
Honeymoon-type Adhesives for Wood Products based on Acetoacetylated PVA and Diamines

Effect of Diamines and Degree of Acetoacetylation

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Background

Request for Wood Adhesive of Low VOC

Strategy

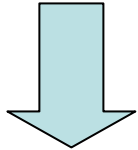
Solventless (Hot-melt, Self-bonding)

Water Based

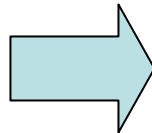
Others

Problems associated with Low VOC Adhesives

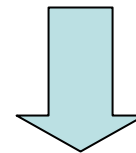
Low VOC



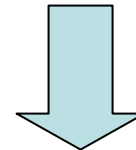
Water Base



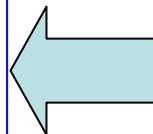
- Low Water Resistance
- Long Time for Bonding



Introduction of Cross-linking

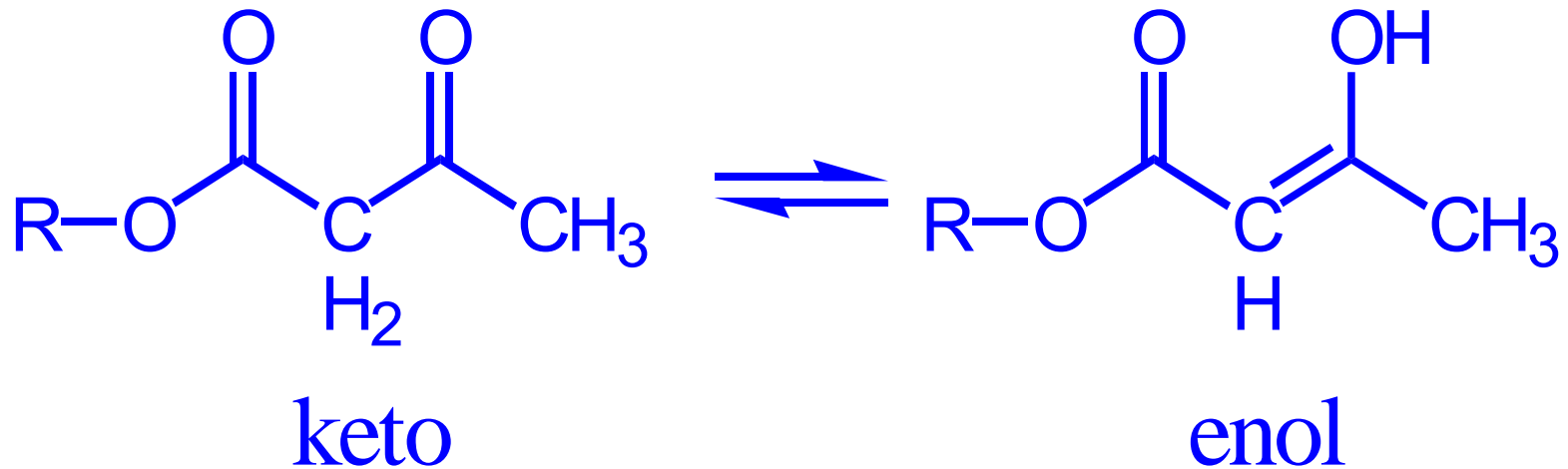


**Water Resistant
Fast Bonding**

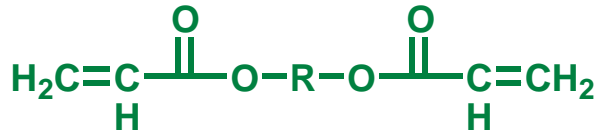
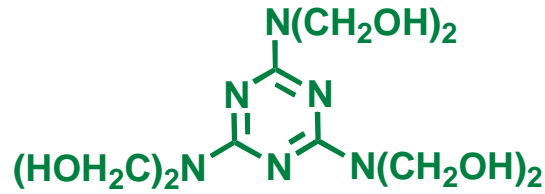
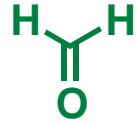


Utilization of Acac Group

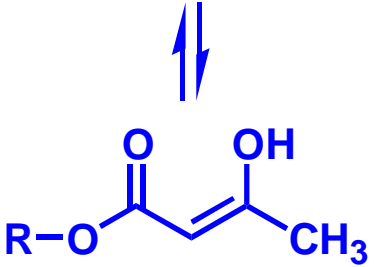
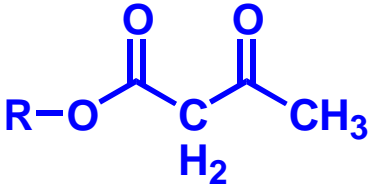
Structure of AA Group



acetoacetyl group

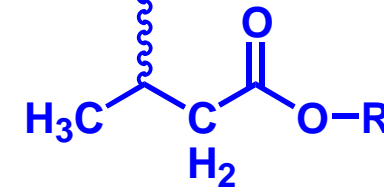
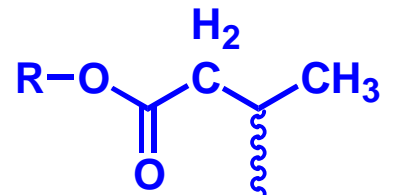
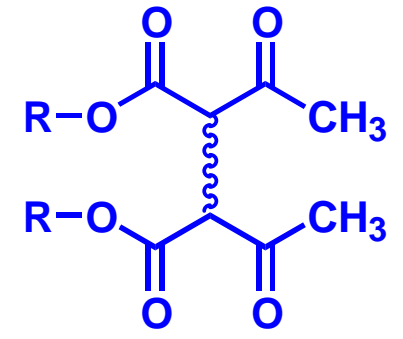


Crosslinking agent



+

⇒
Crosslink



Cross-linking Reactions of Acetoacetyl Group

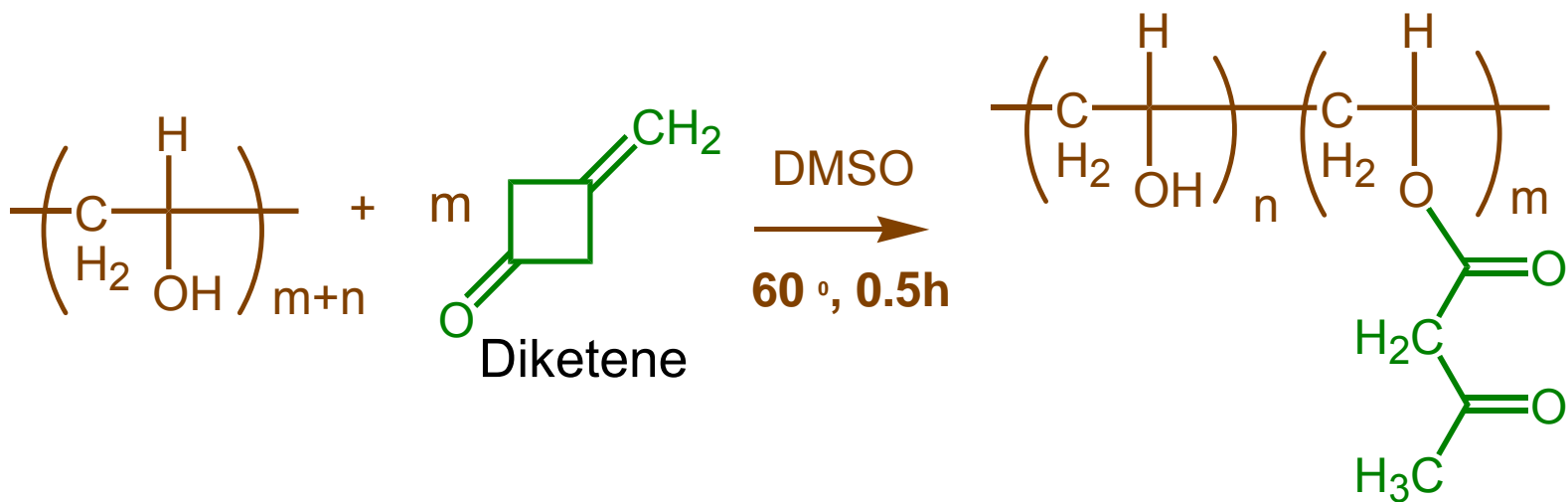
This work presents:

I . Development of Honey-Moon Type
Aqueous Adhesive using AAPVA

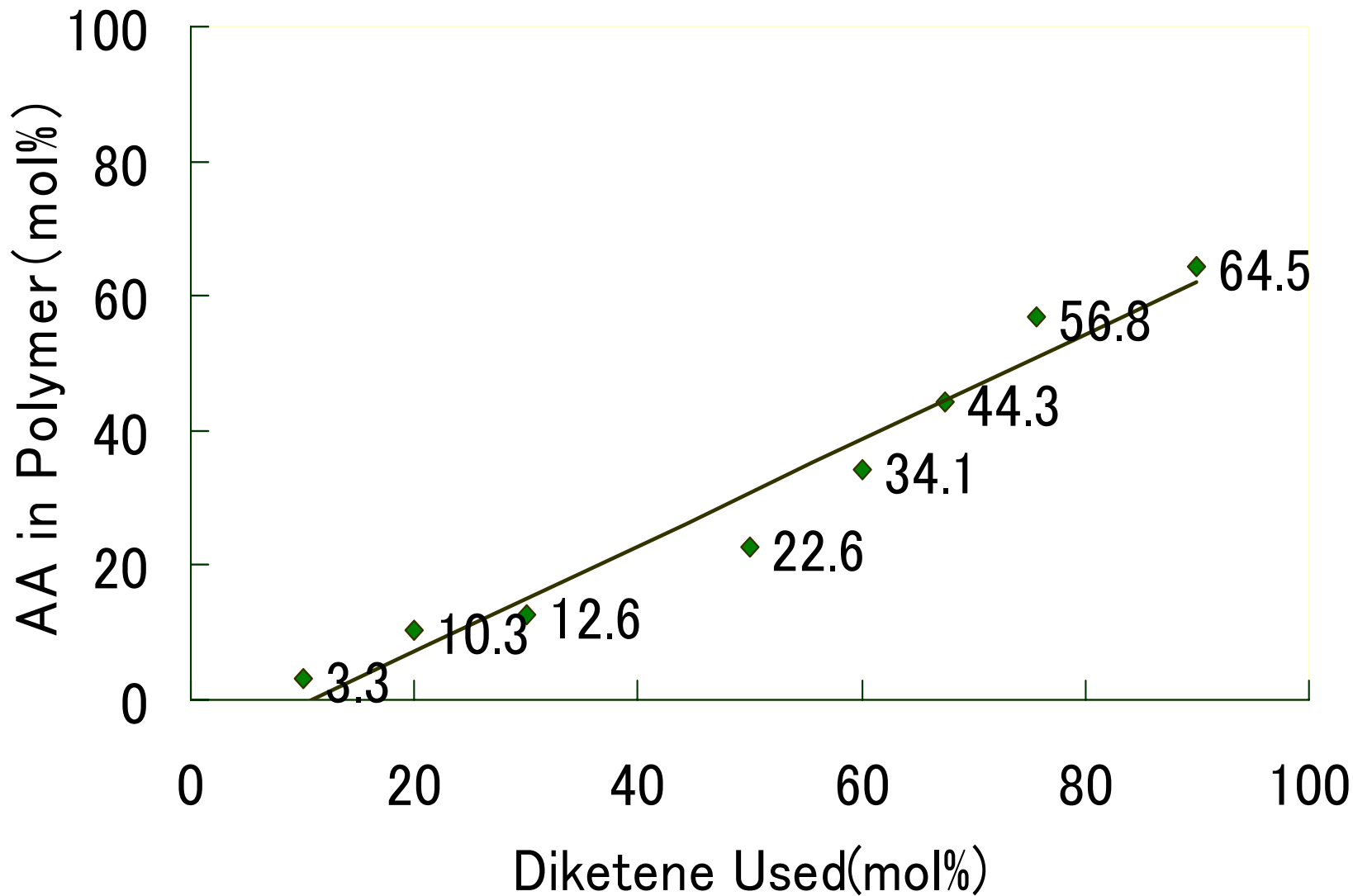
II . Synthesis of Acrylic Emulsion Stabilized
by AAPVA and Development of Room-
temp. Curing Emulsion-type Adhesive
Bonding through Cross-linking (Honey-
moon Type)

I . Development of Aqueous Honey-Moon Type Adhesive using Acetoacetylated PVA



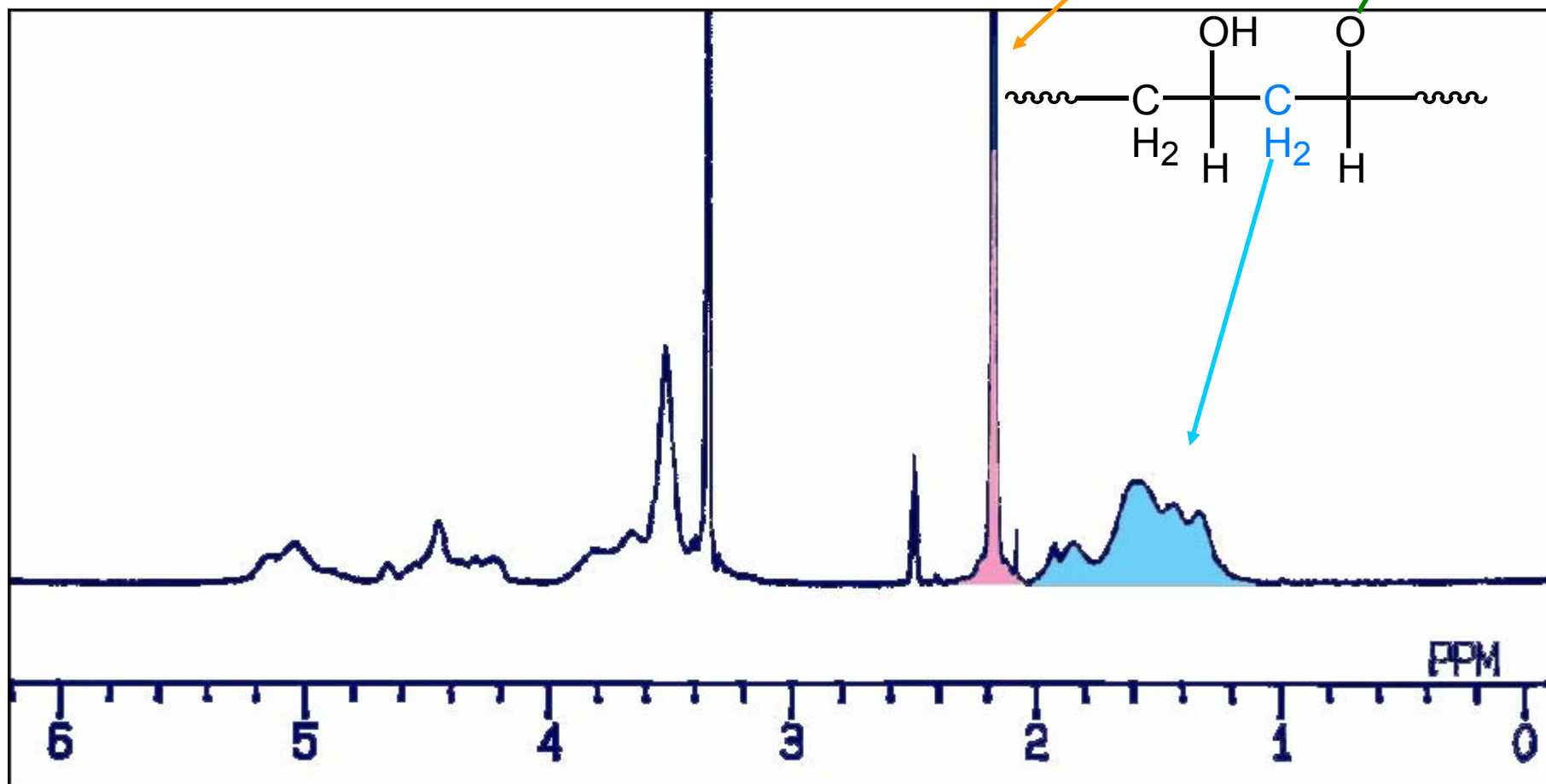
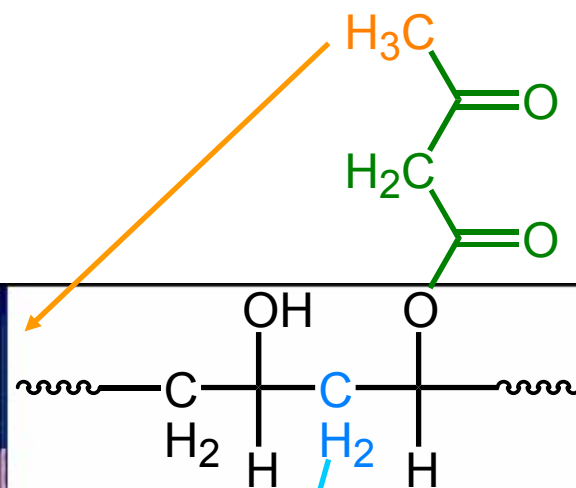


Homogeneous Synthesis of AAPVA

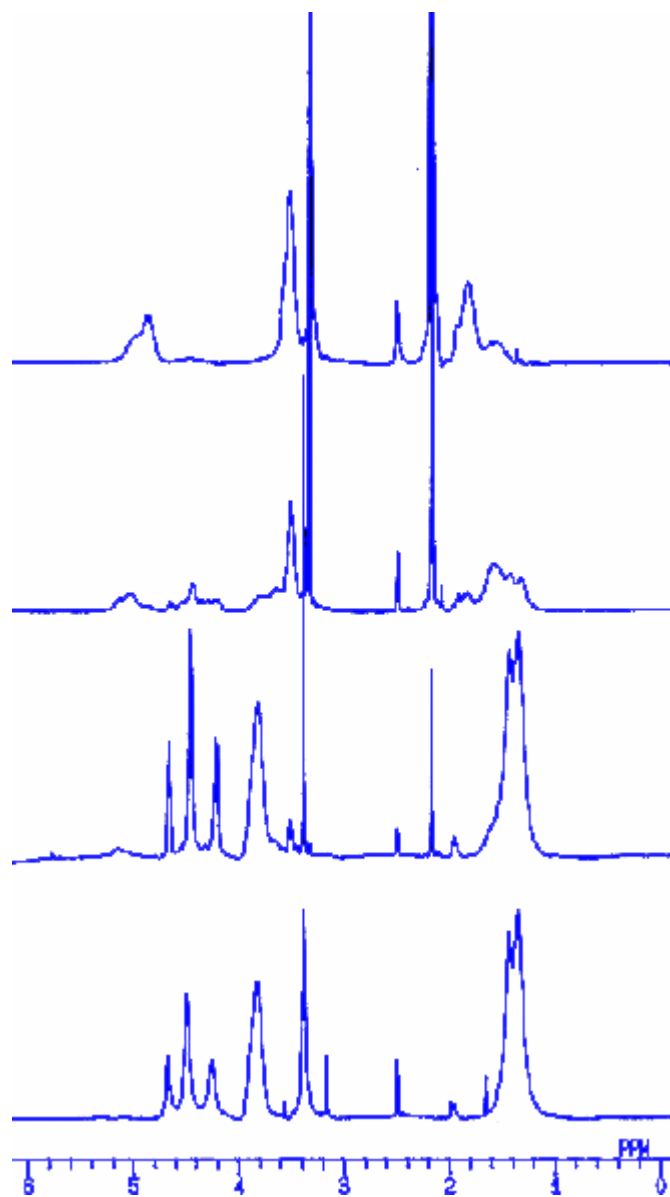


Relationship between AA in Polymer vs used Diketene

$$\text{Degree of Acetoacetylation (mol\%)} = \frac{2 \times \text{H (Methyl of Acac)}}{3 \times \text{H (Methylene of PVA)}} \times 100$$



$^1\text{H-NMR}$ of AAPVA

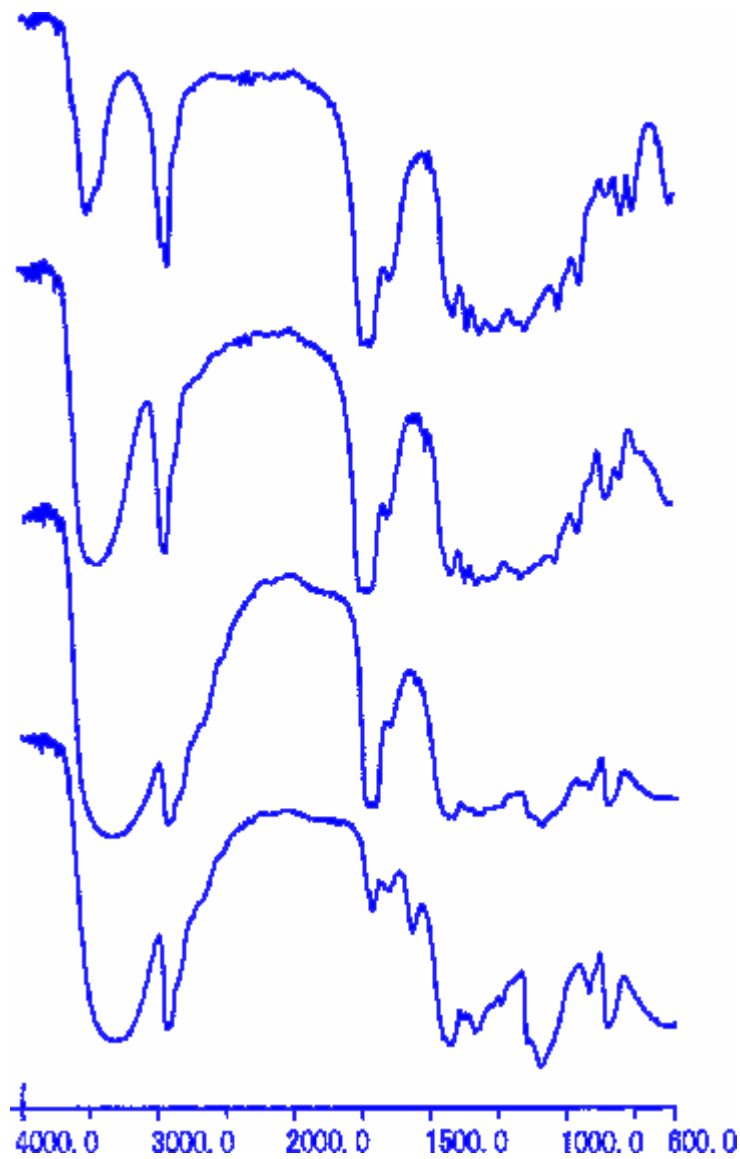


AAPVA
(92.7mol% AA)

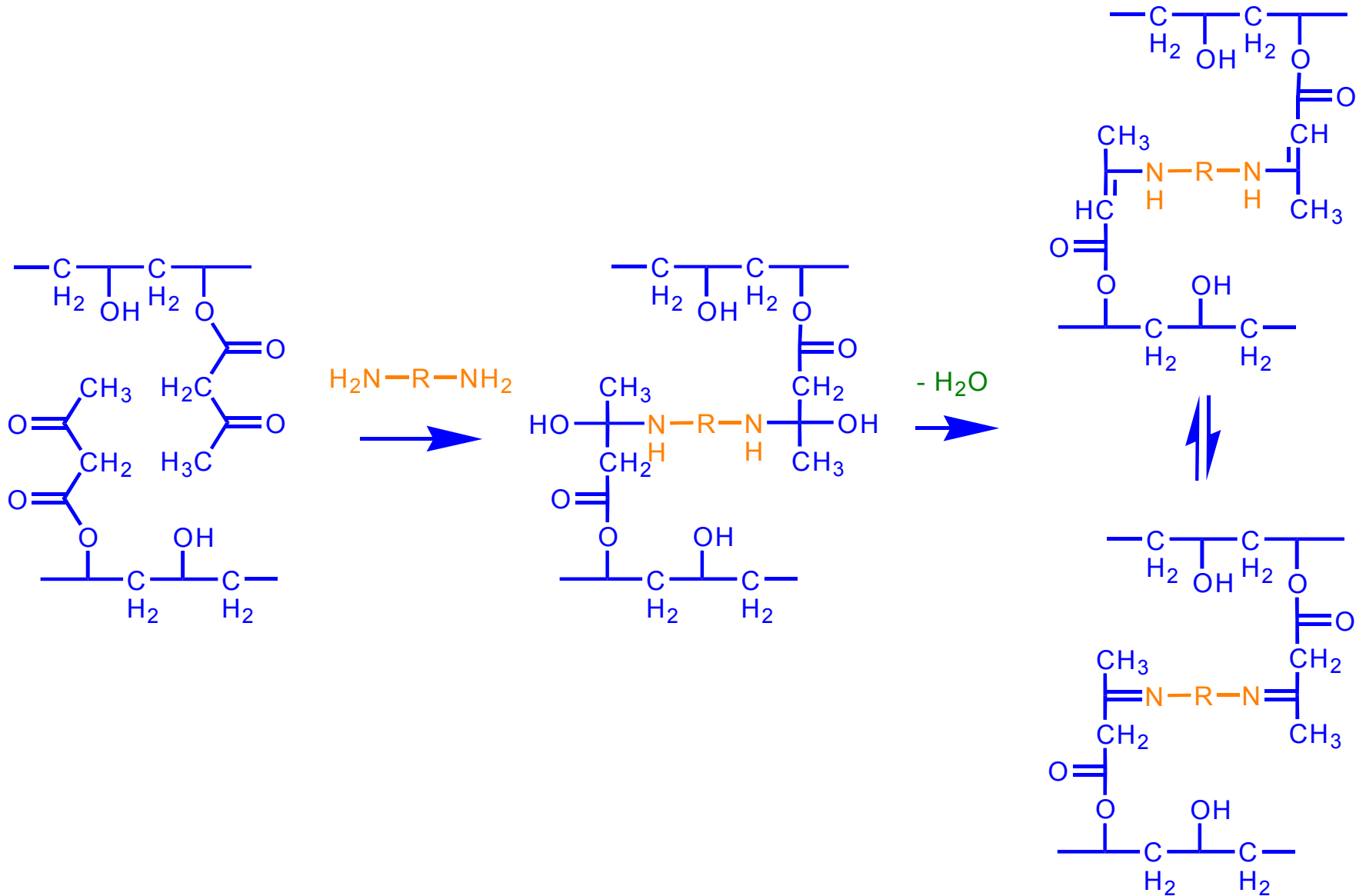
AAPVA
(37.1mol% AA)

AAPVA
(3.3mol% AA)

PVA
(0 mol% AA)

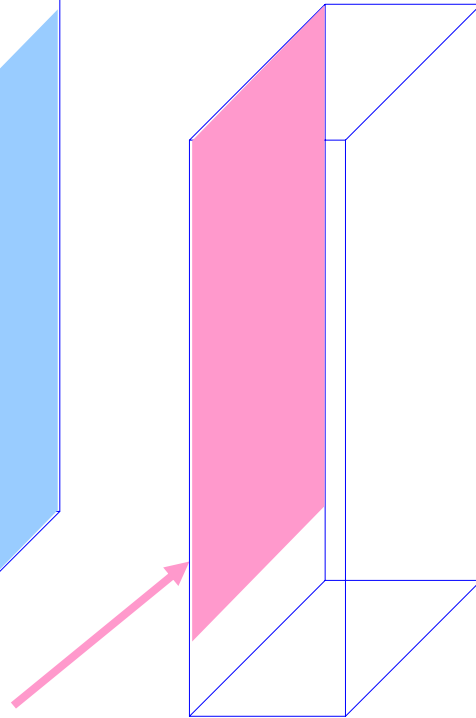
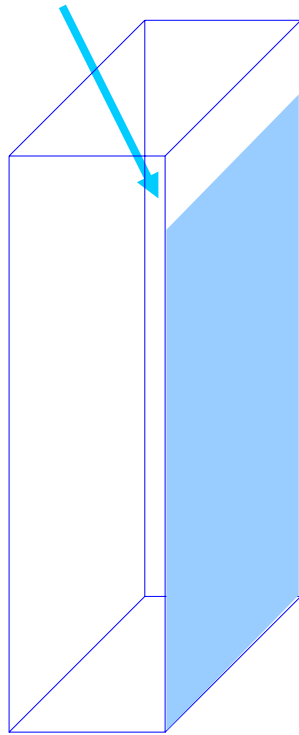


$^1\text{H-NMR/FT-IR}$ Spectra of AAPVA

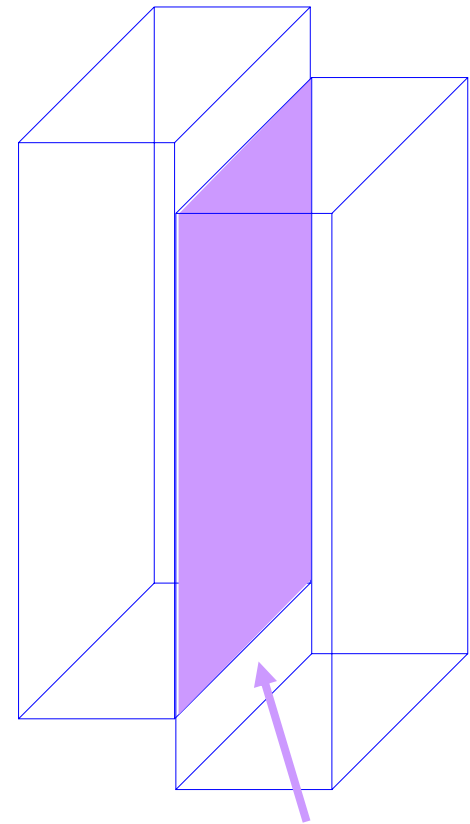


Cross-linking between AAPVA and Diamino-compound

Adhesive



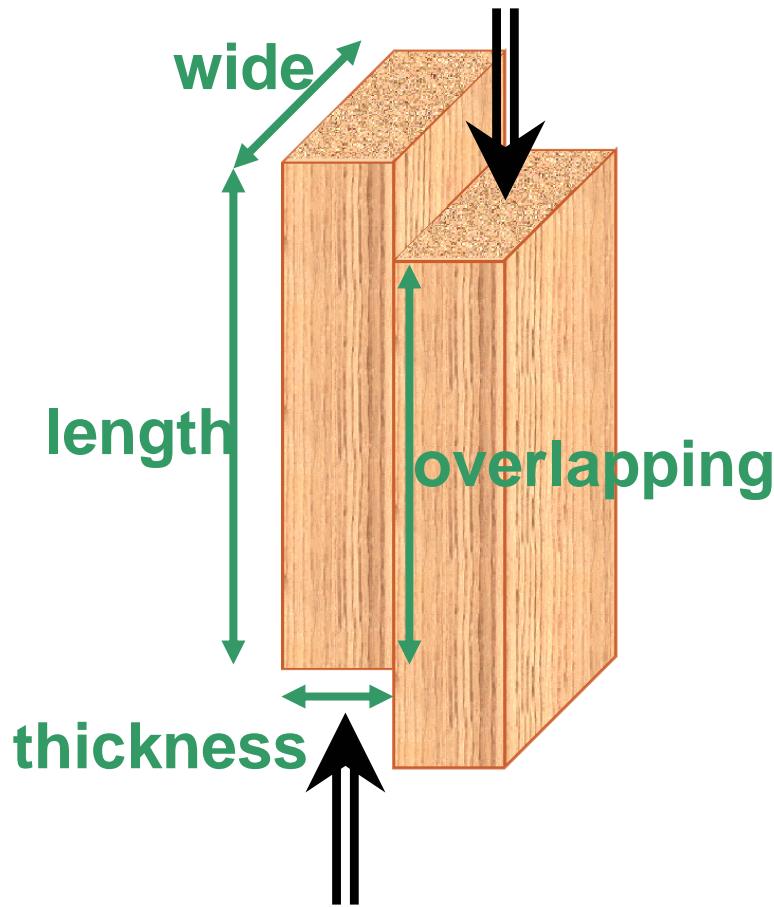
Bonding



Cross-linker

Gelled Adhesive

A Honey-moon Type Bonding
(Two Liquid Type Adhesive)



Size of test piece

length: 30 mm
wide: 15, 20, 25 mm
thickness: 10 mm
overlapping: 25 mm

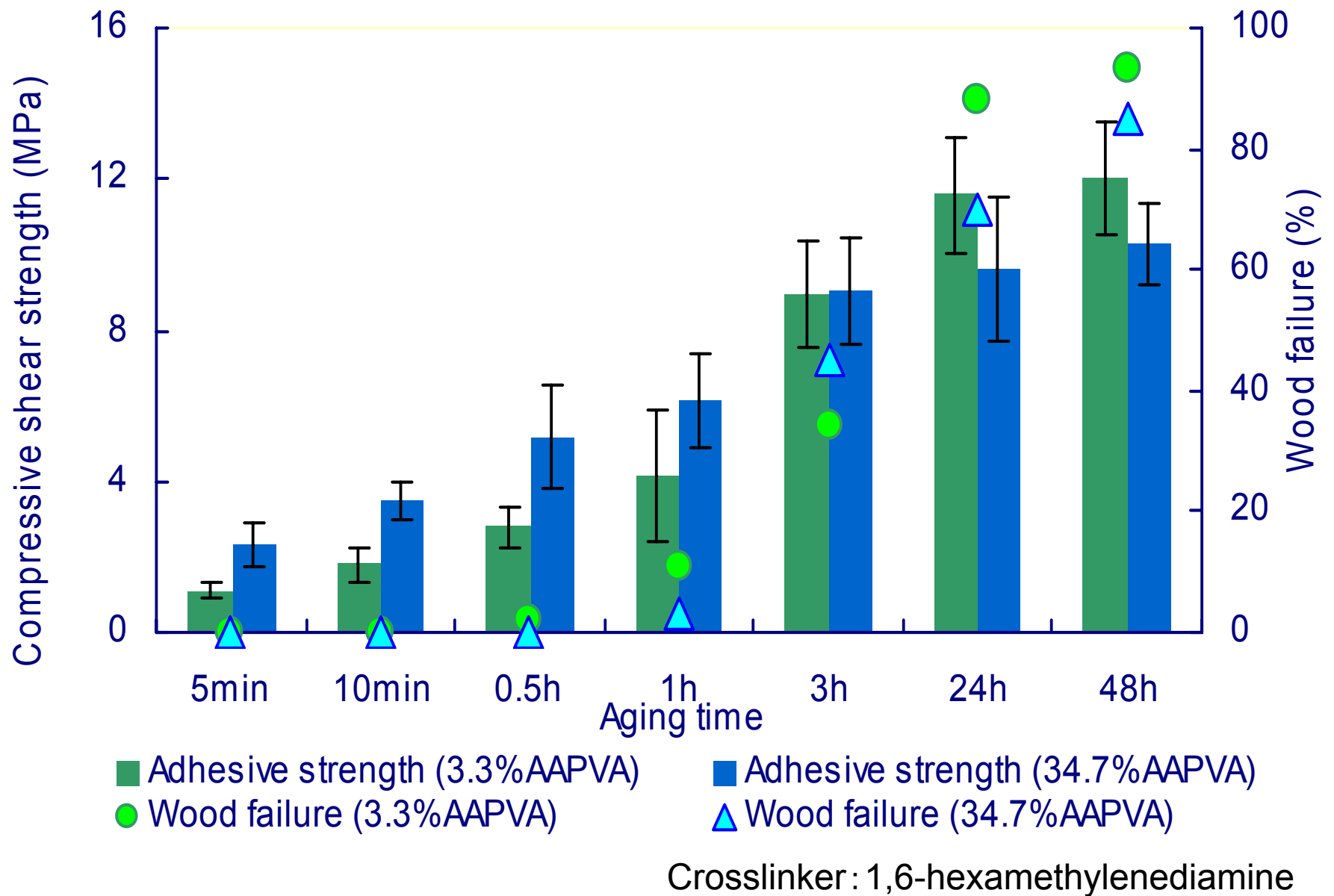
Press Condition

Pressure: 0.49, 0.7 MPa
Time of press: 5 min, 24h
Temp of press: room temp

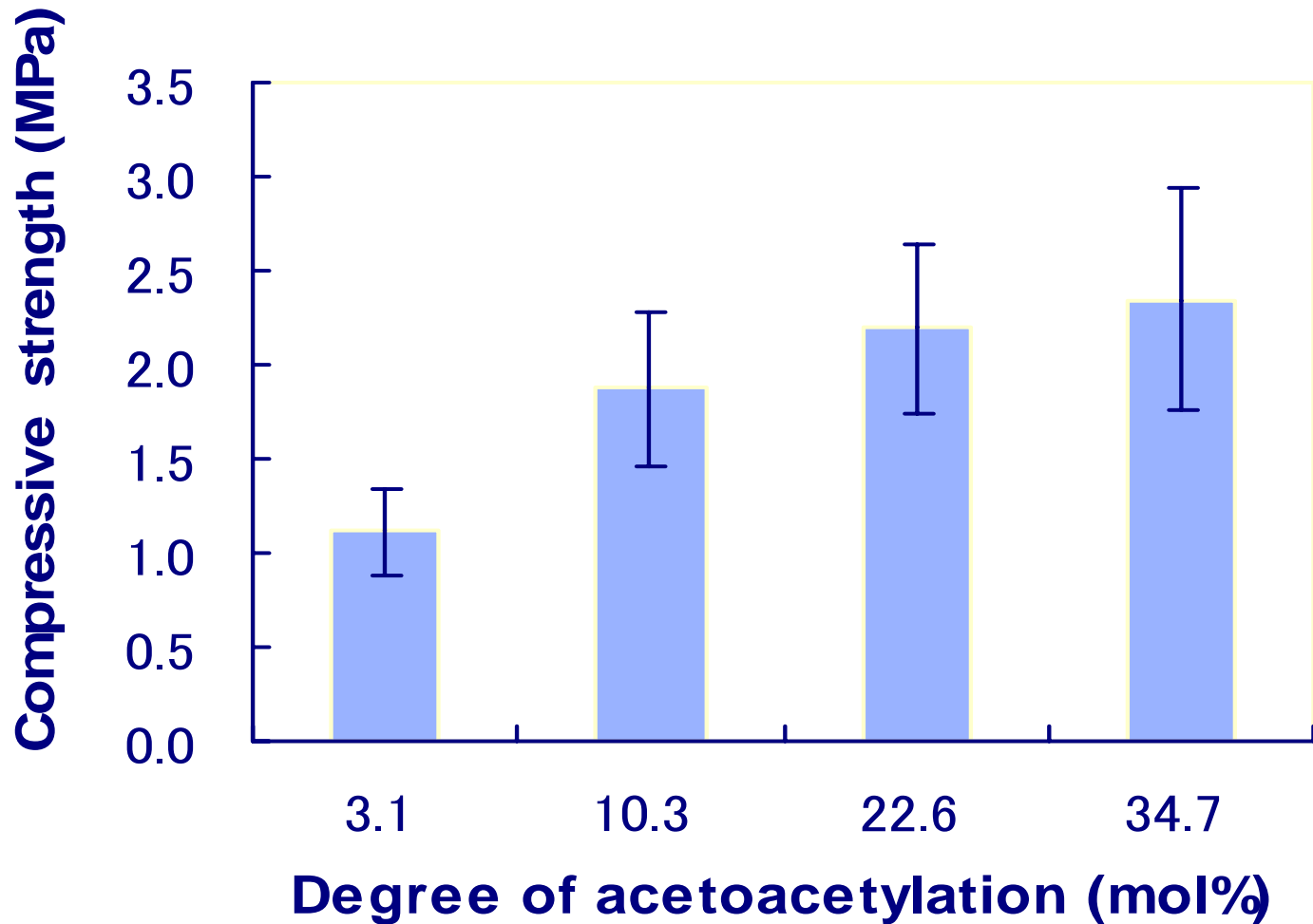
Compression Test of AAPVA Adhesive (JIS6852)

Bonding Test of AAPVA

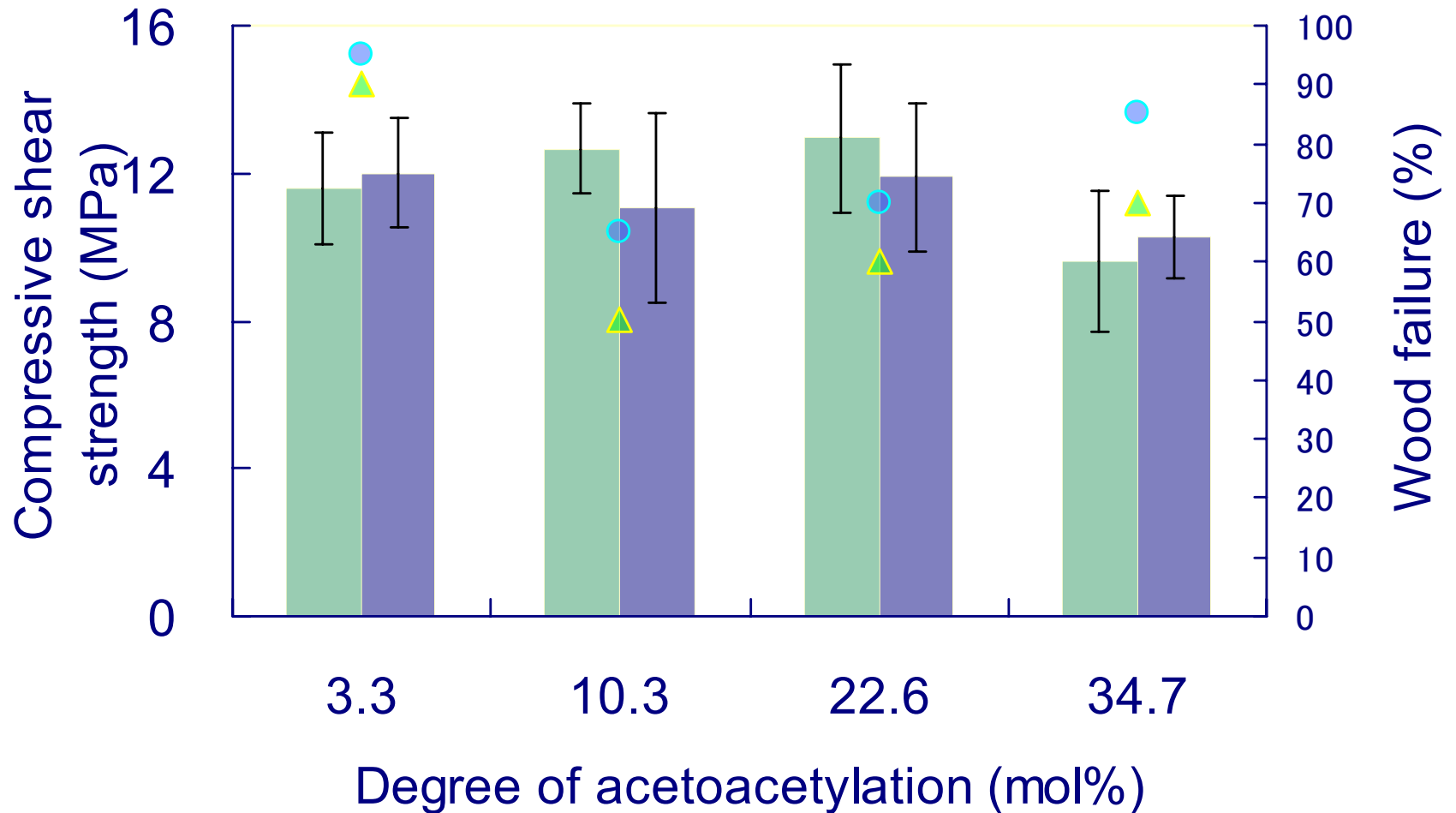
- Concentration of Cross-linker
- Initial Bonding Strength
- Time Dependence of Bonding Strength
- Final Bonding Strength
- Sort of Cross-linker



Time Dependence of Bonding Strength



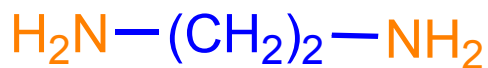
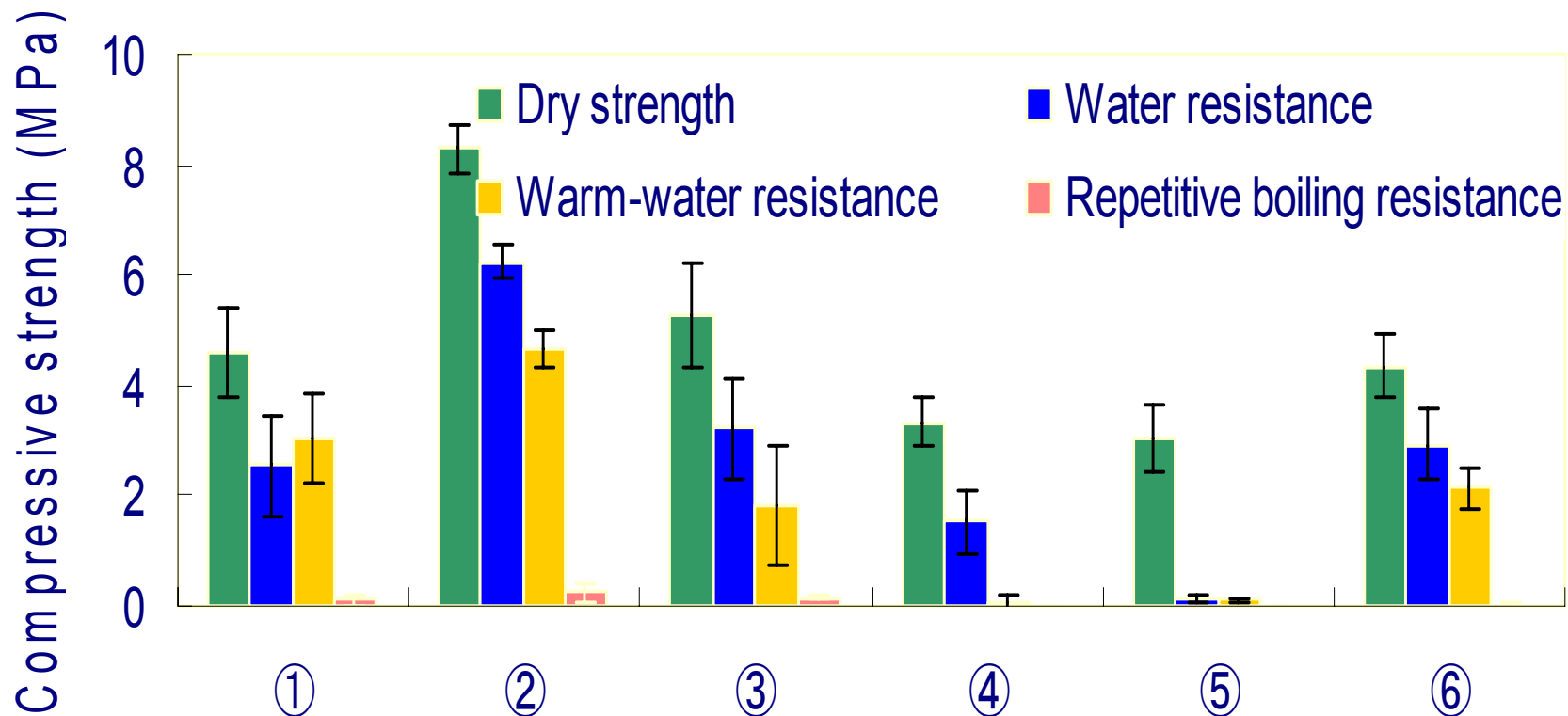
Effect of AA on Initial Bonding Strength
(5 min. after bonding)



- Compressive shear strength (24h)
- Compressive shear strength (48h)
- ▲ Wood failure (24h)
- Wood failure (48h)

Effect of AA on Final Bonding Strength

- Initial Bonding Strength is increased by Honey-moon type Adhesive using AAPVA
- Effect of Acetoacetylation decreases with Extent of Acetoacetylation
- Final Bonding Strength is independent of Acetoacetylation



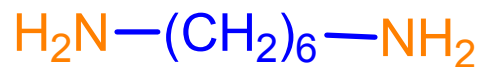
① 1,2-ethylenediamine



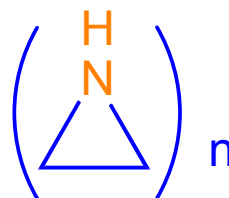
③ diethylenetriamine



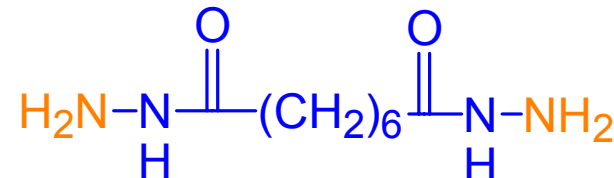
⑤ piperazine



② 1,6-hexamethylenediamine



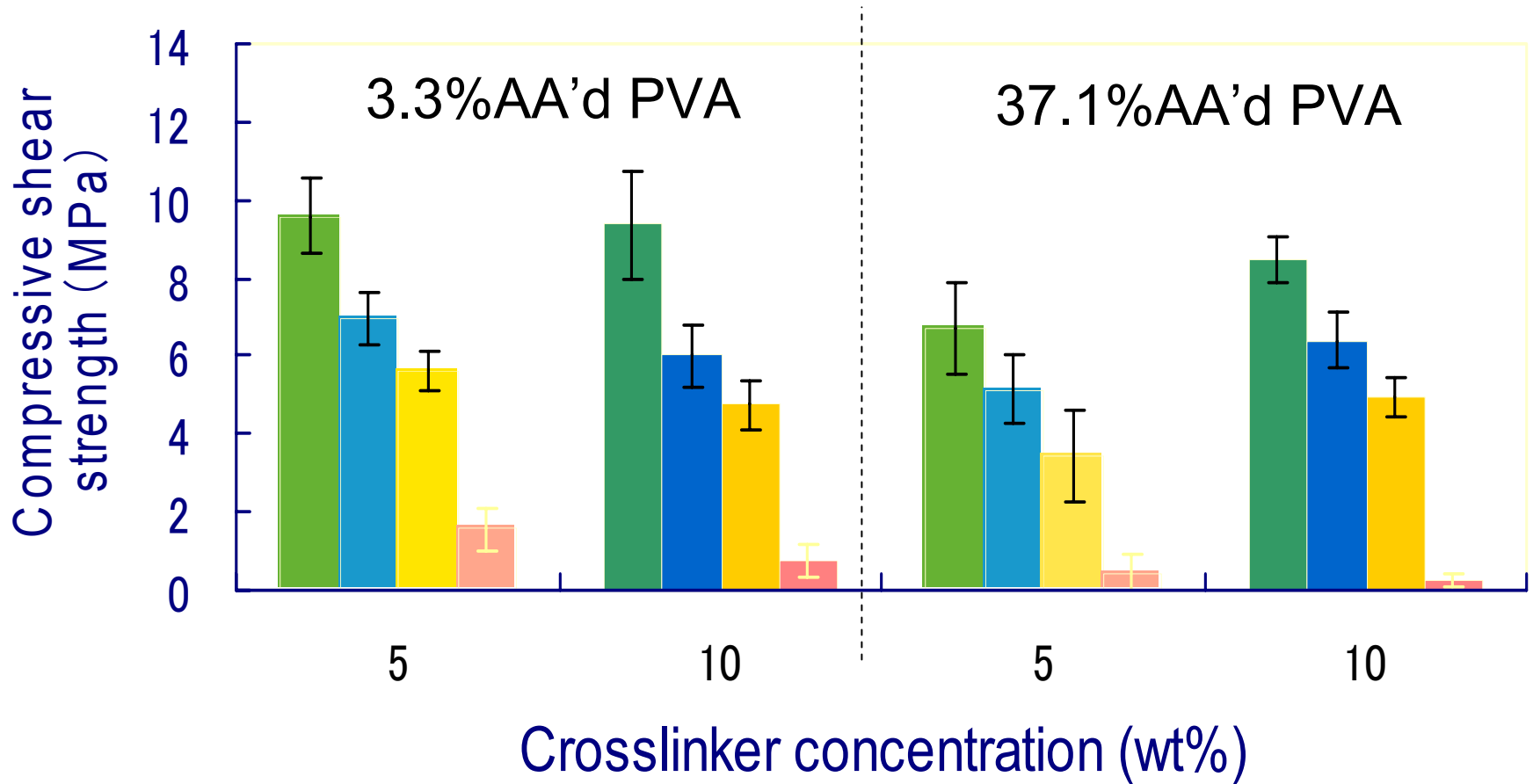
④ Poly ethyleneimine



⑥ adipic acid dihydrazide

Effect of Diamino Cross-linker

AAPVA (37.1mol% AA)



- Normal
- Water resistance
- Warm-water resistance
- Repetitive boiling resistance

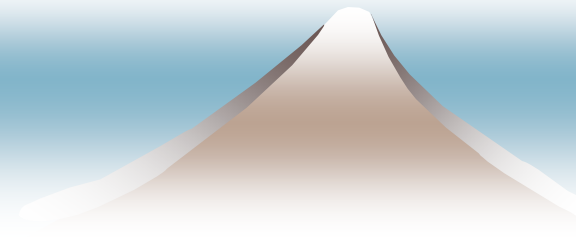
Effect of of Cross-linker Concentration

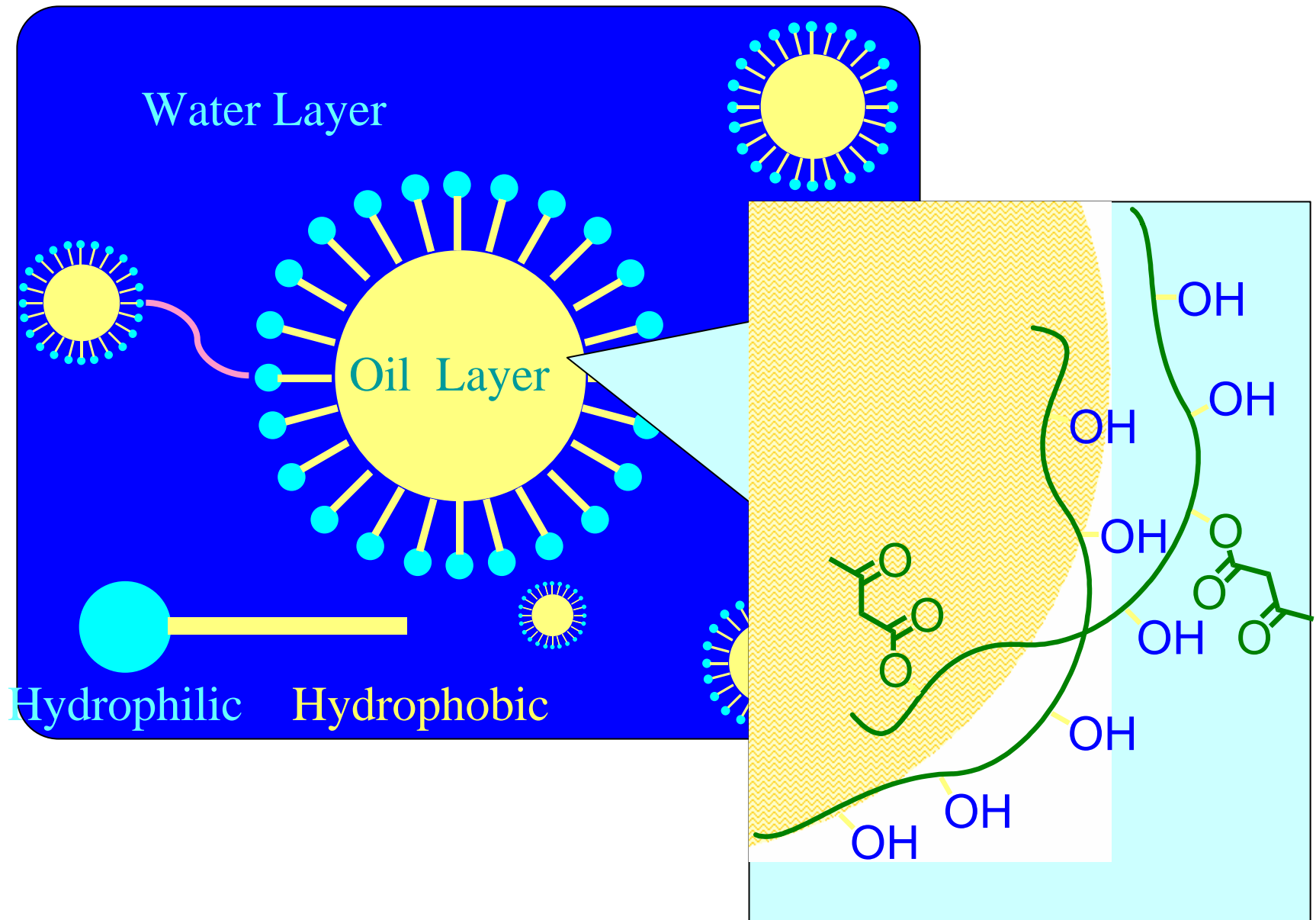
- Water Resistance is improved by introducing Acetoacetyl Group to PVA
- Chemical Structure of Cross-linker influences on Bonding Strength
- Degree of Acetoacetylation had little Effect on the Water Resistance

Summary I

- Cross-linking using Acetoacetyl Group is effective for increasing Initial Bonding Strength and Final Water Resistance
- The Effect become smaller with Extent of Acetoacetylation
- Cross-linker having 1ry Amino Group showed higher Bonding Strength
- Suitable Distance between two Amino Groups is important

II. Synthesis and Performance of Acrylic Emulsion Stabilized by AAPVA as Protecting Colloid





Degrees of Acetoacetylation and Saponification of AAPVA used in this work

	PVA		Acetoacetylation (mol%)
	DP	Saponification (mol%)	
AAPVA1	500	96<	2.1, 4.4, 6.7, 10.6, 13.2, 17.5, 28.0
AAPVA2	1000	96<	4.6, 7.7, 20.7
AAPVA3	500	86.5 – 89.0	3.2, 9.7, 13.3, 21.1
AAPVA4	1000	86.0 – 89.0	7.5, 12.0, 10.8, 17.1

Preparation of (Meth)Acryl Copolymer Emulsion

← **AAPVA 15 g**

← H₂O 85g

← **MMA 22.5 g**

BA 30.5 g

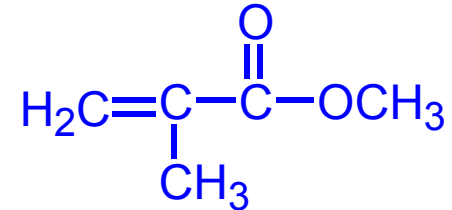
70°C 600rpm 45min

N₂

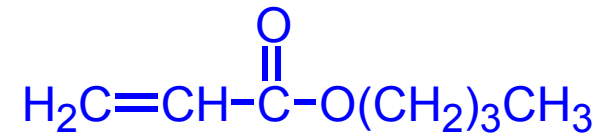
70°C 600rpm 15min

← AIBN 0.15 g

70°C 600rpm 3h



MethylMethacrylate (MMA)



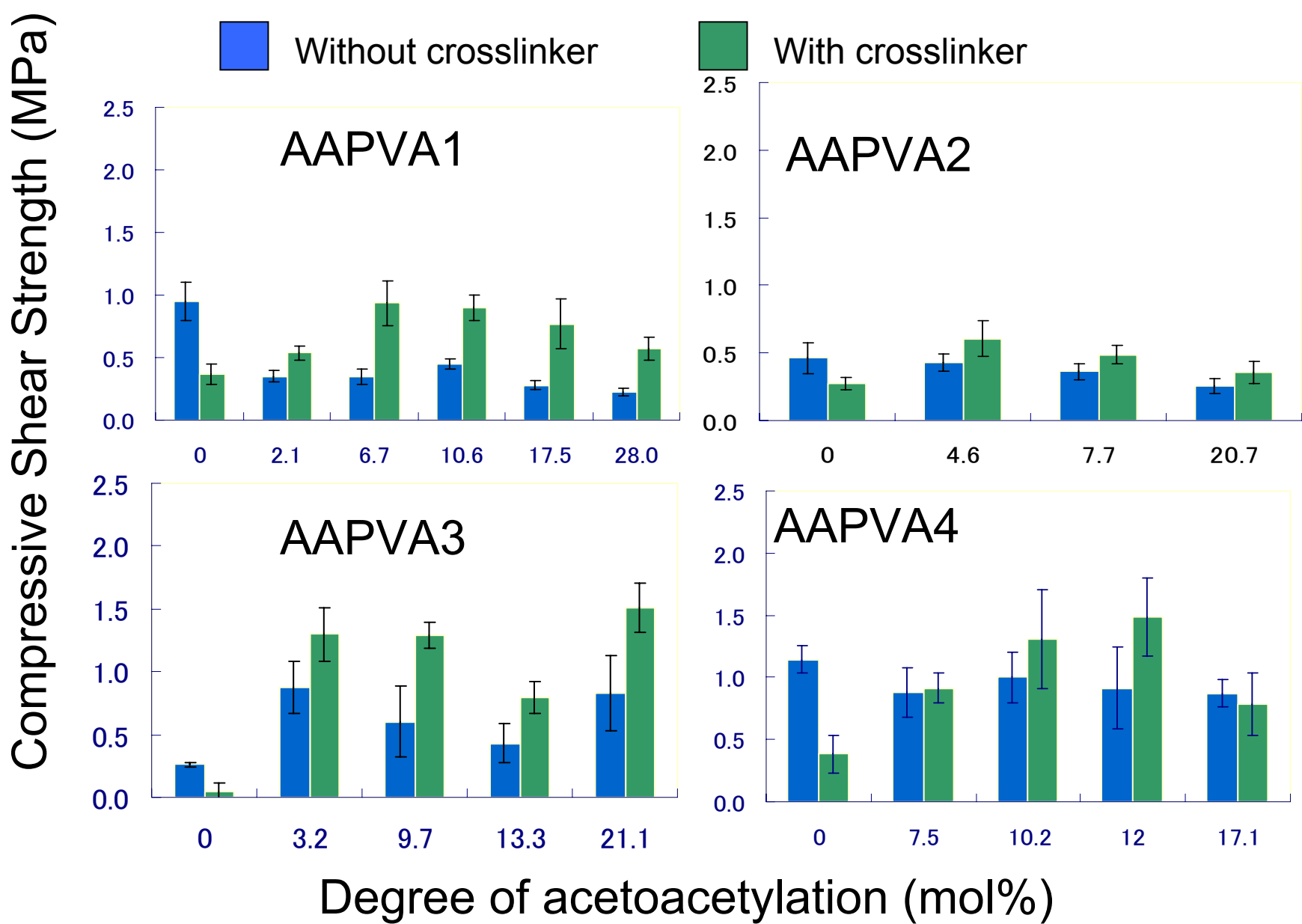
Butyl Acrylate (BA)

(Final Conc:

44% Solid in Emulsion)

Adhesive Strength of Acrylic Emulsion using AAPVA as Protective Colloid

- Bonding Test of Honey-Moon Adhesion of Acryl Copolymer Emulsion
 - Initial Bonding Strength
 - Final Bonding Strength
 - Water Resistance
- Cross-linker:
Adipic Acid Dihydrazide 10wt% aq soln



Effect of Degree of Acetoacetylation to Initial Bonding

Compressive Shear Strength (MPa)

Compressive shear strength

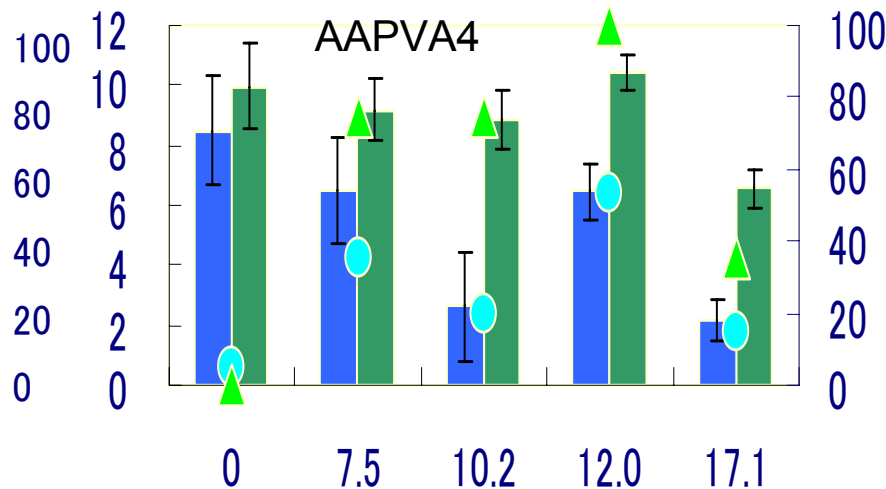
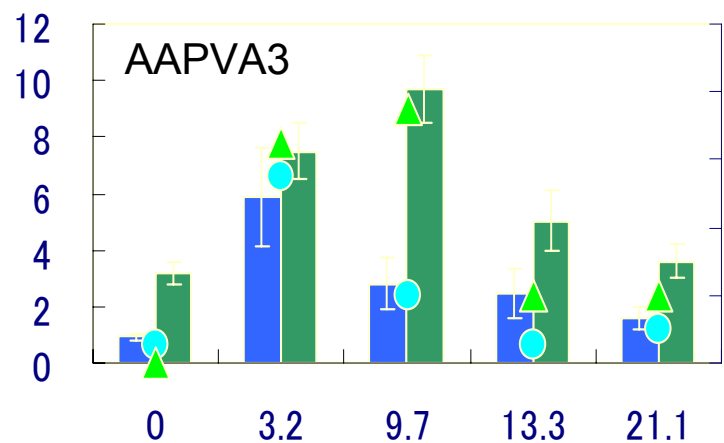
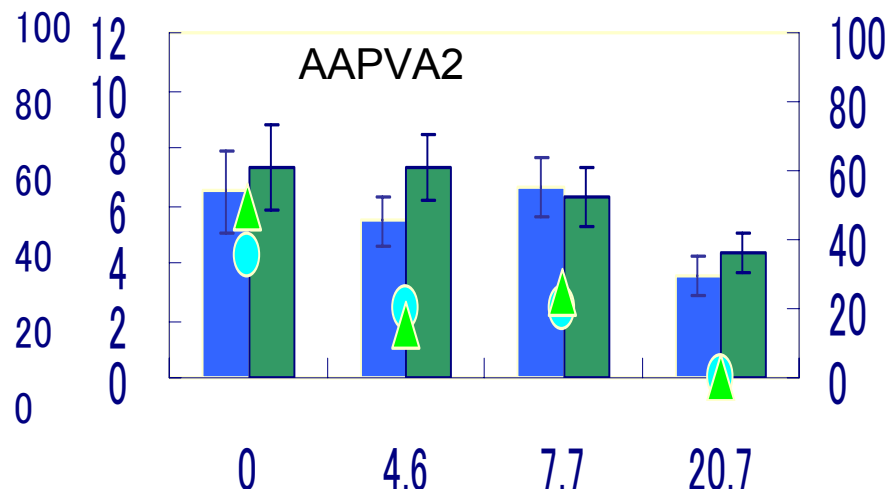
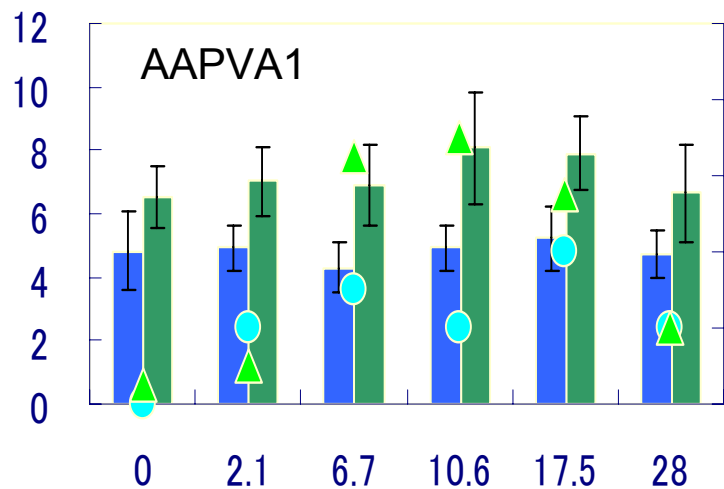
without crosslinker

with crosslinker

Wood failure

without crosslinker

with crosslinker



Wood Failure (%)

Degree of acetoacetylation (mol%)

Effect of Degree of Acetoacetylation to Final Bonding

Compressive Shear Strength (MPa)

Shear Strength

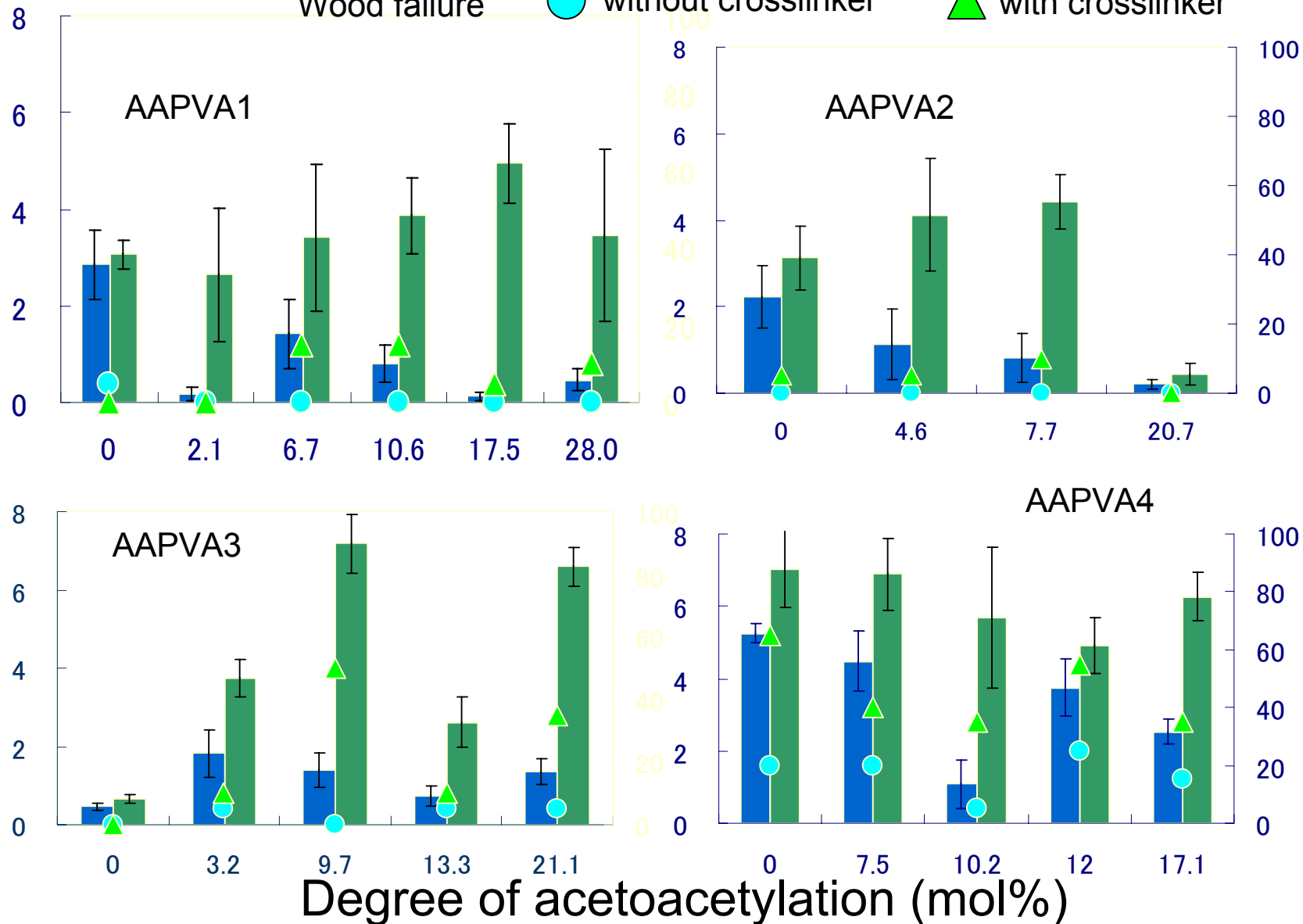
without crosslinker

with crosslinker

Wood failure

without crosslinker

with crosslinker



Wood Failure (%)

Effect of Degree of Acetoacetylation to Water Resistance

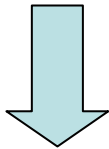
Summary II

- Acryl Emulsion stabilized with AAPVA showed Improved Performance in Honey-Moon Type Initial and Final Bonding Strengths, and Water Resistance
- Degree of Acetoacetylation has little Influence on Bonding Performance of Emulsion

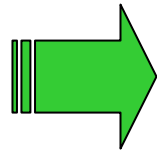
Conclusion

Cross-linking by Introducing Acetoacety Group to Polymer is effective for Improving Performance of Aqueous Adhesive

(Carbohydrate polymer such
as Starch, Cellulose, and so on)



Low VOC
Utilization of
Natural Resources
Biodegradable



**Environmentally
Friendly Adhesive
for Sustainable
Society**

**Thank you for your kind
Attention**

Reaction Mechanism of Acetoacetyl (AA) Group

