

# A Honeymoon-Type Adhesive for Wood Products Based on Acetoacetylated Poly(vinyl alcohol) and Diamines: Effect of Diamines and Degree of Acetoacetylation

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**ABSTRACT:** The honeymoon-type adhesive for wood products based on acetoacetylated poly(vinyl alcohol) (AAPVA) was investigated focusing on the effect of acetoacetylation on performance, and that of amino compounds as a crosslinking agent. AAPVAs with different degrees of acetoacetylation were synthesized by the addition reaction of diketene in dimethylsulfoxide. Adhesive tests were carried out using aqueous solutions of AAPVA and six kinds of amino compounds, spread separately on test pieces of red meranti selected as the adherend. The mechanical strength of the bonded test pieces was then analyzed. It was found that the adhesive strength increased together with the de-

gree of acetoacetylation at least until 3 h after the application of the adhesives. The degree of acetoacetylation had little effect on water resistance within the range 3.3–37.1%, and as a crosslinking agent, diamines containing primary amino groups were effective, although secondary amines and polyethyleneimine were not. It is assumed that the chemical structure of the amine influenced the crosslinking reaction at the adhesion interface. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 2966–2972, 2004

**Key words:** acetoacetyl; adhesives; crosslinking; poly(vinyl alcohol) (PVA); water-soluble polymers

## INTRODUCTION

As the demand for wood adhesives with low emissions of VOCs (volatile organic compounds) increases, the use of water-soluble polymers that do not require organic solvents in paints, adhesives, and so on has increased in recent years. In this context, the importance of poly(vinyl alcohol) (PVA) is increasing. PVA has been widely used as an aqueous adhesive and also as a protective colloid for aqueous emulsion adhesives. However, the use of PVA in adhesives results in a lack of water resistance after bonding. It also requires a long press time. As one solution to these problems, the introduction of acetoacetyl groups that are highly reactive with PVA has been attempted.<sup>1</sup> It was reported that the water resistance of the emulsion stabilized by PVA is improved<sup>2</sup> just by introducing acetoacetyl groups to PVA (AAPVA). Furthermore, an acetoacetyl group has two kinds of reaction sites: an active methylene group and a carbonyl carbon. Therefore acetoacetyl groups may react easily with an amine, a methylol melamine, an isocyanate, an aldehyde, an  $\alpha,\beta$ -unsaturated carbonyl compound, and so on.<sup>3</sup> Coatings and adhesives with improved immediate adhesion and/or water resistance have been de-

veloped by using this function and inducing crosslinking among the polymers.<sup>4</sup>

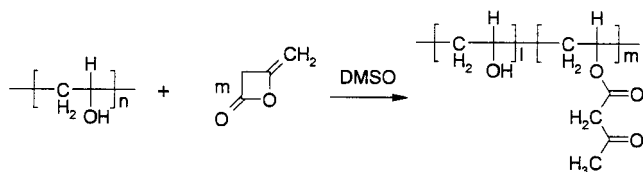
In this study, we attempted to clarify the influence of the chemical structures of amines as a crosslinking agent and the degree of substitution of –OH by an acetoacetyl group on wood adhesion. For this purpose, honeymoon-type adhesives were prepared using AAPVAs acetoacetylated to various degrees, and their adhesive forces examined. To obtain homogeneously substituted AAPVA, a homogeneous preparative method was used adding diketene to a homogeneous solution of PVA.<sup>5</sup>

## EXPERIMENTAL

### Materials

PVA (average degree of polymerization: 400–600; saponification > 96 mol %), diketene, dimethylsulfoxide (DMSO), and dialysis membranes (size 36) were obtained from Wako Pure Chemical Industries (Osaka, Japan). Ethylenediamine, 1,6-hexanediamine, diethylenetriamine, and piperazine 6-hydrate were obtained from Kishida Chemical Co. (Tokyo, Japan). Polyethyleneimine (polymer, 30% in water,  $M_w$  60,000–80,000) was obtained from Nacalai Tesque, Inc. Adipic acid dihydrazide was obtained from Tokyo Kasei Kogyo Co. (Tokyo, Japan). Reagents were used without further purification.

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Scheme 1 Acetoacetylation of PVA in DMSO.

### Modification of PVA

A four-neck flask equipped with a mechanical stirrer, a reflux condenser, a dropping funnel, and a thermometer was charged with 52.8 g (1.2 mol, based on  $-\text{CH}_2-\text{CHOH}-$  as the unit) of PVA and 450 mL of DMSO. The temperature of the reaction mixture was raised to 60°C with agitation under a nitrogen atmosphere. After the PVA had dissolved completely, diketene was added dropwise to the solution with agitation. After the addition, the mixture in the flask was agitated for 1 h, and then poured into ethanol or ethanol/hexane to precipitate the acetoacetylated PVA as a product. When the degree of acetoacetylation was very high, the reaction mixture was poured into water instead of ethanol to precipitate the polymer. The reaction is shown in Scheme 1.

The product was purified as follows. The precipitate was isolated by filtration and dissolved in water. This aqueous solution thus prepared was dialyzed using a dialysis membrane, and then the purified acetoacetylated PVA was obtained by freeze-drying the dialysate. When the product was insoluble in water, such as in the case of a very high degree of acetoacetylation, the polymer was dissolved in THF and then reprecipitated with water. The polymer was purified by repeating these procedures several times and then dried under vacuum.

### Characterization of AAPVA

The  $^1\text{H-NMR}$  of AAPVA was measured by a JEOL-EX270 apparatus (JEOL, Tokyo, Japan) using  $\text{DMSO-}d$  as a solvent. The FTIR was measured with a Shimadzu FT-IR 8200D (Shimadzu, Kyoto, Japan) using a thin film of AAPVA. The molecular mass of the AAPVA, together with the degree of acetoacetylation 92.7%, was determined by the GPC method with a Shodex 80M  $\times$  2 and 802.5 column (Showa Dekno, Tokyo, Japan) using tetrahydrofuran (THF) as the solvent at 40°C, with a flow rate of 1 mL/min and taking polystyrene as a standard.

### Adhesion of wood

Five aqueous solutions of AAPVA with different degrees of acetoacetylation were prepared as adhesives, and six amine solutions were prepared as crosslinking

agents. The adhesives and crosslinking agents used in this study are described in Table I.

Test pieces of red meranti [ $30 \times 25 \times 10$  mm (length  $\times$  width  $\times$  thickness)] were prepared for adhesion tests in general and  $30 \times 10 \times 10$  mm for the time dependency test of adhesive strength. The area of overlap between test pieces was  $25 \times 25$  mm in adhesion tests in general and  $25 \times 10$  mm in the time dependency test of adhesive strength. The spread amount of the AAPVA aqueous solution was  $100 \text{ g/m}^2$  and that of the crosslinking agent was  $50 \text{ g/m}^2$ . The aqueous solutions of AAPVA and the crosslinking agent were spread separately on test pieces. The test pieces were immediately pressed together under a pressure of 0.49 MPa for 5 min at room temperature to give a test specimen for immediate adhesion test. Compressive shear strength was measured according to JIS K 6852. Then the compressive shear strength of each test specimen was measured again after 0.5, 1, 3, 24, and 48 h. Dry strength was determined after ageing for 48 h without further treatment. Water resistance was measured after immersing the 48-h specimens into water at  $30 \pm 1^\circ\text{C}$  for 3 h, and then into water at  $20 \pm 1^\circ\text{C}$  for 10 min. The test was carried out in a wet state. Resistance in warm water was measured with specimens aged for 48 h by immersing them in water at  $60 \pm 3^\circ\text{C}$  for 3 h, and then in water at room temperature until they had cooled. The specimens were tested in a wet state. A repetitive boiling test was performed for specimens aged 48 h, after immersing them in boiling water for 4 h, drying them in air at  $60 \pm 3^\circ\text{C}$  for 20 h, boiling them again for 4 h, and then immersing them in water at room temperature until cooled. The specimens were tested in a wet state.

## RESULTS AND DISCUSSION

### Synthesis and characterization of acetoacetylated PVA

The degree of acetoacetylation of AAPVA, which could be controlled by the amount of diketene added in the synthesis of AAPVA, was determined by  $^1\text{H-NMR}$  measurement from integrals of the signals according to the following equation:

TABLE I  
AAPVA and Crosslinking Agents Studied

AA-PVA acetoacetylation (%)	Crosslinking agent
3.3	1,2-Ethylenediamine
10.3	1,6-Hexamethylenediamine
22.6	Diethylenetriamine
34.1	Polyethyleneimine
37.1	Piperazine
	Adipic acid dihydrazide

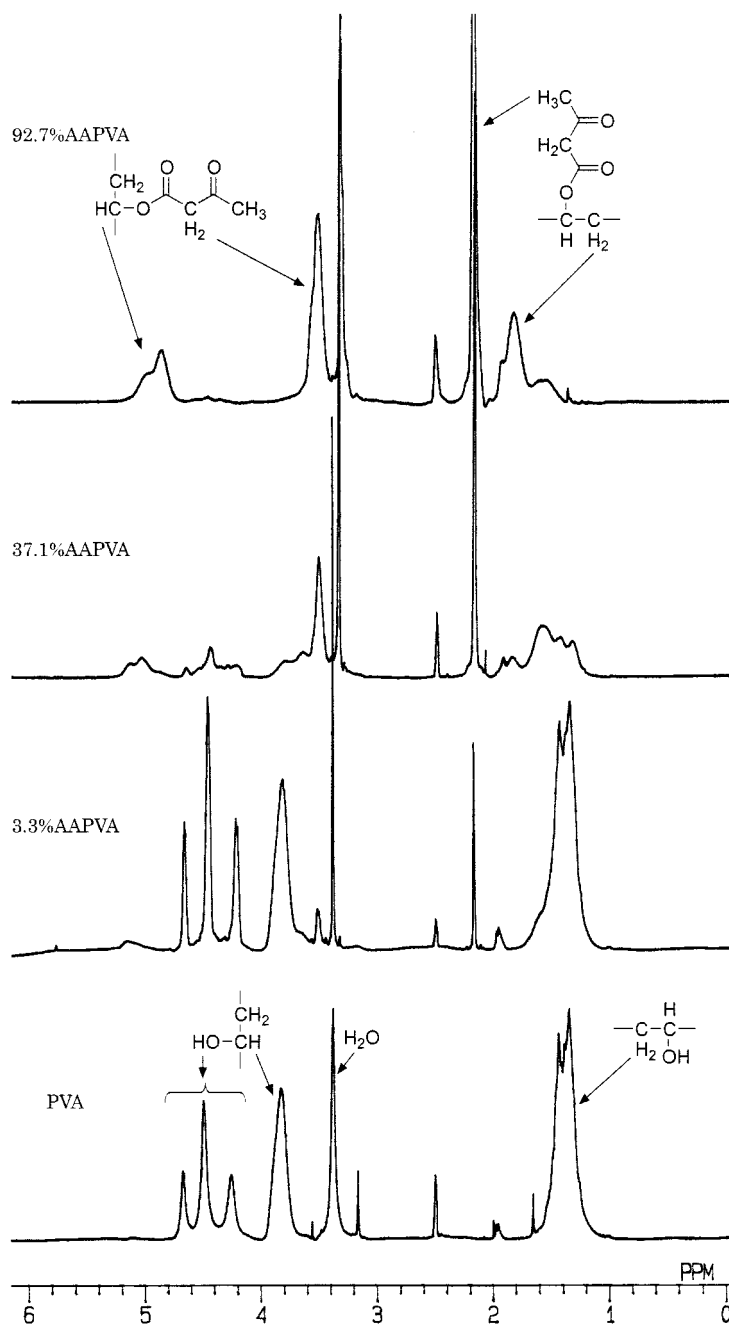


Figure 1 NMR spectra of AAPVAs with various degrees of acetoacetylation.

Degree of acetoacetylation (%)

$$= \frac{\text{Methyl proton of acetoacetyl group at 2.25 ppm}}{1.5 \times \text{methylene proton of PVA at 1.2-2.0 ppm}} \times 100$$

In Figure 1, the corresponding  $^1\text{H-NMR}$  spectra of AAPVA obtained at different degrees of acetoacetylation are shown. As the amount of diketene added to the synthetic reaction increased, so too did the signals at 2.2 and 3.5 ppm, corresponding to the methyl and methyl-

ene protons in an acetoacetyl group, respectively. However, the peak of methyne protons of PVA at 3.8 ppm and the triad peaks of a hydroxyl proton at 4.1–4.7 ppm decreased. At the same time, the broad peak of methylene protons of PVA at 1.1–1.7 ppm shifted partially downfield, and the peak was separated.

In Figure 2, the corresponding IR spectra of AAPVA with different degrees of acetoacetylation are shown. As the degree of acetoacetylation increased, the absorption of two carbonyl groups in an acetoacetyl group at  $1710$  and  $1730\text{ cm}^{-1}$  increased. However, the

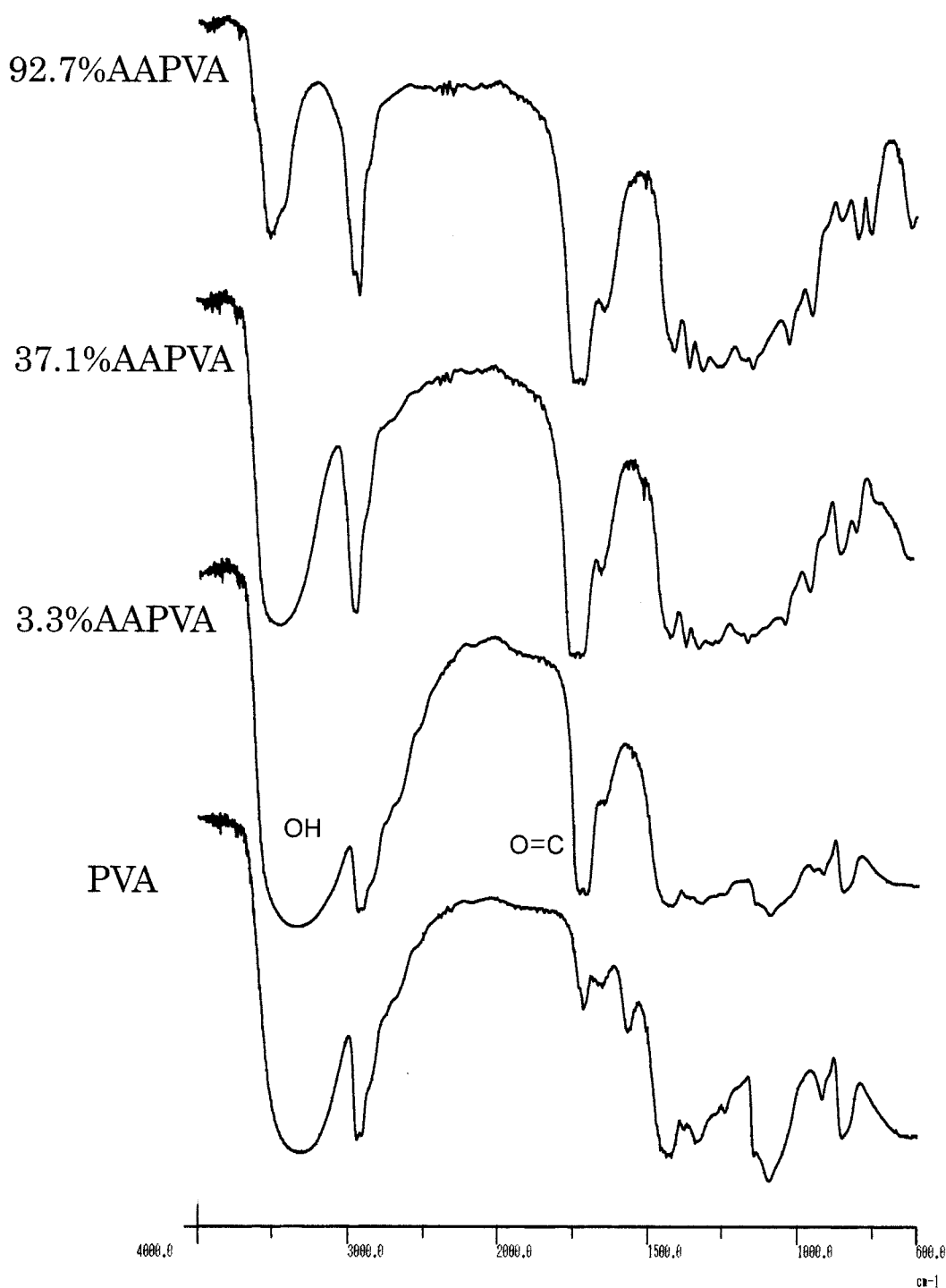


Figure 2 FTIR spectra of AAPVAs with various degrees of acetoacetylation.

absorption of a hydroxyl group of PVA at around  $3400\text{ cm}^{-1}$  gradually decreased.

The GPC measurement of AAPVA with 92.7% acetoacetylation showed number- and weight-average molecular weights of  $M_n = 42,400$  and  $M_w = 191,300$ , respectively. (The theoretical value calculated on the basis of the degree of acetoacetylation was 32,400–48,600.) These values suggest that there was little in-

crease in molecular weight attributed to intermolecular crosslinking during the synthesis, purification, and drying processes.

#### Adhesion of wood

The water solubility of the synthesized polymer decreased when the degree of acetoacetylation exceeded

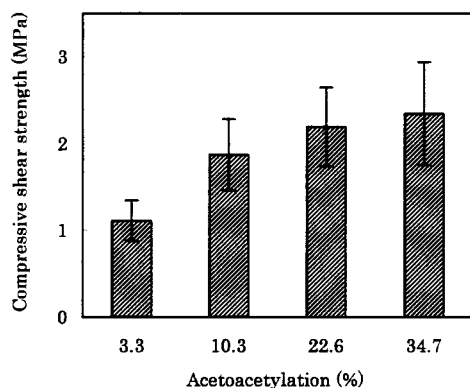


Figure 3 Immediate adhesion of wood by AAPVA.

about 40%. Because we were seeking suitable conditions for preparing a water-based adhesive, the adhesion test was carried out using water-soluble AAPVA, which had  $\leq 37.1\%$  acetoacetylation.

#### Test of immediate adhesion

The results of the immediate adhesion are shown in Figure 3. The adhesive strength increases together with the degree of acetoacetylation, and at 34.7% AAPVA was about twice that at 3.3% AAPVA. This result shows that the increase of acetoacetyl groups in the adhesive is effective in improving immediate adhesion. However, the effect of acetoacetylation on the adhesive strength was not linear and became saturated at a high degree of acetoacetylation.

#### Test of the time dependency of the adhesive strength of honeymoon-type adhesives

The results of the time dependency of the adhesive strength of honeymoon-type adhesives are shown in Figure 4. As for the time dependency of adhesive strength, 34.7% AAPVA showed greater adhesive strength than that of 3.3% AAPVA when tested after

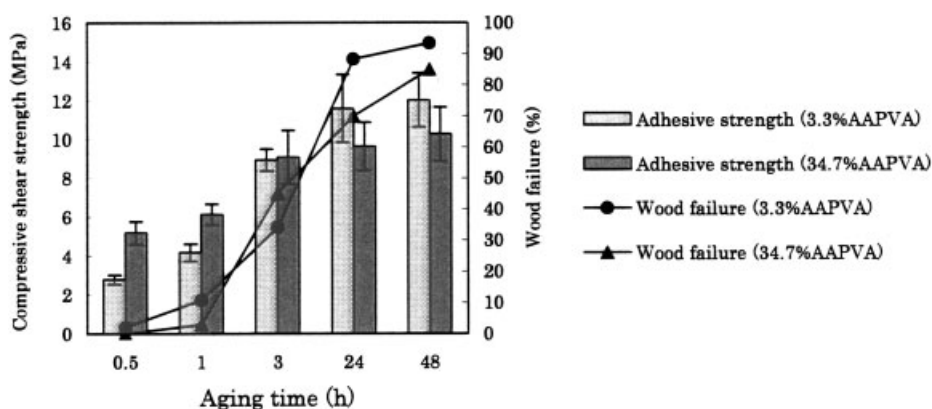


Figure 4 Time dependency of adhesive strength (AAPVA/1,6-hexamethylene diamine) after attachment.

1 h of bonding. However, the adhesive strength of 3.3% AAPVA increases sharply during ageing from 1 to 3 h, to almost the same degree as that of 34.7% AAPVA. It is assumed that the adhesive force increases because of a decrease of water in the adhesive interface. After 3 h, the adhesive strength of 3.3% AAPVA was greater than that of 34.7% AAPVA. From this result, increasing covalent bonds with increasing acetoacetyl groups may not contribute much to the final adhesive strength of AAPVA.

#### Effect of the kinds of amine compounds

To study the effect that the kind of crosslinking agent has on the adhesive strength of a honeymoon-type adhesive, the compressive shear strength test was carried out with several kinds of crosslinking agents. For preparation of base resin 37.1% AAPVA was used, and the crosslinking agent was a 10% solution (by weight) of several amine compounds. Tests were carried out on dry strength, on water resistance, on warm water resistance, and on repetitive boiling resistance. The results are shown in Figure 5.

All strength values were low with piperazine and polyethyleneimine as the crosslinking agent. No improvement in adhesion by crosslinking was observed with these two amines. Because piperazine did not show gelation on mixing with an aqueous solution of AAPVA, it may be concluded that no secondary amine has reactivity for crosslinking with the acetoacetyl group. However, when polyethyleneimine was mixed with the aqueous solution of AAPVA, gelation was observed. Still, there was no effect of polyethyleneimine as a crosslinking agent in the honeymoon-type adhesion. The dispersion and self-mixing of polyethyleneimine might occur quite slowly at the adhesive interface. Other amine compounds had some effect on crosslinking in all tests. These results suggest that small molecules having two or more primary amino groups in their structure are preferred as crosslinking agents.

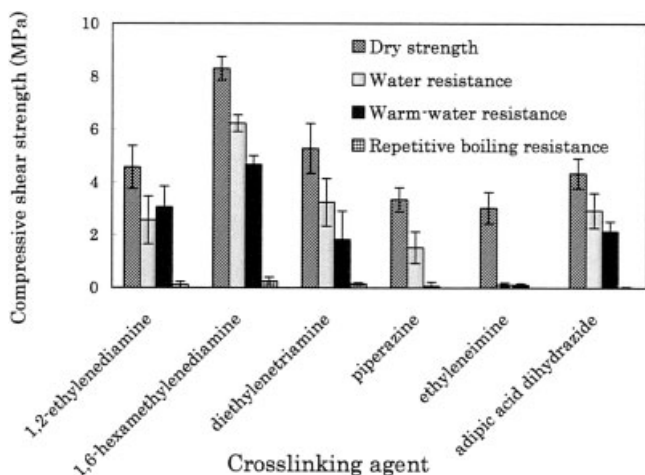


Figure 5 Effect of various diamines on adhesive strength.

When 1,6-hexamethylenediamine was used as the crosslinking agent, the results of all tests except for the boiling repetition experiment were very good. Given that 1,6-hexamethylenediamine has a relatively long nonpolar aliphatic chain, which consists of six carbon atoms between two amino groups, its flexible structure may contribute to the crosslinking reaction of an amino group on a polymer with a remote acetoacetyl group by increasing the mobility of the remaining amino group of bonded 1,6-hexamethylenediamine attributed to the hexamethylene group, and thus have a substantial effect on the crosslinking for adhesion (see Scheme 2).

**Effect of amine concentration on the strength of honeymoon-type adhesion**

To study the effect of the concentration of the crosslinking agent on adhesion, the compressive shear strength test was carried out using various amounts of the agent: 3.3% AAPVA and 37.1% AAPVA were selected as the base resin polymer for the test, and crosslinking agents containing 5 or 10% 1,6-hexamethylenediamine by weight were used. Tests were per-

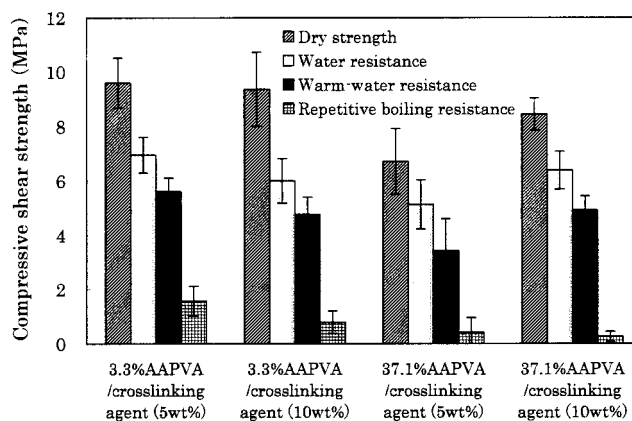
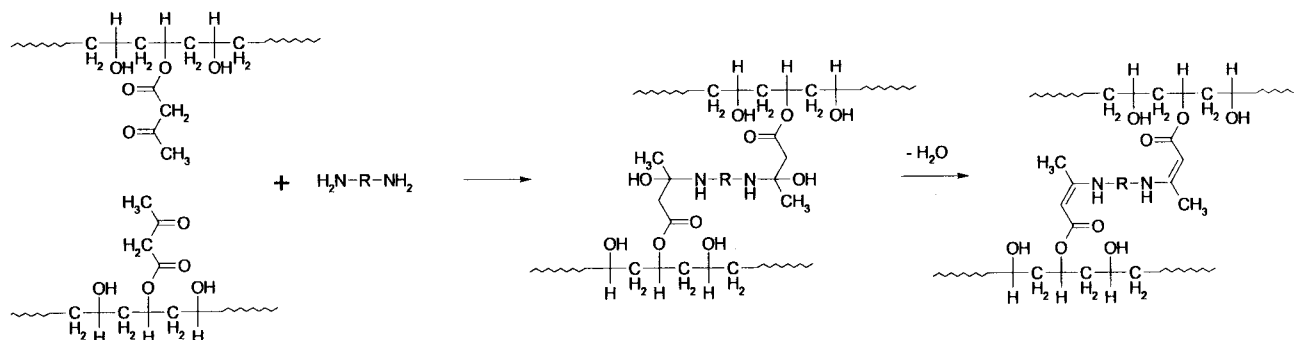


Figure 6 Effect of amine concentration and degree of acetoacetylation on bonding strength.

formed on dry strength, on water resistance, on warm water resistance, and on repetitive boiling resistance. The results are shown in Figure 6. The effect of the amount of crosslinking agent was not clear when 3.3% AAPVA was used. However, when 37.1% AAPVA was used as adhesive, the adhesive strength improved in all tests together with the amount of crosslinking agent from 5 to 10%. From these results it is clear that the crosslinking reaction between acetoacetyl groups and some amino compounds as a crosslinking agent is effective in improving the adhesive strength and also the water resistance, but only if the degree of acetoacetylation of AAPVA is sufficiently high. However, the results of the strength tests for the adhesives using 37.1% AAPVA was almost the same as for the adhesives with 3.3% AAPVA. These observations might suggest that the effect of increasing the amounts of crosslinking agent to improve water resistance cannot exceed the inherent water resistance of highly saponified PVA.

**CONCLUSIONS**

Acetoacetylated AAPVAs were synthesized, and the effects of the degree of acetoacetylation and amines as



Scheme 2 Crosslinking between acetoacetyl groups by diamine.

crosslinking agents on honeymoon-type adhesives for wood products were investigated. It was found that the compression shearing strength on immediate adhesion was improved with the increase of acetoacetyl groups in AAPVA. It was also suggested that the water resistance upon the introduction of acetoacetyl groups into PVA cannot exceed the inherent water resistance of highly saponified PVA and also that the adhesive strength of honeymoon-type adhesives using AAPVA is dependent on the chemical structure of the crosslinking agent.

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