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

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

**Abstract** In a series of studies, development of a new aqueous emulsion-type adhesive for use with wood or paper, which does not release formaldehyde or volatile organic solvents, was attempted. For the purpose of increasing both initial and final adhesive strengths, we selected a system consisting of acrylic monomers copolymerized with functional monomers such as diacetone acrylamide and some cross-linking agents such as dihydrazide or polymeric methylene diphenyl diisocyanate (pMDI). It was found that dihydrazide cross-linker was effective for both the initial and final adhesive strengths, suggesting contribution of hydrazone bonds to the bonding strengths. Cross-linking with pMDI might be slow and was not important in the initial bonding. However, its cross-linking effect might develop gradually, because the adhesive showed good final strengths using pMDI as a cross-linker.

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

### Introduction

The accepted mechanism of adhesion<sup>1</sup> involves the combined action of mechanical bonding, physical interaction, and chemical interaction to generate total binding strength (or force). Mechanical bonding is otherwise called the anchor effect, and is important in the bonding of porous adherends, such as wood, paper, and leather. Physical bonding is due to the intermolecular interaction of constituents (second-order bonding) such as van der Waals forces

(London dispersion force), and constitutes the basic force of adhesion. Chemical interaction means hydrogen bonding and the first-order bonding between adhesive and adherend.

During the course of our study on the development of a non-formaldehyde-type adhesive for use with wood or paper, an aqueous emulsion of acrylic copolymers with both rapid room-temperature curing properties and strong permanent adhesive strength was examined. According to our strategy, the immediate adhesive strength after bonding was given through the cross-linking reaction 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 due to some acrylic monomers. Final strength would be given by the full condensation of the keto groups with amines and also full development of hydrogen bonding after the free water of emulsion is lost. As described in the preceding article,<sup>2</sup> diacetone acrylamide (DAAM) was selected as the acrylic monomer having a keto group,<sup>3</sup> and acetoacetylated poly(vinyl alcohol) (AAPVA)<sup>4–7</sup> was used as the colloid stabilizer for the above purpose. The effects of monomer composition and the kind of cross-linkers on the final adhesive properties were examined in light of the above mechanisms of adhesion.

### Experimental

Syntheses of adhesives (series A to E) are described in the preceding article.<sup>2</sup> Final adhesive strengths were determined by compression lap shear test using the test piece shown in Fig. 1. The size of a test piece was 2.0 (W) × 3.0 (L) × 1.0 (H)cm with the bonded area of 2.0 × 2.5cm. The number of test pieces examined per test was 15. Water resistance and repeated boiling tests were carried out according to the procedures of JIS K6852. Bonding strength by the compression lap shear test was measured with a crosshead speed of 2mm/min.

Two bonding methods were used depending on the use of cross-linking agent. When bonding without the cross-

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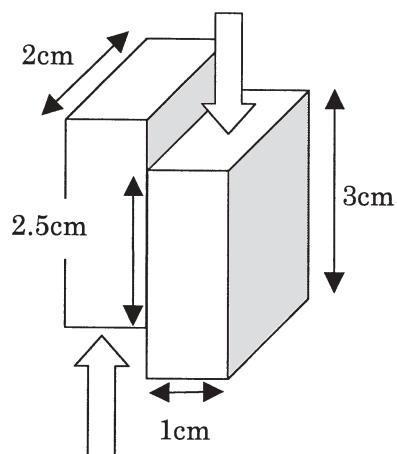


Fig. 1. Test piece for the compression lap shear test

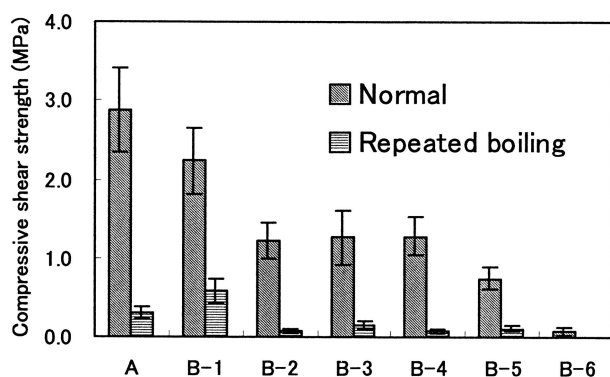


Fig. 2. Final adhesive strengths of adhesives A and B. Error bars show standard deviations

linking agent, 0.1 g of adhesive was spread evenly on a piece, which was then bonded with another piece. The assembled test sample as in Fig. 1 was pressed at 0.69 MPa for 24 h, and aged for 1 week at 25°C after pressing. When the cross-linking agent was used, 0.04 g of cross-linker was spread evenly on a piece, and the other piece was coated with 0.1 g of adhesive. The two pieces were then bonded together and treated similarly as above.

## Results and discussion

The results of final bonding strengths and repeated boiling tests of adhesives A and B by using 10% adipic acid dihydrazide (ADH) as a cross-linker are shown in Fig. 2.

The results can be interpreted as follows: when a cross-linker was not used, the final bonding strengths of the adhesives examined here are expected to arise mainly from mechanical bonding, hydrogen bonding, and physical interaction of intermolecular bonding forces. In the presence of a cross-linker, however,  $\text{NH}_2$  groups of nucleophilic hydrazide react with the carbonyl group of the adhesive, leading to hydrazone formation and increased bonding strength.

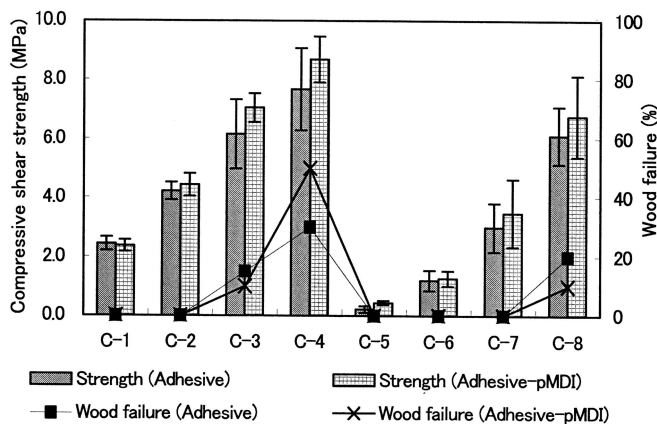
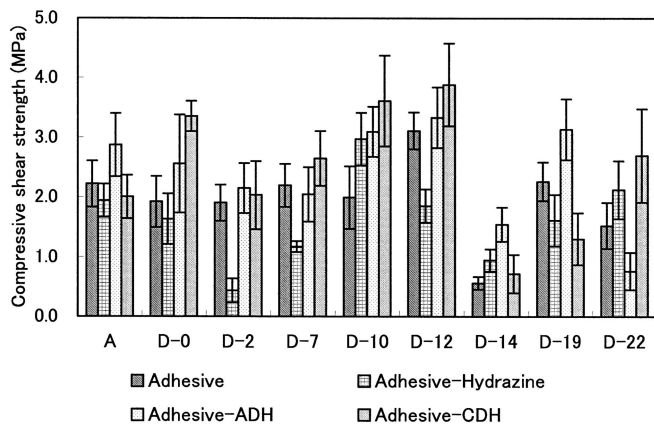


Fig. 3. Final adhesive strengths and wood failures of adhesive C. Error bars show standard deviations. pMDI, polymeric methylene diphenyl diisocyanate

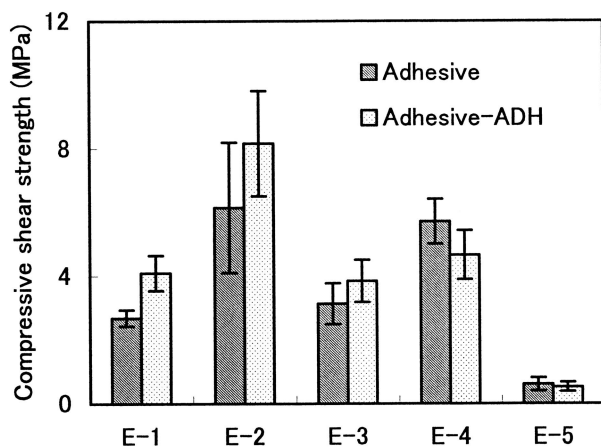
Experiments with the adhesive B series were carried out to see the contribution of each monomer on the total performances of the adhesive. The performances of adhesives prepared from four types of monomers were compared with that of adhesives prepared from five components [ethyleneglycol dimethacrylate (EDMA), glycidyl methacrylate (GMA),<sup>8</sup> DAAM, styrene, and butyl acrylate (BA)]. In general, the bonding strength of A was higher than those of the B series, and B-1 was the highest in the B series. The latter tendency is similar to the initial bonding strengths reported in the preceding publication.<sup>2</sup> These results suggest that each component of the mixed monomers has its own contribution to the final adhesive strength and BA had the most significant influence on the initial adhesive strength. ADH was effective as a cross-linking agent for increasing not only initial bonding described earlier, but also the final bonding. After repeated boiling, however, all adhesives that were examined showed very limited strength.

The results for the adhesive C series are summarized in Fig. 3. In these experiments, the cross-linker was 10% aqueous polymeric methylene diphenyl diisocyanate (pMDI). Final bonding strengths of the C series indicate that the strengths increased with the amount of acrylamide (AM). This observation can be interpreted as the effect of increasing hydrogen bonding of the amide group on the final bonding strength and/or increased conversion of adhesives with higher concentrations of AM. pMDI, used as the cross-linker, increased final adhesive force, but the effect was not significant. The samples bonded with adhesives C-3, C-4, and C-8 showed wood failure, indicating sufficient bonding strengths. After repeated boiling, however, all adhesives that were examined did not show measureable strength.

Figure 4 shows the results for the adhesive D series. In this series, three cross-linkers, 10% ADH, 10% carbodihydrazide (CDH), and 10% hydrazine solutions, were used and their efficiencies were compared. Final bonding strength increased with both hydrazide cross-linkers, ADH and CDH, suggesting the formation of hydrazone cross-linking. Although ADH was a little more effective



**Fig. 4.** Final adhesive strengths of adhesive D (normal). Error bars show standard deviations. ADH, adipic acid dihydrazide; CDH, carbodihydrazide



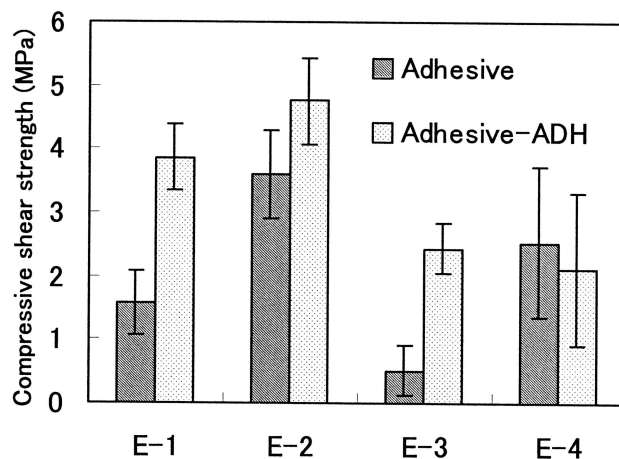
**Fig. 5.** Final adhesive strengths of adhesive E (normal). Error bars show standard deviations

than CDH in initial bonding strength, final bonding strength was higher with the latter. Again, hydrazine was not effective as a cross-linker and final bonding strength decreased in many cases when hydrazine was used as a partner of honeymoon bonding, probably because of the same reason stated in the preceding report<sup>2</sup> for the initial strength.

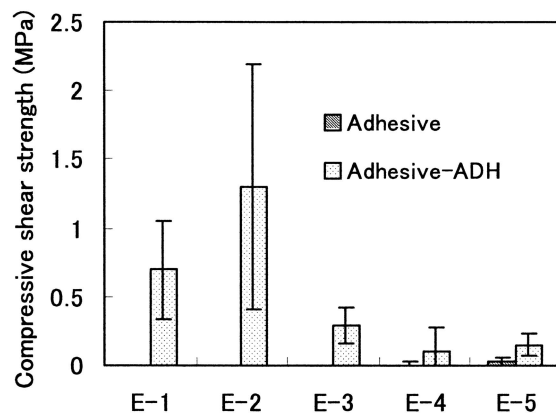
There appears to be an optimum concentration of acetoacetyl group (O-AA) in AAPVA for the final adhesive strength. Increased substitution of OH groups by O-AA increased the final bonding strength up to 12.6% of substitution, but the strength then decreased with more substitution.

Results for the adhesive E series are shown in Fig. 5. The effect of ADH as a cross-linker is significant for the initial strength, but is less significant for the final strength. These results suggest that the contribution of hydrogen bonding is important for the final strength.

The results of water absorption tests and repeated boiling tests for the E series are shown in Figs. 6 and 7, respectively. The results show that cross-linking is effective for the water resistance of final bonding, although proper flowability of adhesive after bonding is also important.



**Fig. 6.** Final adhesive strengths of adhesive E (water resistance). Error bars show standard deviations



**Fig. 7.** Final adhesive strengths of adhesive E (repeated boiling). Error bars show standard deviations

Similar results were obtained in the repeated boiling test, but it is interesting that even after repeated boiling in water for 4h with a intervening drying process (60°C, 20h) (repeated boiling test, JIS K6852), the cross-linked adhesive maintained significant bonding strength. However, almost no adhesive strength was observed without ADH as a cross linker, suggesting that intermolecular bonding is considerably strong in the normal test, but is not tolerant toward repeated boiling. It may be concluded that some hydrazone linkages formed by the reaction of ADH with the keto group can survive even after repeated boiling.

For the purpose of improving water resistance, we further tested some additives such as a wax emulsion or a coating material. However, the results were not reproducible and were not significant.

## Conclusions

For the development of a new non-formaldehyde-type aqueous emulsion adhesive possessing room-temperature adhesion properties and both high initial tack and final

adhesive strength, several acrylic emulsions were prepared and their adhesive properties examined. This article describes the factors controlling final adhesive strength and water resistance.

It was found that 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 the contributions to the initial adhesive strength by the hydrogen bonding of amide groups, the sufficiently fast formation of hydrazide, and the rather small contribution of the first-order bonding by pMDI, which generates a urea or biuret bond through the interaction of isocyanate with an amino or amide group.

Final bonding strength did not correlate with the initial bonding strength. This suggests that the cross-linking reaction between adhesive polymers is effective for initial adhesive strength, but final adhesive strength is dependent on interfacial interaction between adhesive polymers and the adherend.

In the presence of dihydrazide cross-linker, the behavior of the final adhesive strength was almost the same as the initial adhesive strength, and showed the contribution of the formation of hydrazone bonding. pMDI cross-linking was slow and not important in the initial bonding, but increased the final strength. Some adhesives that are newly developed in this study showed sufficient normal adhesive strength,

but insufficient strength for use under repeated boiling conditions. Nevertheless, this characteristic may be useful in environmental protection and recycling in that it can be removed easily by immersion in warm water after the main purpose of adhesion is over.

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