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## Development of room-temperature curing aqueous emulsion-type acrylic adhesive I: effect of monomer composition on the initial adhesive strength

Received: September 10, 2003 / Accepted: December 22, 2003

**Abstract** For the purpose of developing a new aqueous emulsion-type adhesive for wood or paper use that does not release formaldehyde or volatile organic solvents, a honeymoon-type acrylic adhesive was examined. An adhesive system consisting of acrylic monomers copolymerized with functional monomers and a cross-linking agent was selected for the purposes of increasing initial adhesive strength and ensuring room-temperature curing. The initial adhesive strength increased by the use of cross-linkers such as dihydrazides and also polymeric methylene diphenyl diisocyanate (pMDI). Thus an adhesive with reasonable to good initial adhesive strength and room-temperature curing was obtained. The effect of pMDI on the initial adhesive strength was not significant and decreased when the amount of acrylamide in a copolymer was high.

**Key words** Acrylic emulsion · Honeymoon · Acetoacetyl · PVA · Diacetone acrylamide · Cross-linking

### Introduction

Demand for safe housing materials of little detriment to the environment is increasing. In particular, there is a public request for a decrease of formaldehyde emissions from housing materials prepared using conventional wood adhesives, such as urea and phenol resins, and volatile organic materials, such as xylene and toluene. Solutions for such a problem involve the use of formaldehyde catchers and development of nonformaldehyde adhesives and aqueous emulsion-type adhesives.

During the course of our study on the development of non-formaldehyde-type adhesives for wood or paper use, we examined an aqueous emulsion of acrylic copolymers with both rapid room-temperature curing properties and a strong final adhesive strength. According to our strategy, the adhesive strength immediately after jointing arises through the interaction of keto groups, copolymerized in the acrylic copolymer or present in a colloid stabilizer of the emulsion, with amino groups of cross-linkers, in addition to the tack of some acrylic monomers. Final strength would be generated by the full condensation of the keto groups with amines. Diacetone acrylamide (DAAM) is selected as the acrylic monomer having a keto group,<sup>1</sup> and acetoacetylated poly(vinyl alcohol) (AAPVA)<sup>2–4</sup> is used as the colloid stabilizer for the above purpose (Fig. 1).<sup>5</sup> The effects of monomer composition and cross-linker on the initial adhesive properties are described in this report.

### Experimental

All chemicals used were commercial reagents and were used as received unless specifically described.

A typical procedure for preparation of AAPVA was as follows: to a 1-liter four-neck flask equipped with a mechanical stirrer, a reflux condenser, a dropping funnel, and a nitrogen gas inlet, was added 52.8 g of poly(vinyl alcohol) (PVA; average degree of polymerization, 400–600; saponification, more than 96 mol%), 450 ml of dimethyl sulfoxide (DMSO), and 2.4 g of acetic acid as a catalyst. The mixture was warmed to 60°C and stirred under nitrogen until complete dissolution was attained. Diketene (25.21 g, 25 mol% to OH groups of PVA) was added dropwise to the solution, and the mixture was stirred at 500 rpm for 1 h. Then ethanol and hexane were added to the solution, and the insoluble polymeric material generated was collected by filtration. The polymeric precipitate was dissolved in distilled water, and dialyzed through a dialysis membrane (size 36). AAPVA product was obtained after freeze-drying of the dialyate (Fig. 2). The degree of acetoacetylation of

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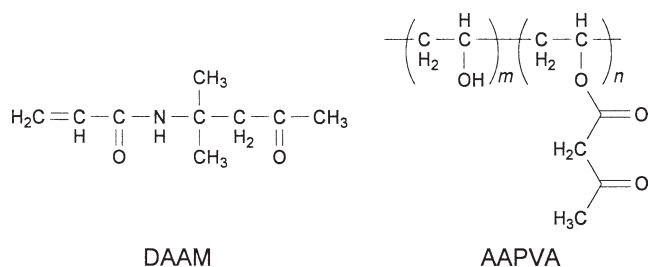
**Table 1.** Monomer composition of base-resin varnish<sup>a</sup>

Symbol	Initiator		Monomers mixture						Additives after solvent removal		Additive after dissolution
	DTBP	DTBP	MMA	MAA	EA	BA	DAAM	AM/H <sub>2</sub> O	Water	25% aq NH <sub>4</sub> OH	Water
A, D	0.32	0.5	5	20	10	61	20	–	100	16	250
B	0.35	0.5	–	20	–	60	20	–	100	15	250
C	0.35	0.5	–	20	–	60	–	20/20	100	15	450
E	0.35	0.5	–	10	–	60	30	–	100	6	250

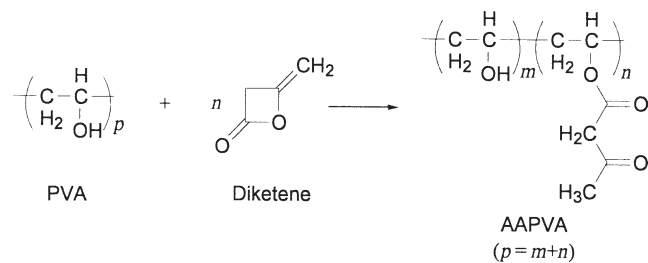
Data given as mass in grams

DTBP, di-*t*-butyl peroxide; MMA, methyl methacrylate; MAA, methacrylic acid; EA, ethyl acrylate; BA, *n*-butyl acrylate; DAAM, diacetone acrylamide; AM, acrylamide; aq, aqueous

<sup>a</sup>1,2-propanediol methyl ether acetate (60 g) was used as a solvent during polymerization and removed afterwards



**Fig. 1.** Carbonyl substrate. *DAAM*, diacetone acrylamide; *AAPVA*, acetoacetylated poly(vinyl alcohol)



**Fig. 2.** Acetoacetylation of poly(vinyl alcohol) (*PVA*)

*AAPVA* [ $D_{AA}$  (%)] was determined by <sup>1</sup>H nuclear magnetic resonance (NMR) spectroscopy from the percentage ratio of peak area due to acetyl protons at 2.2 ppm to the area of methylene proton peaks of the *PVA* main chain appearing in the range of 1.2–2.0 ppm multiplied by 1.5. The  $D_{AA}$  of the sample prepared as above was 10.6%.

### Synthesis of adhesives

The adhesives were prepared by a two-step procedure. The base-resin varnish was prepared first, and then the adhesive was prepared in the presence of the base-resin varnish.

Preparation of base-resin varnish A: to a 500-ml four-neck separable flask equipped with a mechanical stirrer, a reflux condenser, a dropping funnel, and a nitrogen inlet, was added 1,2-propanediol methyl ether acetate (*PMA*)

**Table 2.** Monomer composition of adhesive B<sup>a</sup>

Adhesive	BRV-B	BA	Styrene	DAAM	GMA	EDMA
B-1	25	62.5	10	11	0.25	0.5
B-2 <sup>b</sup>	25	62.5	10	11	0.25	–
B-3	25	62.5	10	11	–	0.5
B-4	25	62.5	10	–	0.25	0.5
B-5	25	62.5	–	11	0.25	0.5
B-6	25	–	10	11	0.25	0.5

Data given as mass in grams

BRV-B, base-resin varnish B; GMA, glycidyl methacrylate; EDMA, ethylene dimethacrylate

<sup>a</sup>H<sub>2</sub>O 6 g was added with BRV-B

<sup>b</sup>An extra 50 g of water was added

and the mixture was heated to 140°C under nitrogen. Then a solution of di-*t*-butyl peroxide (DTBP) in a small portion of *PMA* was added dropwise to the flask and the nitrogen flow was stopped. A mixture of DTBP, methacrylic acid (MAA), methyl methacrylate (MMA), ethyl acrylate (EA), butyl acrylate (BA), and DAAM was added to the flask over 3 h. Stirring was continued for a further 3 h after the addition was completed. *PMA* was removed from the solution under reduced pressure, and the residue was dissolved in dilute aqueous ammonium hydroxide to give base-resin varnish A (BRV-A).

Preparation of adhesive A: to a reaction flask similar to that described above was added BRV-A (25 g), distilled water (6 g), triethylamine (1 g), a small amount of 2,2'-azobis(4-methoxy-2,2'-dimethylvaleronitrile) (AMVN), and ammonium peroxodisulfate (APS), at 55°C under nitrogen. Then a mixture of BA 62.5 g, styrene 10 g, DAAM 10 g, ethylene glycol dimethacrylate (EDMA) 0.5 g, and glycidyl methacrylate (GMA) 0.25 g was added to the flask dropwise and stirring was continued for 5 h with occasional additions of AMVN and APS to give adhesive A.

Other base-resin varnishes and adhesives were prepared similarly according to the monomer compositions in Tables 1–5.

Conversions of monomers and solid contents of adhesives were determined according to the industrial test method JIS K6833 and the results are summarized in Table 6.

**Table 3.** Monomer composition of adhesive C<sup>a</sup>

Adhesive	BRV-C	BA	AM	Styrene	GMA	EDMA
C-1	25	62.5	5	10	0.25	0.5
C-2	25	62.5	10	10	0.25	0.5
C-3	25	52.5	20	10	0.25	0.5
C-4	25	42.5	30	10	0.25	0.5
C-5	25	62.5	5	–	–	–
C-6	25	62.5	10	–	–	–
C-7	25	52.5	20	–	–	–
C-8	25	42.5	30	–	–	–

Data given as mass in grams

BRV-C, base-resin varnish C

<sup>a</sup>H<sub>2</sub>O (15 g) and ethanol (15 g) were added with BRV-C

**Table 4.** Monomer composition of adhesive D<sup>a</sup>

Adhesive	DAAM	AAPVA $D_{AA}$
A	10	–
D-0	–	10 (0%)
D-2	–	10 (2.5%)
D-7	–	10 (7.5%)
D-10	–	10 (10.2%)
D-12	–	10 (12.6%)
D-14	–	10 (14.3%)
D-19	–	10 (19.6%)
D-22	–	10 (22.6%)

Data given as mass in grams

AAPVA, acetoacetylated poly(vinyl alcohol);  $D_{AA}$ , degree of acetoacetylation

<sup>a</sup>Other ingredients are the same as adhesive A, except for use of base-resin varnish D instead of base-resin varnish A

**Table 5.** Monomer composition of adhesive E<sup>a</sup>

Adhesive	DAAM	AM	H <sub>2</sub> O
E-1	10	10	30
E-2	20	20	110
E-3	–	10	30
E-4	–	20	100
E-5	10	–	30

Data given as mass in grams

<sup>a</sup>Other ingredients are the same as adhesive A, except for use of base-resin varnish E instead of base-resin varnish A

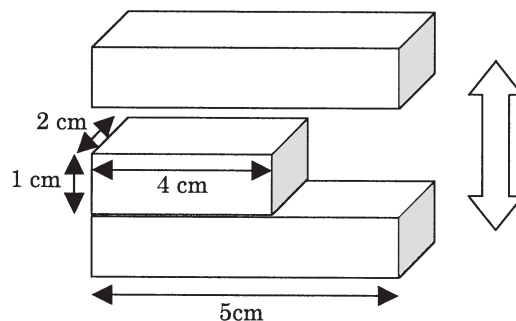
### Adhesive strengths

Initial bonding strengths were determined by the cleavage test. Red meranti was used as the adherend throughout the work. The test sample is shown in Fig. 3; the size of the upper and lower pieces were 2.0(W) × 5.0(L) × 1.0(H) cm, and that of the middle piece was 2.0(W) × 4.0(L) × 1.0(H) cm. The lower piece and the middle piece were bonded with a conventional epoxy resin. Fifteen samples were examined per test.

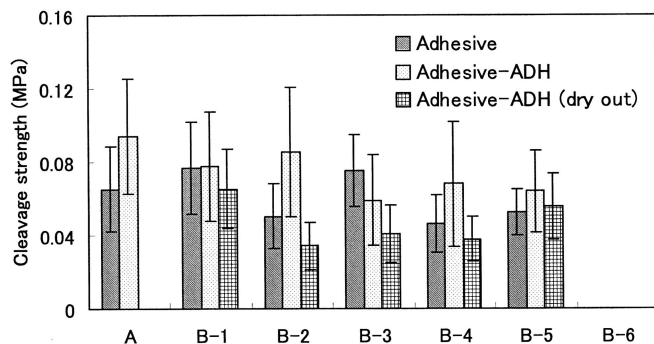
Two types of bonding methods of test samples were used depending on the use of a cross-linking agent or not. When bonding without the cross-linking agent, 0.08 g of adhesive

**Table 6.** Solid contents and monomer conversions of adhesives

Adhesive	Solid content (g)		Conversion (%)
	Dried for 24h	Theoretical	
A	53.7	55.7	96.5
B-1	58.8	55.0	106.9
B-2	44.4	43.1	103.2
B-3	56.2	55.0	102.2
B-4	52.3	52.1	100.2
B-5	51.5	52.4	98.2
B-6	30.4	31.6	96.5
C-1	39.7	57.4	69.2
C-2	43.2	58.3	74.0
C-3	44.8	58.3	76.9
C-4	52.5	58.3	90.0
C-5	38.3	55.2	69.3
C-6	39.4	56.3	70.0
C-7	37.8	56.3	67.2
C-8	46.1	56.3	81.9
D-0	42.3	55.7	75.9
D-2	48.4	55.7	87.0
D-7	48.1	55.7	86.5
D-10	41.0	55.7	73.7
D-12	41.5	55.7	74.6
D-14	30.6	55.7	55.1
D-19	33.4	55.7	60.0
D-22	38.0	55.7	68.3
E-1	42.7	49.4	86.5
E-2	31.4	40.2	78.0
E-3	39.8	47.0	84.6
E-4	27.1	37.5	72.2
E-5	48.5	47.0	103.2

**Fig. 3.** Test piece for the cleavage test

was spread evenly on the middle piece (see Fig. 3), and the piece was allowed to dry for 1 min (open release time). Then the coated middle piece was bonded with the upper piece. The assembled sample was left for 2 min and then pressed at 0.98 MPa for 30 s. One minute after the release of pressure, the initial bonding strength of the sample was measured by the cleavage test with a crosshead speed of 100 mm/min. In the case of using cross-linking agent, the upper piece was coated evenly with 0.032 g of cross-linker, and 0.08 g of adhesive was spread on the middle piece as described above. Both pieces were left for 5 min and the two were then jointed and treated as above.



**Fig. 4.** Initial adhesive strengths of adhesives A and B. Error bars show standard deviations. ADH, adipic acid dihydrazide

## Results and discussion

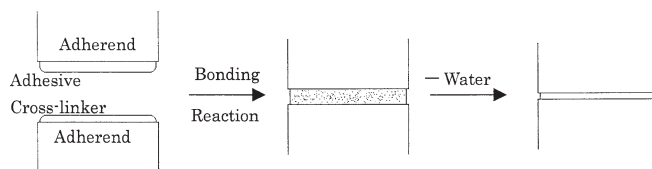
Solid contents and total conversions of monomers of the prepared adhesives are summarized in Table 6. Conversions of adhesives in the A and B series almost attained theoretical values, suggesting that the polymerization proceeded successfully to the end. However, conversions of the C and D series were low, and indicate the presence of some inhibitory effects in these monomer systems. Conversion increased with AM content in the C series, and the increase of  $D_{AA}$  of AAPVA in the D series resulted in rather lower conversion.

### Initial bonding strength

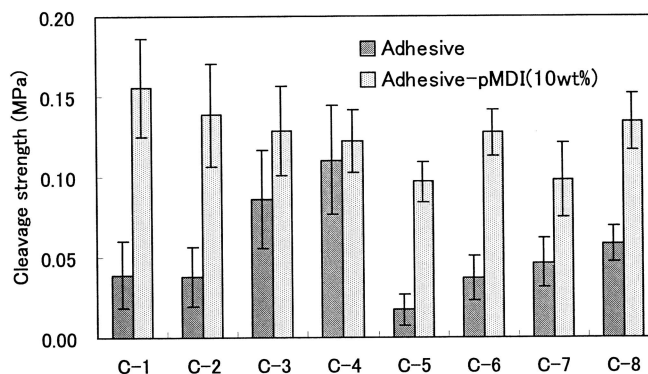
The results for initial bonding strength tests of adhesives A and B are shown in Fig. 4.

The results indicate that the initial adhesive strength increased by reaction of the adhesive with adipic acid dihydrazide (ADH) as cross-linker through the reaction of carbonyl groups with the nucleophilic  $NH_2$  groups of hydrazide, even several minutes after jointing, although it is not clear at present whether the interaction was due to complete hydrazone formation. For this test, “dry out” means that jointing was carried out after drying out the cross-linker by leaving the piece for 1 day at room temperature after coating.

In general, the bonding strength of A was higher than those of the B series, and B-1 showed the best bonding strength in the series. B-6 showed no initial adhesive strength. These results suggest that each component of the mixed monomers has its own contribution to the adhesive strength of A or B-1, and BA contributed much to the initial adhesive force because of its characteristic high tack. ADH was effective as a cross-linking agent for increasing initial bonding except in B-3, which suggests not only reaction with the keto group but also the reaction of the cross-linker with the epoxide group contributes to the initial adhesive strength.<sup>6</sup> Drying out the cross-linker before bonding resulted in a similar or a slightly weaker strength than bonding without the cross-linker. It may be suggested that the



**Fig. 5.** Bonding mechanism of aqueous honeymoon adhesive



**Fig. 6.** Initial adhesive strengths of adhesive C. Error bars show standard deviations. pMDI, polymeric methylene diphenyl diisocyanate

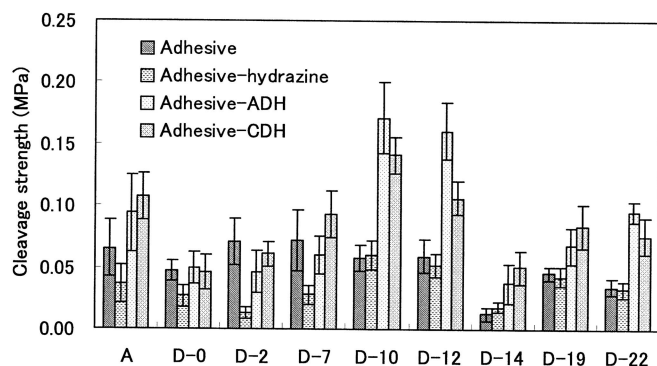
aqueous medium contributes to the reaction of cross-linker through better diffusion of cross-linker to the reaction site, and subsequent diffusion of water into the adherend developed the bonding strength, as shown in Fig. 5.

The results for adhesive C are summarized in Fig. 6. In these experiments, the cross-linker was changed to 10% aqueous polymeric methylene diphenyl diisocyanate (pMDI).

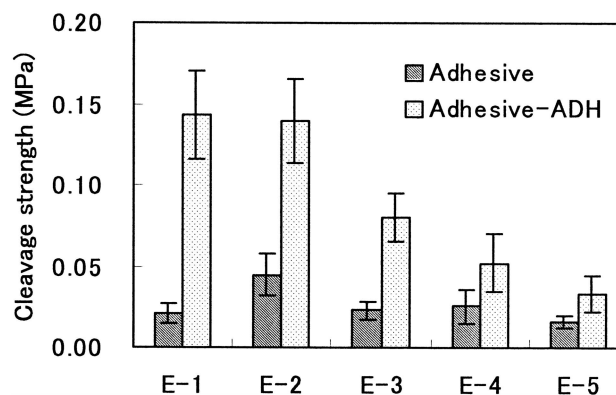
The results for bonding with the C series adhesives indicate that the initial adhesive strengths increase with the amount of AM monomer. Because strong hydrogen bonding of the amide group is well documented, this observation may be interpreted as the effect of hydrogen bonding of the amide group on the initial bonding strength. However, as described above, the conversion of acryl monomers in the polymerization process also increased with the amount of AM. Thus, part of the observed strengthening effect of AM may be ascribed to the higher conversion.

When pMDI is used as the cross-linker, the initial adhesive force of adhesive C increased significantly, as was observed with C-1. However, the initial bonding strength decreased with the amount of AM. We have no reasonable explanation for this observation yet, but urea and biuret bonds generated from the reactions of isocyanate with an amide group of AM may not be as effective as an amide group for hydrogen bonding.

Figure 7 shows the results for adhesive D. In this series, three cross-linkers, 10% ADH, 10% carbodihydrazide (CDH), and 10% hydrazine aqueous solutions, were used and their efficiencies were compared. Initial bonding strength was increased with ADH or CDH, which suggests the formation of hydrazone cross-linking. ADH was found



**Fig. 7.** Initial adhesive strengths of adhesive D. Error bars show standard deviations. CDH, carbodiimide



**Fig. 8.** Initial adhesive strengths of adhesive E. Error bars show standard deviations

to be more effective than CDH based on the results of D-10 and D-12. However, hydrazine itself was not effective as a cross-linker, with results showing that bonding strength decreased when hydrazine was used as a partner of honey-moon bonding. Hydrazines react with carbonyl groups to form hydrazones, but their nucleophilicity is high enough to also react with ester groups, causing cleavage of the ester linkage. The results obtained indicate that the latter effect prevailed in this system.

Regarding the effect of acetoacetyl group concentration ( $D_{AA}$  (%)) of AAPVA on the bonding strength, concentrations of acetoacetyl group higher than 7.5% in AAPVA tend to decrease the initial bonding strength. Increased substitution of hydroxyl groups in PVA by acetoacetyl groups results in fewer free OH groups remaining in the adhesive and more hindrance due to the bulky acetoacetyl group for hydrogen bonding between two intermolecular OH groups, decreasing the initial bonding strength.

Results for the adhesive E series are shown in Fig. 8. The effect of ADH as a cross-linker is significant in this series. Initial bonding strength without cross-linker increased by dilution of the adhesive with  $H_2O$ , as can be seen from comparison between E-1 and E-2, or E-3 and E-4, while no such tendency was observed using ADH as a cross-linker. These results clearly indicate the important role of the cross-linking reaction on the initial strength. Without a cross-linker, there was insufficient interaction of adhesive with adherend at the adhesive surfaces of E-1 and E-3 because the adhesives were too viscous to make a sufficient glue line. By increasing water content as solvent or extender, there was some improvement in the adhesive strength, as seen for E-2 and E-4. However, honeymoon-type bonding in the presence of ADH increased the site of interaction and initial bonding strength significantly. The dilution effect did not influence the bonding strength in the presence of ADH. The poor result of E-5 shows the importance of AM monomer as the emulsifying component. Adhesive E-5 did not develop emulsion successfully and was rather inhomogeneous. Thus E-5 had few bonding sites and, as a result, low adhesive strength. These results suggest that DAAM works for cross-linking and initial bonding strength in the presence of an effective partner, and AM works for emulsification and tack. Adhesives involving both

components, such as E-1 and E-2, showed excellent initial adhesion.

## Conclusion

Several acrylic emulsions were prepared for the development of a new non-formaldehyde-type aqueous emulsion having room-temperature adhesion properties and both high initial tack and final adhesive strength. Their adhesive properties were examined and this article describes the factors controlling the initial adhesive strength. It was found that the initial adhesive strength increased significantly by using cross-linkers, such as dihydrazides and pMDI, and with the content of acrylamide. pMDI was effective as a cross-linker, but its effect decreased with the amount of acrylamide. These results indicate that (1) reaction of a hydrazide group with a carbonyl was sufficiently fast to contribute to the initial adhesive strength; (2) hydrogen bonding of an amide group contributes to the initial adhesive strength; and (3) chemical bonding by pMDI forming a urea or biuret bond through interaction of the isocyanate group with amino or amide groups has a rather small contribution to the initial adhesive strength.

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