

添加自由基起始劑對加熱硬化聚醋酸乙烯乳膠耐水性之效應

劉正宇¹ 劉昭吟²

【摘要】本研究乃探討在聚醋酸乙烯乳膠之硬化膠膜中形成架橋或部分三次元之分子構造時，對其膠膜耐水性改良之效果，由試驗結果得知，在PVAc乳膠中加入BPO或AIBN等自由基起始劑，並在加熱及加壓下使其硬化時可改善PVAc乳膠之耐水性。

【關鍵詞】聚醋酸乙烯乳膠、自由基起始劑、架橋反應、耐水性、膠合強度

Effects of The Addition of Free Radical Initiators on The Water-resistance of Heat-setting PVAc Emulsion Adhesives

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【Abstract】This study investigated the effects of crosslinking and partially three-dimensional structure formed in the molecular structure of cured PVAc adhesives film on the improvement of their water resistance. From these results, the water-resistance of PVAc emulsion adhesives were improved by the addition of free radical initiators, such as BPO and AIBN, and cured under heat and pressure.

【Key words】Polyvinyl acetate emulsion adhesive, free-radical initiators, crosslinking reaction, water resistance, bonding strength

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I. Introduction

Polyvinyl acetate emulsion adhesive (PVAc; white glue; cold glue) is one of the most important adhesives used in wood industry (Pizzi · 1983). But due to its low softening point as a result of physical property of thermoplastics (Bergin and Chow · 1974 ; Steiner and Troughton, 1980), and in the existence of hydrophilic Polyvinyl alcohol (PVA) as a protective colloid, there are two major defects for cured PVAc adhesives, i.e., bad heat-resistance and bad waterproof, both of them decreased its value for use. So, we tried to modify its properties and promote its utilization value.

In view of the molecular structure, PVAc belongs to linear and amorphous polymer, because a larger acetate group exist in its molecular structure.

In order to take place the crosslinking reaction among these linear molecule, and form the three-dimensional structure inside the cured PVAc, free-radical initiators such as peroxides and azo com-

pounds were added into PVAc emulsion (Lin, 1988). Once these initiators were added and under heating condition, free radical($R \cdot$) produced from them, and induced the transfer of one hydrogen atom in acetate group of PVAc. This dehydrogen reaction would produce noncovalent electrons, and the covalent bond between two PVAc molecule was formed then.

The three dimensional structure of PVAc molecule formed by crosslinking was shown as figure 1, this structure result in increase its heat and water resistance (Masaharu N., 1971).

In this study the probability of polymerization caused by the formation of chemical bond between the molecule of PVAc at the time that free-radical initiators, such as BPO or AIBN added, and the effects of these initiators on the water and heat resistance of cured PVAc would be investigated.

II. Materials and methods

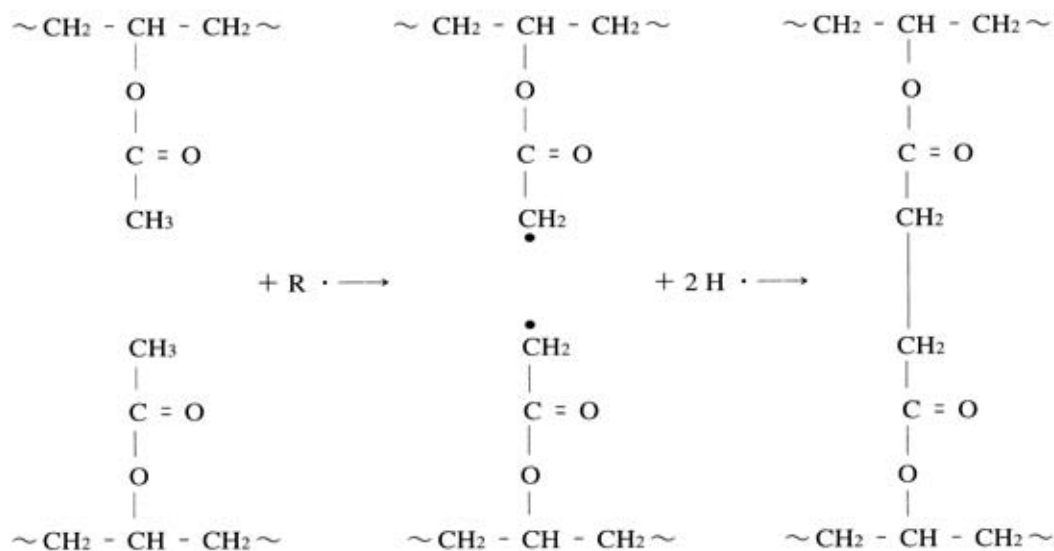


Fig. 1. Crosslinking reaction of PVAc emulsion adhesives

I. Materials

- (1) Benzoyl peroxide (BPO)
- (2) α, α' -azobisisobutyronitrile (AIBN)
- (3) Polyvinyl acetate emulsion adhesives

(PVAc): They were synthesized in laboratory as the following conditions, and detailed in previous reports (Liu and Liu, 1994; 1996).

PVA: Saponification degree 86-89 mole %
Viscosity 5-6 cps (20°C)

PVA/H₂O = 10% PVA/VAc = 15%

VAc/H₂O = 66.7%

K₂S₂O₈/VAc = 0.5%

NaHSO₃/VAc = 0.2%

- (4) Wood: *Tectona grandis* and
Swietenia mahagoni
26 cm × 2.5 cm × 1.0 cm

2. Methods

(1) The PVAc emulsion, 0.4%, 0.7% and 1.0% by weight of BPO and AIBN powder was added respectively, spreaded right after complete mixing.

(2) Glue was spreaded on each side of two match adherend, and 200 g/m² of gule rate at single gluline was used.

(3) The glued strips were pressed with pressure of 10 kgf/cm² and kept in oven at 60°C and 80°C for 24 hours, respectively. After being released, they were kept at a constant temperature and humidity room (20°C, 65% R.H.) for 7 days.

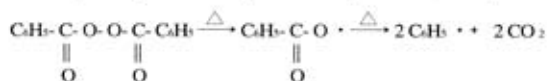
(4) Specimens for block shear bonding strength were prepared with 2.5 cm × 2.5 cm of shearing area, and tested at dry condition and after soaked in 30°C and 60°C water for 3hr., respectively.

III. Results and discussions

1. Crosslinked-PVAc adhesive with BPO

There was -O-O- chemical bonding in the structure of molecule of BPO.

It broke down into benzoyl oxyradical (C₆H₅COO ·) and phenyl radical (C₆H₅ ·), and became initiators (Shiue, 1982). The decomposition of BPO under heat was as follow, the total rate of decomposition of BPO was only slightly affected when phenyl radical produced (Shiue, 1985).



The half-life of BPO is shown in Table 1.

Table 1. Half-life of BPO

Temperature (°C)	Half-life (hr.)
60	80.0
70	13.0
72	10.0
92	1.0
100	0.4

The decomposition of BPO occurred at 50~100°C and formed free-radical (Paul, 1967). The previous research showed that PVAc emulsion added with free-radical initiator and cured under 60°C could improve its wet bonding strength, but there was no effect when the heating temperature was only 40°C (Liu and Chen, 1981). So, in this study, we cured the glued specimens under 60°C and 80°C for 24 hr.. The results were shown in Table 2. Because the half-life of BPO under 60°C was 80 hr., there was no satisfying amount of free-radical produced in such a short time, so the bonding strength of specimens cured under 60°C was less than those cured under 80°C. Increment of the amount of BPO could increase the bonding strength.

The wet bonding strength after soaked in 60°C water for 3 hr. of the specimens bonded by PVAc with 1% of BPO and cured under 80°C was three times higher than those glued by PVAc with no BPO added.

Table 2. The effect of various addition amount of BPO and curing temperature on the bonding strength of PVAc emulsion adhesives

		Shear bonding strength (kgf/cm ²)						
		<i>Tectona grandis</i>			<i>Swietenia mahagoni</i>			
curing temperature No.	(°C)	BPO added (%)	Dry	3hr soak in 30°C water	3hr soak in 60°C water	Dry	3hr soak in 30°C water	3hr soak in 60°C water
			1	60	0.4	83.1 (95)	62.4 (87)	22.6 (29)
2	60	0.7	90.2 (96)	69.2 (89)	25.7 (30)	120.9 (85)	72.5 (87)	44.4 (34)
3	60	1.0	90.2 (97)	70.7 (90)	35.2 (35)	123.7 (90)	82.0 (90)	45.0 (35)
4	80	0.4	92.6 (95)	86.4 (90)	29.0 (34)	121.1 (91)	98.0 (80)	41.6 (33)
5	80	0.7	95.9 (92)	86.4 (92)	37.6 (40)	131.0 (92)	105.4 (82)	55.1 (45)
6	80	1.0	107.0 (93)	104.7 (92)	48.3 (48)	134.8 (95)	108.2 (94)	67.1 (50)
7	—	0	79.7 (68)	45.7 (36)	15.6 (7)	101.0 (34)	54.4 (19)	21.2 (7)

*() wood failure (%)

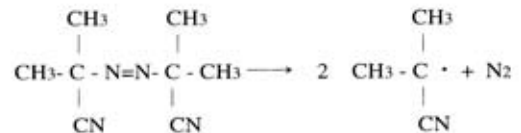
From Table 2, it showed that the best bonding strength would be gained by 1% of BPO added and cured under 80°C, and the bonding strength of *Swietenia mahagoni* were better than *Tectona grandis*.

2. Crosslinked-PVAc adhesive with AIBN

AIBN was an heat initiator which effective and commonly used. It had lower decomposition temperature and no oxidation trend. Its decomposition reaction under heat was as follow (Billmeyer, 1984 ; Lin, 1988 ; Rudin, 1982), this decomposition rate goes higher as the temperature elevated.

Its half-life of decomposition is showed in Table 3. (Liao *et al.*, 1988 ; Rudin, 1982 ; Wu, 1979). Owing to this properties, AIBN could be stored safely for a long time in low temperature, but it was decomposed under suitable heating, then accelerated and accomplished the polymerization of monomer.

In this study, we found that the viscosity of glue emulsion went up as the amount of AIBN



increased. This was owing to its total rate of polymerization was in positive relationship with the concentration of initiator (Tsay, 1978).

As shown in Table 4, the bonding strength of specimens guded by PVAc added with AIBN was higher than that glued by PVAc alone, this phenomenon appeared not only for dry condition, but especially for specimens that were soaked in 30

Table 3. Half-life of AIBN

Temperature (°C)	Half-life (min.)
0	1 × 10 ⁷ (about 20 years)
64	600.0
70	250.0
100	5.5

°C or 60°C water, which had more than two times of wet bonding strength for specimens guled by PVAc added with AIBN than none AIBN added. Both bonding strength and wood failure in dry or wet test would increase as the amount of AIBN increased for specimens guled by PVAc added with AIBN and cured under 60°C heating, but it showed negative trend for specimens cured under 80°C. Comparison of the bonding strength between these two curing temperatures, specimens cured under 80°C had bonding strength higher than those cured under 60°C. Comparison between wood species, the bonding strength of *Swietenia mahagoni* was better than *Tectona grandis*

From the results in the former discussion, the effect of BPO and AIBN added on the improvement of water resistance was about the same, but BPO needed essential long half-life, so the amount of BPO used should be more than AIBN when cured under 80°C.

IV. Conclusions

There would be significant improvement in the water resistance of cured PVAc adhesives when 1% of BPO or 0.3% of AIBN were added into glue emulsion before spreading and cured under 80°C.

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Table 4. The effect of various addition amount of AIBN and curing temperature on the bonding strength of PVAc emulsion adhesives

		Shear bonding strength (kgf/cm ²)						
curing temperature No.	AIBN added (°C)	AIBN (%)	<i>Tectona grandis</i>			<i>Swietenia mahagoni</i>		
			Dry	3hr soak in 30°C water	3hr soak in 60°C water	Dry	3hr soak in 30°C water	3hr soak in 60°C water
1	60	0.3	90.9 (90)	62.4 (70)	15.6 (17)	104.6 (88)	94.1 (89)	14.8 (13)
2	60	0.6	93.0 (90)	68.8 (78)	33.0 (33)	118.7 (97)	101.7 (90)	30.1 (20)
3	60	0.9	103.7(100)	76.9 (78)	35.1 (44)	137.4 (95)	90.2 (85)	33.8 (24)
4	80	0.3	149.0 (99)	118.2 (94)	54.0 (37)	147.3 (98)	140.5 (92)	66.8 (37)
5	80	0.6	126.7 (98)	117.3 (88)	42.2 (34)	144.6 (95)	114.3 (78)	49.5 (36)
6	80	0.9	123.1 (98)	113.8 (89)	41.8 (33)	143.2 (93)	114.2 (71)	45.7 (30)
7	—	0	79.5 (68)	45.7 (36)	15.6 (7)	99.0 (34)	54.4 (19)	21.2 (7)

*() wood failure (%)

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