mixed glue change synchronously.

Therefore, our 'volume–time curve' testing method for potlife of API is as follows: (1) The mixed adhesive is sealed in an transparent volume measuring tool, and the liquid adhesive volume is continuously tested at a certain interval of time (3–5 min) at constant temperature. (2) Plot the liquid adhesive volume ($V$) *versus* time ($t$), and the time where the volume of mixed glue increases abruptly is taken as the potlife of API.

The 'volume–time curve' method has the advantages of easy operation and is cost-effective. Zhao [15] validated that this measurement had high accuracy for the potlife of API compared with that of strength–time curve according to ASTM D1338, by a great deal of experiments, where the test results between the 'volume–time curve' method and 'strength–time curve' method were less than 10%.

### 2.3.2. Curing Time

Similar to the potlife, the existing test standards for aqueous polymer isocyanate adhesive are not adequate for evaluating the curing time. Because the hardness of polymer depends on structural parameters of molecular chains such as flexibility and cross-linking density, the hardness test is considered a quick method for mechanical performance. It is well known that nanoidentation is the most accurate measurement for the hardness of polymer film, but it is too expensive. Therefore, the pencil hardness test, which is a simple and effective technique to evaluate the hardness of many coatings, was used to evaluate the curing time of API adhesives as follows: (1) The surfaces of rosewood plates were ground with 600-mesh sand paper and then cleaned with acetone. (2) API adhesives were coated on the surface of the rosewood plate after the acetone had volatilized. The thickness of the API coating is about 0.2 mm. (3) After the coated rosewood samples dried for 2 h at constant temperature (23 ± 1°C), the pencil hardness of the API films were continuously measured at a certain interval of time (15–20 min) according to ASTM D3363. The time of maximum hardness is accordingly the curing time of the adhesive.

### 2.3.3. Bonding Performance and Water Resistance

API adhesives were evaluated by measuring the compression shear strength and percent wood failure of bonded specimens at ambient temperature, and the resistance to warm water and boiling water according to Japanese industrial standards JIS K6806 and JIS K6852. Load at failure was recorded for subsequent computation of shear strength. After each specimen was broken, the individual shear block halves were separated and evaluated for percent wood failure. The amount of wood failure was calculated by judging the percentage of the surface area of the joint that exhibited fibers torn away from the opposing surface.

The rosewood specimen is a cuboid of 30 mm (L) × 25 mm (W) × 10 mm (T) with adhesive area of $25 \times 25\,\text{mm}^2$, and the specimens were prepared based on the bonding technique guidelines listed in Table 3 according to JIS K6806. In addition, the water resistance method is shown in Table 4.

## 2.4. Instrument and Apparatus

1) Super Constant Temperature Water Bath, Model: CH-1015 made by Shanghai Balance Instrument Company (Shanghai, China), where temperature range is (room temperature) + 5°C to 95°C, stability

**TABLE 3** Bonding Technique Guidelines

| Parameter | Value |
|---|---|
| Room temperature (°C) | 20–25 |
| Amount of adhesive (g/m$^2$) | 250–300 |
| Time of pressure applied (h) | 24 |
| Pressure applied (kg/mm$^2$) | 10–15 |
| Moisture content of wood (%) | 6–10 |
| Storage time at room temperature after pressure released (h) | 72 |

is +0.05°C, and control mode is computer control proportional, integral, and derivative (PID) adjustment.

2) Constant Temperature & Constant Humidity Digital Controlled Box, Model 101 A, made by Shanghai Gaochao Automation Control Equipment Company (Shanghai, China).
3) Pencil Hardness Gage, made by Shanghai Changfeng Instrument Company (Shanghai, China).
4) Universal Test Machine: Instron 8032 (Instron, Norwood, MA, USA) under displacement control with loading rate of 1 mm/min.

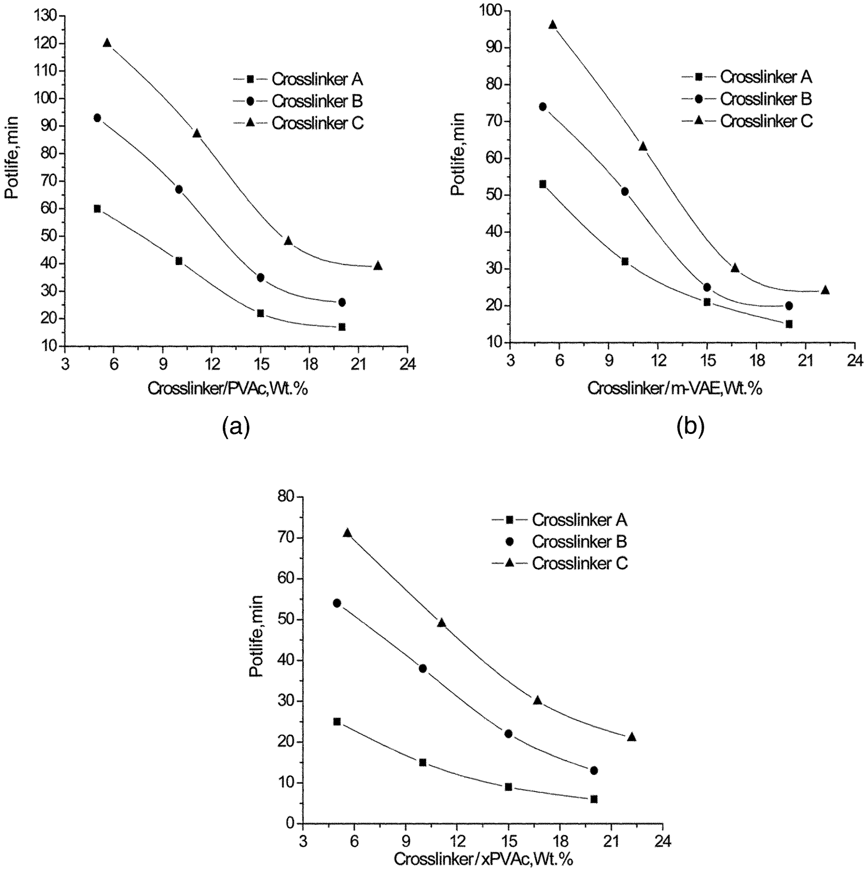
## 3. RESULTS AND DISCUSSIONS

### 3.1. Potlife

As shown in Figure 2, with the increase of p-MDI cross-linker loading, the potlife of aqueous polymer emulsion shortens. The adhesive mixed with aqueous emulsifiable p-MDI (cross-linker A) has the shortest pot-life. That means the cross-linker A, in which is the p-MDI modified

**TABLE 4** Water-Resistance Test Method

| Test | Result |
|---|---|
| Warm water | The specimens shown in Table 3 are dipped in warm water at 60 ± 3°C for 4 h, and then compression shear strength and percent wood failure of these specimens are measured after they are cooled down in water at ambient temperature. |
| Boiling water | The specimens shown in Table 3 are dipped in boiling water for 4 h, blown by hot air at 60 ± 3°C for 20 h, and dipped in boiling water for 4 h again. Then compression shear strength and percent wood failure of these specimens are measured after they are cooled down in water at ambient temperature. |



(a) (b)

(c)

**FIGURE 2** Effect of p-MDI on the potlife of API. (a) Main component: vinyl acetate homopolymer latex, PVAc; (b) Main component: modified vinyl acetate–ethylene copolymer latex, m-VAE; (c) Main component: vinyl acetate/butyl acrylate/hydroxypropyl methacrylate tri-copolymer latex, xPVAc.

by a hydrophilic group, has quicker dispersion and penetration ability in aqueous polymer emulsion. The water molecules in the emulsion will fully contact a the –NCO group in short time so that the potlife of this adhesive is decreased sharply. With the protection of a hydrophobic organic solvent, it is more difficult for the –NCO group to be wetted by sufficient $H_2O$ molecules because of the barrier of tiny liquid drops composed of isocyanate and solvent. In addition, with the same type of cross-linker, the potlife of API is compared

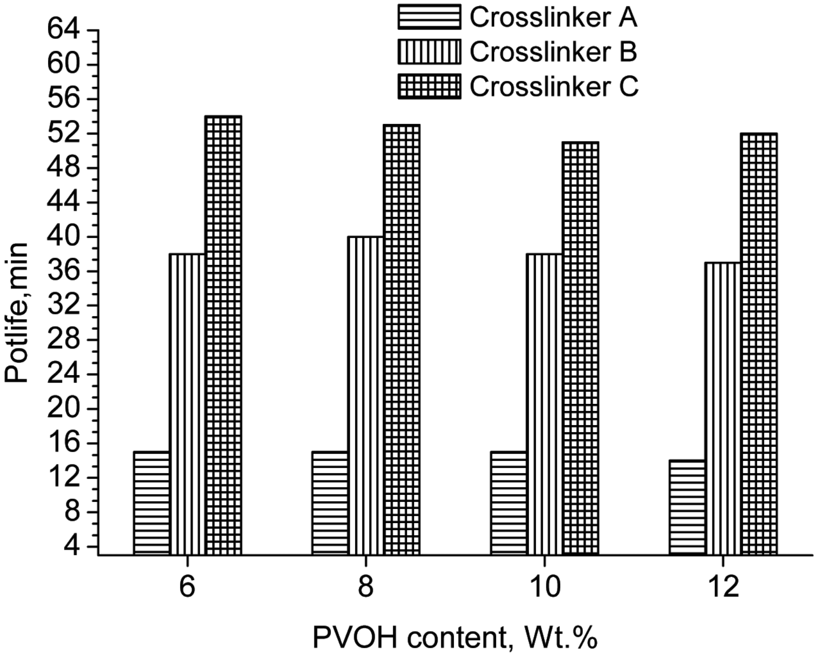


**FIGURE 3** Effect of PVOH content of the aqueous latex on the potlife of API ($-NCO/xPVAc = 15\%$).

in sequence according to the main components, as follows: PVAc > m-VAE > xPVAc.

As shown in Figure 3, with the increase of PVOH content, no statistically apparent differences in the potlife of API were found with the same cross-linker. This suggests that $-NCO$ groups cannot react with the hydroxyls of PVOH because great excesses of water exist in the aqueous polymer latex. Therefore, the PVOH content of the main component has no obvious effect on the potlife of API adhesive.

## 3.2. Curing time

After API-mixed adhesives were coated on the surface of rosewood specimen, as the $H_2O$ is evaporated to the environment, absorbed by wood, and reacted with $-NCO$, the water content in the coating layer decreases and tiny particles of polymer form a film gradually while hydroxyl groups cross-link with the isocyanate group. Meanwhile, at the interface between adhesive layer and wood, vinyl polymer will embed itself into the porosity of the wood surface to leave many tiny "glue nails," and p-MDI can penetrate further into the wood interior

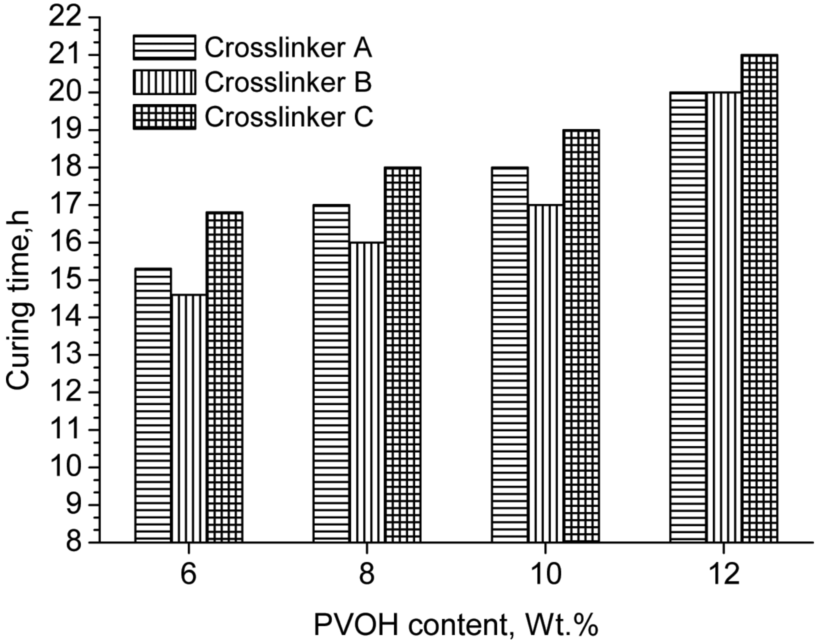


**FIGURE 4** Effect of PVOH content of the aqueous latex on the curing time of API (–NCO/xPVAc = 15%).

where chemical reactivity with hydroxyl groups in wood can occur. Thus, greater adhesion forces (mechanical and chemical bond) are developed. When the water in adhesion layer fully disappears and –NCO groups are exhausted, the surface hardness of the API adhesion film increases gradually up to the maximum. When the hydroxyl groups of aqueous vinyl polymer increase, the amount of –NCO reacted with $H_2O$ molecules relatively reduces; consequently, the drying rate of the adhesive layer decreases. Therefore, the curing time of API increases with increasing PVOH content of the main components, as shown in Figure 4.

As shown in Figure 5, with the increase of p-MDI loading, the curing time of mixed adhesives reduces remarkably. The curing time of API with the same main component is ranked as follows: cross-linker B < cross-linker A < cross-linker C. That is, unmodified p-MDI, in which –NCO groups directly contact $H_2O$ in the main components, has a higher reaction rate; thus, the adhesive layers lose the water and quickly form films. As to the aqueous polymer emulsion modified by cross-linker C, the organic solvent markedly prolongs the curing time of the adhesive. It is noted that the curing time of this aqueous emulsion modified by cross-linker A is not the shortest one, although

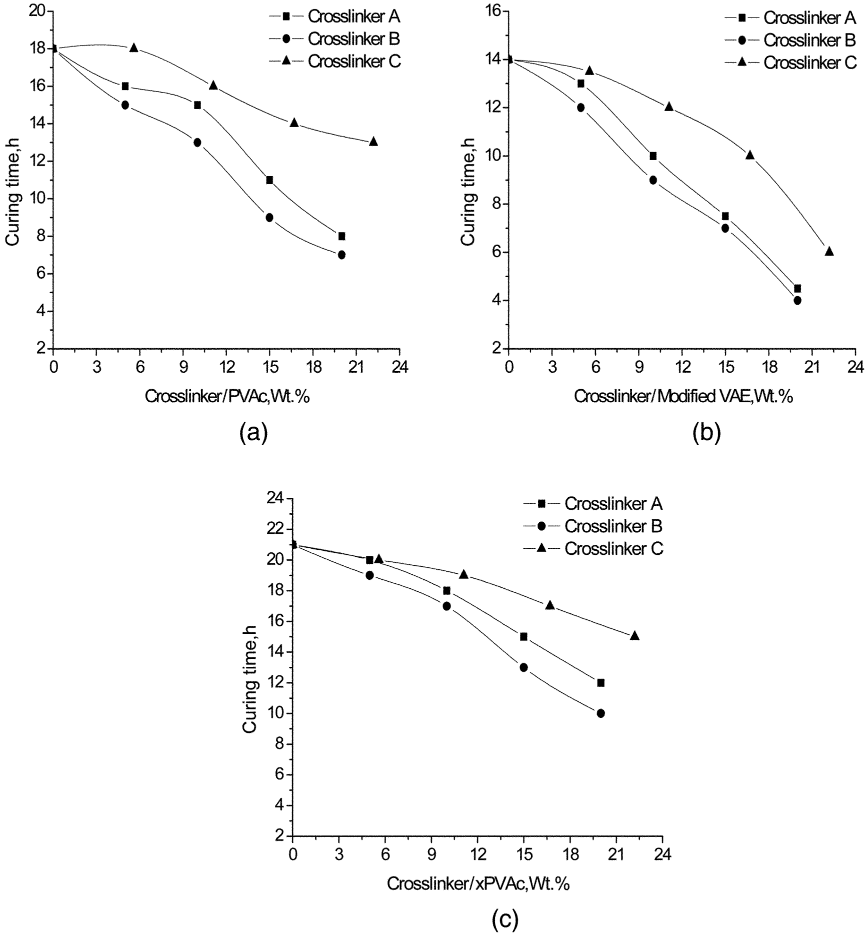


**FIGURE 5** Effect of p-MDI on the curing time of API. (a) Main component: vinyl acetate homopolymer latex, PVAc; (b) Main component: modified vinyl acetate–ethylene copolymer latex, m-VAE; (c) Main component: vinyl acetate/butyl acrylate/hydroxypropyl methacrylate tri-copolymer latex, xPVAc.

aqueous emulsifiable isocyanate has the best dispersion. This phenomenon may be explained by the aqueous emulsifiable isocyanate having better wood penetration, so a great number of –NCO groups in cross-linker A move toward the interface between the API coating layer and wood, while isocyanate concentration in the adhesive layer is relatively lower. Consequently, the drying rate of the adhesive layer is lower than that of unmodified p-MDI. In addition, with the same cross-linkers and loadings, the curing time of API is ranked as

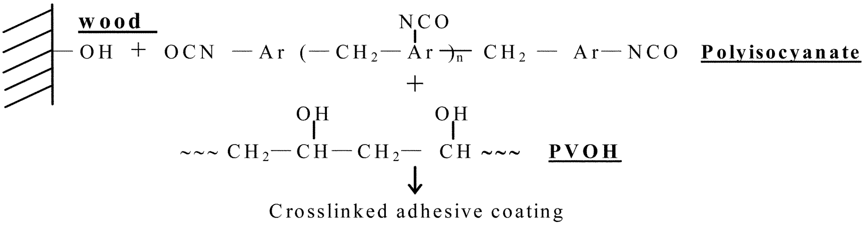


**FIGURE 6** Chemical bonding mechanism of API.

follows: m-VAE < PVAc < xPVAc, which is coincident with the features of API without cross-linker. Therefore, the curing time of API adhesive depends on the water-loss rate of the adhesion layer and penetration and cross-linking ability of isocyanate.

## 3.3. Bonding Performance at Ambient Temperature

With evaporation of water from the emulsion, small particles of API polymer migrate into the porosity of the surface. The isocyanate groups of the cross-linker cannot only react with hydroxyl groups in the wood but also cross-link with PVOH in the emulsion; the result forms the urethane bond, shown in Figure 6. Thus, the compression shear strength and percent wood failure of the specimens glued by API at ambient temperature increase as the PVOH content of aqueous latex increases from 6% to 12%, but the extent of increase gradually decreases (see Fig. 7)

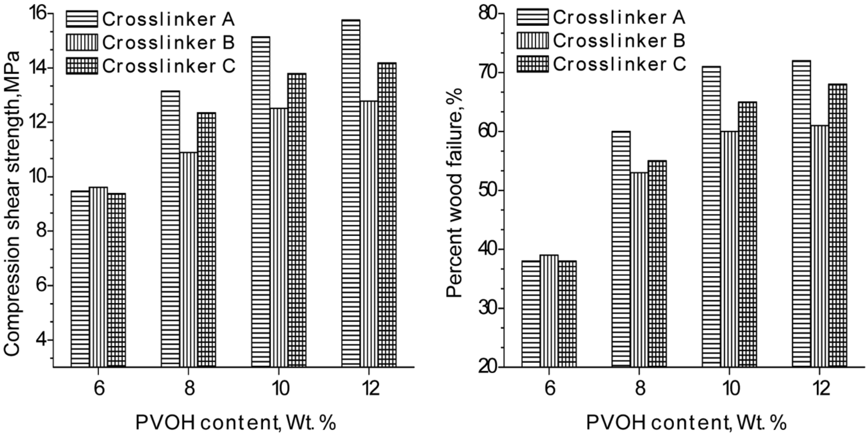


**FIGURE 7** Effect of PVOH content of the aqueous latex on the bonding performance of API at ambient temperature (–NCO/xPVAc = 15%).

Suitable amounts of cross-linker can improve the bonding performance of API at ambient temperature and result in significant differences between both the compression shear strength and percent wood failure in PVAc/p-MDI, m-VAE/p-MDI, and xPVAc/p-MDI, shown as Figure 8. Because steric hindrance between alternate acetate groups restricts movement of the molecules, the coating film of PVAc homopolymer latex is fairly hard and brittle. With the increase of weight ratio of cross-linker, the curing film of API hardens while its elasticity reduces, and the residual stress arising the from curing shrinkage of the adhesive layer grows; hence, excess isocyanate loadings may obviously damage the bonding performance of API. That is why the compression shear strength of PVAc emulsion cross-linked by isocyanate enhances first and then weakens if the loading of p-MDI added exceeds the critical value ($X_{cr}^{NCO}$), as shown in Figure 8a. The main chains of VAE polymer soften because of vinyl copolymerizing with ethylene, where the distances between acetate groups are lengthened, VAE are softer and more flexible than the straight PVAc. Therefore, as the loading of cross-linker increases ($0 \rightarrow 20\%$), the residual stress arising from curing shrinkage of the adhesive layer is relatively small, and the compression shear strength of m-VAE cross-linked by p-MDI rises continuously (see Figure 8b). As for the xPVAc latex, where butyl acrylate is introduced to internally plasticize polyvinyl acetate grafted by hydroxypropyl methacrylate (hard monomer), the elastic modulus of its adhesive film is between PVAc and VAE. Therefore, the compression shear strength and percent wood failure curves of xPVAc/p-MDI at ambient temperature are similar to that of PVAc/p-MDI, except that $X_{cr}^{NCO}$ of xPVAc/p-MDI is much higher (Fig. 8c).

At ambient temperature, with increasing cross-linker loading, the aqueous emulsifiable isocyanate (cross-linker A) gives the best results for the three latex polymer emulsions tested, whereas cross-linker B and cross-linker C are equivalent. However, p-MDI with protection of organic solvent was shown to have better performance at high loadings, whereas there was a decrease with the other two cross-linkers. That is because the organic solvent can relatively reduce excess isocyanate reaction with water, and the microdefects in the coating layer are accordingly diminished. In addition, the aqueous vinyl polymer can be externally plasticized to some extent by the organic solvent in cross-linker C. Accordingly, the curing film will soften while its elasticity increases, and the residual stress arisen from curing shrinkage of adhesive layer will decrease. Therefore, the bonding performance of API adhesives is improved.

At normal ratio (main component/cross-linker = 100/15), the compression shear strength and percent wood failure of m-VAE/p-MDI and xPVAC/p-MDI at ambient temperature can reach the

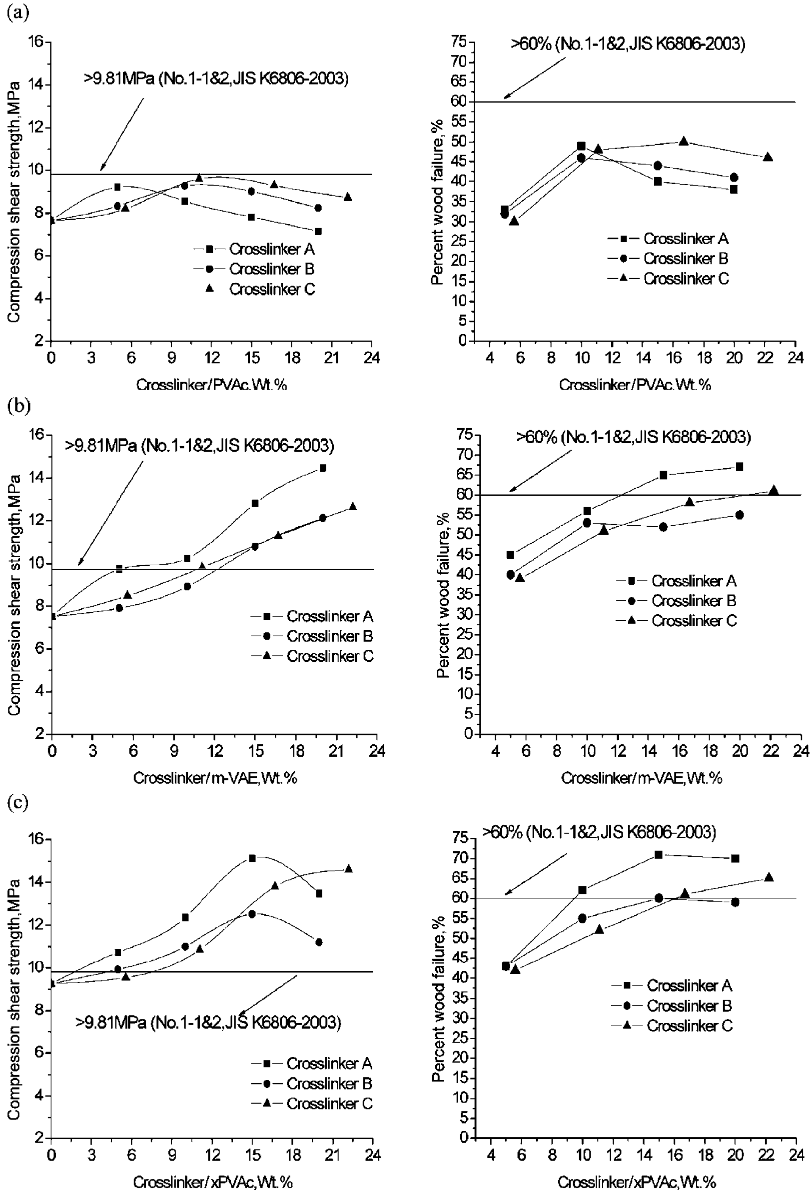


**FIGURE 8** Effect of p-MDI on the bonding performance of API at ambient temperature. (a) Main component: vinyl acetate homopolymer latex, PVAc; (b) Main component: modified vinyl acetate–ethylene copolymer latex, m-VAE; (c) Main component: vinyl acetate/butyl acrylate/hydroxypropyl methacrylate tri-copolymer latex, xPVAc.

requirements of JIS K6806. For xPAVc, in fact only a small amount of cross-linker ($\geq 7\%$) needs to be added. However, the bonding performance of PVAc cross-linked by all three kinds of isocyanates at all loadings (0–20%) cannot meet all the requirements outlined in JIS K6806.

## 3.4. Resistance to Warm Water and Boiling Water

When the hydroxyl groups in polymer of emulsion are cross-linked by isocyanate groups, the curing films of aqueous vinyl latex are transferred from thermoplastic polymer to thermoset resin that is stronger. Moreover, the energy of chemical bonds in the interface between adhesive layer and wood increases, so the resistance to warm water and boiling water increases (see Figs. 9 and 10). The improvement of the isocyanates can be ranked as follows: cross-linker A > cross-linker C > cross-linker B. It is noted that, at higher loadings of p-MDI, the water resistance of API does not show the trend of weakening, which is very different from the results of bonding strength of API at ambient temperature shown in Figures 8a and 8c. That is because the residual stress of cross-linked cured polymer at higher loading of p-MDI may be released because of the penetration of, and plasticization by, water molecules.

As shown in Figures 9 and 10, statistically significant differences were found between PVAc/p-MDI, m-VAE/p-MDI, and xPVAc/p-MDI for compression shear strength and percent wood failure of samples aged by water immersion. The warm- and boiling-water resistances of PVAc/p-MDI are very poor. Conversely, m-VAE/p-MDI and xPVAc/p-MDI have high water resistance, and Figures 9b and 9c show that the warm-water resistance of m-VAE and xPVAc cross-linked by p-MDI at 15% loading is larger than 5.88 MPa: *i.e.* the bonding performance meets the requirements of JIS K6806 for solid-wood lamination and finger jointing (No. 1-2). Figure 10 shows that only the xPVAc cross-linked by aqueous emulsifiable isocyanate (cross-linker A) with a loading of 20% can meet the boiling-water resistance as specified by JIS K6896 (No. 1-1) and can then be used as a structural glue for wood.

Figures 9 and 10 also show that the aqueous vinyl latex modified by cross-linker A (aqueous emulsifiable isocyanate) has better resistance to warm and boiling water than the other two cross-linkers. The p-MDI mixed with organic solvent (cross-linker C) was next in performance.

To investigate further the effect of isocyanate on bonding properties of aqueous polymer latex, the warm and boiling water resistance of the rosewood samples bonded by xPVAc/p-MDI where the PVOH content is from 6% to 12% were tested. From the test results shown in

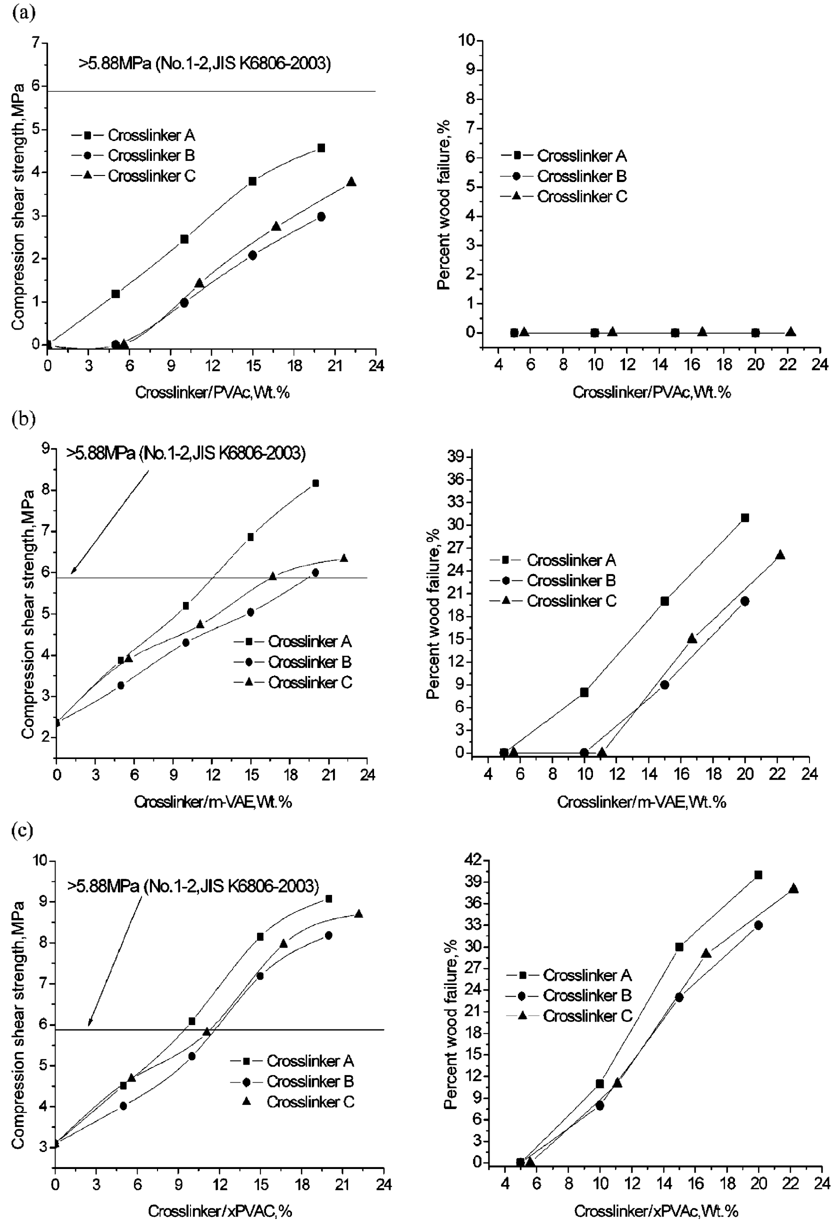


**FIGURE 9** Effect of p-MDI on the warm-water resistance of API. (a) Main component: vinyl acetate homopolymer latex, PVAc; (b) Main component: modified vinyl acelate-ethylene copolymer latex, m-VAE; (c) Main component: vinyl acetate/butyl acrylate/hydroxypropyl methacrylate tri-copolymer latex, xPVAc.

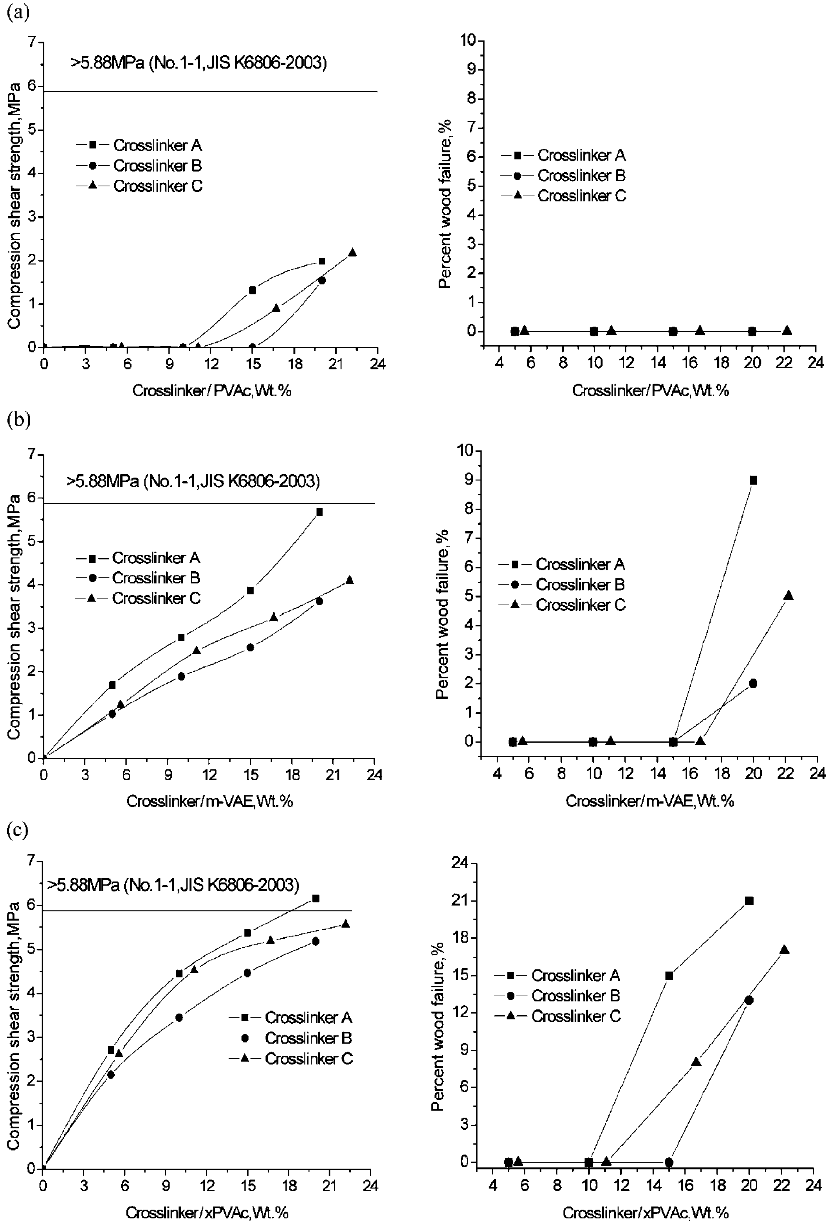
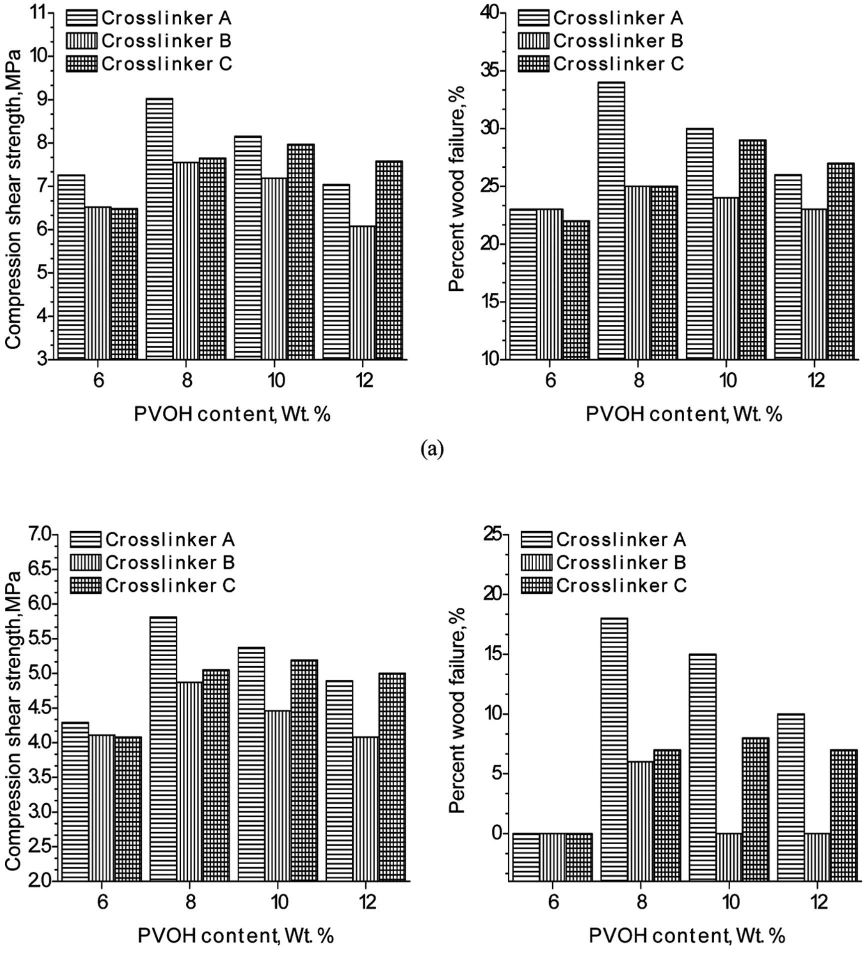


**FIGURE 10** Effect of p-MDI on the boiling resistance of API. (a) Main component: vinyl acetate homopolymer latex, PVAc; (b) Main component: modified vinyl acetate–ethylene copolymer latex, m-VAE; (c) Main component: vinyl acetate/butyl acrylate/hydroxypropyl methacrylate tri-copolymer latex, xPVAc.



(a)

(b)

**FIGURE 11** Effect of PVOH content of the aqueous latex on water resistance of API (–NCO/xPVAc = 15%). (a) Warm water (b) Boiling water.

Figure 11, the compression shear strength and percent wood failure increase with increasing amounts of hydroxyl groups when the PVOH content is less than the critical value ($X_{\mathrm{cr}}^{\mathrm{PVOH}}$), and the compression shear strength and percent wood failure decreases with excess PVOH ($>X_{\mathrm{cr}}^{\mathrm{PVOH}}$). The reason is that when the PVOH $< X_{\mathrm{cr}}^{\mathrm{PVOH}}$, the urethane bonds increase as the PVOH content increases; thus, the water resistance of API is improved. Conversely, the isocyanate groups are not enough to react with the excess PVOH, resulting in weakening the water resistance of API. In addition, Figure 11 indicates that the value of $X_{cr}^{PVOH}$ for cross-linker C is higher than that for cross-linker A and B. Because of the barrier of tiny liquid drops composed of isocyanate and solvent in the cross-linker C, the rate of reaction of –NCO groups with water will decrease, and the more –NCO groups of the cross-linker can react with the hydroxyl groups of PVOH.

## 4. CONCLUSIONS

1) The type of cross-linker and its loadings have marked influences on potlife and curing time of API. With increase of –NCO content, the potlife and curing time of API shorten sharply. Moreover, p-MDI cross-linker modified by water emulsification has reduced the potlife of API and blending with organic solvent can prolong the usable time of mixed adhesive, and the two modification methods for p-MDI both reduce the curing speed of API to different extents, in which the organic-solvent shielding method has the more obvious impact.
2) With the increase of PVOH content, the curing time of API accordingly increases, but no statistically apparent differences in the potlife of API were found.
3) Suitable loadings of p-MDI improve remarkably the compression shear strength and percent wood failure of aqueous polymer emulsion at ambient temperature. Nevertheless, excess cross-linker loading cannot maintain its enhancing effect and will even result in weakening of the adhesive layer. At lower loadings of cross-linker, the aqueous polymer latex modified by aqueous emulsifiable isocyanate shows the best performance. At extremely high loading, the best performance is with p-MDI protected by organic solvent.
4) With the increase of cross-linker loadings, the warm-water and boiling-water resistance of API are improved remarkably. Aqueous emusifiable isocyanate shows the best performance, and p-MDI protected by organic solvent is the second best.
5) With the increase of PVOH content, the bonding performance of API is improved. However, the excess PVOH will weaken the warm- and boiling-water resistance of the joint.
6) The bonding strength and water resistance of API, in which the main component is VAE or xPVAc, are far better than those using PVAc; that is, choosing the types of isocyanate is very important, but cross-linking polymerization of appropriate aqueous polymer latex may be the decisive factor for high-performance API.

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## REFERENCES

[1] Terbilcox, T. F. and Luckman, E. R., *Elastomerics* **116**(10), 28–28 (1984).
[2] Lix, S. X. and Liu, Y. J., *Polyurethane Adhesives* (Chemistry Industry Publishing Company, Beijing, 1998), 2nd ed., Chap. 7, pp. 301–304 (in Chinese).
[3] Pagel, H. and Luckman, E. R., *Adhesives Age* **24**(10), 34–39 (1981).
[4] Vick, C. B. and Larsson, P. C., *International Journal of Adhesion and Adhesives* **13**(3), 139–149 (1993).
[5] Gardner, D. J., Davalos, J. F., and Munipalle, U. M., *Forest Products Journal* **44**(5), 62–66 (1994).
[6] Mototani, Y. and Nakano, T., *Mokuzai Gakkaishi* **42**(2), 140–148 (1996) (in Japanese).
[7] Qiao, L. J., and Easteal, A. F., Clive, F., Coveney, P. K. and Franich, R. A., *Pigment Resin Technology* **29**(4), 229–237 (2000).
[8] Vrazel, M. and Sellers, T., *Forest Products Journal* **54**(3), 66–75 (2004).
[9] Kilmer, W. R., and Blankenhorn, P. R., Labosky, P., and Janowiak, J. J., *Wood and Fiber Science* **30**(2), 175–184 (1998).
[10] Miyazaki, J. and Nakano, T., *Mokuzai Gakkaishi* **48**(3), 184–190 (2002) (in Japanese).
[11] Johnson, F. and Wooler, A. M., US Patent 3996154 (1976).
[12] Papadopoulos, A. N., Hill, C. A. S., and Traboulay, E A., and Hague, J. R. B., *Holz als Roh- und Werkstoff* **60**, 81–83 (2002).
[13] Papadopoulos, A. N., Traboulay, E. A., and Hill C. A. S., *Holz als Roh- und Werkstoff* **60**, 394–396 (2002).
[14] Martin, M., Michael, S., and Claus, K., *Progress in Organic Coatings* **40**, 99–109 (2000).
[15] Zhao, J. J., *Investigation on Bonding Mechanics Performance of Aqueous Polymer Latex Modified by Polymeric Methylene Diisocyanate*, Master's thesis, Shanghai University (2005).