Note

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New Curing System of Urea-Formaldehyde Resins with Polyhydrazides I.

Curing with dihydrazide compounds*[1]

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ポリヒドラジドによるユリア樹脂の新しい硬化法（第１報）

ジヒドラジド化合物による硬化*[1]

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ユリア樹脂を中性域で硬化させる新しい方法を開発した。この方法は，ユリア樹脂とジヒドラジド化合物を混合するだけで実際使用することができる。４種のジヒドラジド化合物を用いて検討し，次の結果を得た。
１）ユリア樹脂中の遊離ホルムアルデヒド量とメチロール基量の和に対するジヒドラジド化合物の当量比が0.1～0.2の範囲で，両者の混合液のゲル化時間は極小値をとる。このことからヒドラジド基はメチロール基あるいはホルムアルデヒドに対し２または３官能性であると考えられる。
２）この方法で作製した合板を用いて接着試験を行ったところ，通常の塩化アンモン硬化法に比べ遜色なかった。特に，芳香族系のイソフタロイルジヒドラジドを硬化剤とした場合には，温冷水浸漬後の性能低下が認められず従来法に勝った。

A nonconventional curing system was developed using a simple mixing of urea-formaldehyde (UF) resins with polyfunctional hydrazide compounds under neutral condition. Several kinds of low molecular-weight dihydrazide compounds were investigated as hardners of the UF resins. Results were as follows:
1) As the minimum gelation times were observed in the range of molar ratios [dihydrazide/(free F+ methylol F)] from 0.1 to 0.2, it was concluded that the hydrazide group has two or three functions with formaldehyde or methylol groups.
2) The adhesive strength of plywood prepared by this system was not inferior to conventional curing with ammonium chloride both in normal tests and in water-soaking tests at 60°C. The aromatic dihydrazide, isophthaloyl dihydrazide, had no decreases in superiority and bond strength after

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water-soaking compared with conventional curing with ammonium chloride.

Keywords: urea-formaldehyde resin, dihydrazide compound, neutral curing.

1. INTRODUCTION

Urea-formaldehyde (UF) resins have been manufactured the most among all the synthetic polymers or plastics. The merits of the resins are their costs and ease of utilization. They have been used as adhesives for making plywood and particleboard and also for molding and other industrial materials. On the other hand, there have some faults such as insufficient water-resistance and the release of formaldehyde from final products. From the environmental aspect, the latter is the most important problem to be solved. The structures of cured UF resins, which may relate to the problem, are considered to depend on the curing method and the nature of liquid resins. However, the cause of emission also is derived from the hydrolysis of the cured resins by the residual acid.[1,2] From this aspect, we wished to develop a new system using crosslinking reagents under neutral conditions.

The hydrazide compounds have been known io react with formaldehyde.[3-5] Orth used dihydrazide-formaldehyde resins as adhesives to fortify conventional glues.[4] Tada developed the synthesis of the resins and their application to wood adhesives.[5] In these works, the resins were synthesized by the reaction of hydrazide compounds with formaldehyde. On the other hand, hydrazides have a great potential as curing agents of UF resins if they are capable of reacting with the methylol groups of these resins to give crosslinking structures.

Our nonconventional approach in this paper is based on a simple curing system by mixing UF resins with polyhydrazide compounds. The low molecular-weight dihydrazide compounds such as malonyl, adipoyl, sebacoyl, and isophthaloyl dihydrazides, which were obtained easily from the corresponding diester of dicarboxylic acids, were used as the crosslinking agents of the UF resins.

2. EXPERIMENTAL

2.1 Urea-Formaldehyde Resins

The commercial UF resin (Ooshikashinko Co. Ltd.) used was characterized as follows: free formaldehyde contents determined by the ammonium chloride method, 2.16%; formaldehyde content determined by iodometry,[3] 17.4%; pH 8.5; solid content determined at 105°C for 3 hrs, 60.5%.

2.2 Dihydrazide Compounds

Each dihydrazide compound was synthesized by the refluxing of the corresponding commercial diester of dicarboxylic acid in an excess amount of hydrazine hydrate for several hours. After cooling, each dihydrazide was obtained as crystals, which were filtered off, and then purified by recrystallization from methanol or ethanol. Identification was made by means of melting point as shown in Table 1.

2.3 Measurement of Gelation Time

Two dihydrazide compounds, malonyl and adipoyl dihydrazides, were added separately to UF resin in various molar ratios. The molar ratio of a dihydrazide compound to formaldehyde was based on the total value of free formaldehyde and methylol group contents, which was determined by iodometry, and calculated by the following equation.

$$\text{Molar ratio} = 3\times10^3\,[h/Mwf]$$

Here, h: weight of dihydrazide compound (g),
M: molecular weight of dihydrazide compound,
w: weight of UF resin (g), and
f: formaldehyde content by iodometry (%).

The mixtures were adjusted at pH 7.8–8.0 and

Table 1. Structure and melting points of dihydrazide compounds.

Dihydrazide compounds	Structures	Melting points (°C)
Malonyl dihydrazide	$H_2NHNOC\text{-}(CH_2)\text{-}CONHNH_2$	164—165
Adipoyl dihydrazide	$H_2NHNOC\text{-}(CH_2)_4\text{-}CONHNH_2$	179—180
Sebacoyl dihydrazide	$H_2NHNOC\text{-}(CH_2)_8\text{-}CONHNH_2$	192—193
Isophthaloyl dihydrazide	$H_2NHNOC\text{-}(C_6H_4)\text{-}CONHNH_2$	221—222

ature at 135 °C was effective at the same amount of dihydrazide, and the large bond strength was held after water-soaking at 60℃. The mixing conditions of the resins seemed to be improved by the higher hot press temperatures. On the other hand, the amount of dihydrazide was effective between 10–15 phr (parts per hundred parts of resins). An excess amount of dihydrazide will cause a stoichiometric unbalance between hydrazide group and methylol groups, and result in smaller crosslinked networks in which a considerable amount of hydrazide groups may remain unreacted.

Table 2. Bond strength test of plywood prepared with the UF resin-dihydrazide curing system.[a)]

Dihydrazide compounds[b)]	Shear strength (Wood failure, %) N/mm^2		
	Normal test	Water-soaking[c)] at 20℃	Water-soaking[d)] at 60℃
Sebacoyl dihydrazide	2.50 (85)	1.67 (29)	1.03 (4)
Adipoyl dihydrazide	2.74 (92)	2.01 (47)	1.29 (7)
Malonyl dihydrazide	2.52 (80)	1.72 (23)	1.18 (2)
Isophthaloyl dihydrazide	2.43 (94)	2.04 (55)	1.57 (15)
Melamine	1.94 (60)	1.57 (22)	1.18 (11)
Control-1[e)]	1.86 (92)	1.52 (95)	1.62 (86)
Control-2[f)]	2.16 (86)	1.88 (51)	0.76 (1)

a) Hot press conditions: temperature, 115℃; pressure, 0.98 N/mm^2; time, 5 min.
b) Dihydrazide compound (4 g) was added to 40 g of UF resin.
c) 20℃ for 3 hrs-dry for 2 hrs.
d) 60℃ for 3 hrs-dry for 2 hrs.
e) Control-1: cured with NH_4Cl.
f) Control-2: cured with NH_4Cl and wheat flour.

Table 3. Results of bond-strength test for the UF resin-adipoyl dihydrazide system.[a)]

Sample no.	Hot-press temperature (°C)	Amount of dihydrazide to UF resin (phr)	Shear strength, N/mm^2 (Wood failure, %)	
			Normal test	Water-soaking[b)]
1	110	10	1.96 (94)	1.23 (7)
2	135	10	2.12 (84)	1.98 (20)
3[c)]	135	10	2.11 (100)	1.42 (3)
4	110	15	2.16 (87)	0.76 (6)
5	135	15	1.99 (89)	1.91 (47)
6[c)]	135	15	2.07 (99)	1.27 (3)
7	110	20	2.01 (85)	1.34 (10)
8	135	20	2.01 (15)	0.76 (26)
9[c)]	135	20	2.01 (99)	1.23 (5)

a) Testing method is the same as noted in Table 2.
b) Water-soaking at 60℃ for 3 hrs.
c) Wheat flour was added.

Table 4. Results of bond-strength test for the UF resin-isophthaloyl dihydrazide system,[a)]

Sample no.	Amount of dihydrazide to UF resin (phr)	Shear strength, N/mm^2 (Wood failure, %)	
		Normal test	Water-soaking test[b)]
1	10	1.76 (97)	1.86 (100)
2	15	1.72 (96)	1.92 (90)
3	20	1.91 (94)	2.04 (70)

a) All systems have common hot-press conditions (temperature, 135°C).
b) Water-soaking at 60℃ for 3 hrs.

maintained at 60°C. Gelation time was determined as the time for the mixture to solidify.

2.4 Preparation and Testing of Plywood

Three-ply lauan plywoods (30×30×48 cm) were prepared. The preparative conditions were generally common as followings unless otherwise stated in the tables: closed assembly time, 15–30 min; spread ratio, 30 g/(30×30) cm^2; hot press temperature, 115°C; press pressure 0.98 N/mm^2; press time 5 min. The amounts of dihydrazide compounds mixed with UF resin are shown in the tables. Just after the mixing of the dihydrazides with UF resin, the mixtures were spread on the veneers without further treatments. The bond strength was measured both in the normal condition and after soaking in water at 20 or 60°C according to Japanese Agricultural Standards (JAS).

3. RESULTS AND DISCUSSION

3.1 Relationship between Gelation Time and Molar Ratio

Figures 1 and 2 show the variations of gelation times for various molar ratios of dihydrazide to formaldehyde in the new system. As both free formaldehyde and methylol groups of UF resin were suggested to react with hydrazide groups, the iodometry values were used to calculate the molar ratios. The malonyl dihydrazide-UF resin system showed a minimum gelation time for the molar ratio from 0.1 to 0.15 at pH 7.8–8.0. Similarly it was observed in the molar ratio from 0.1 to 0.2 in the adipoyl dihydrazide-UF resin system. These compounds have two hydrazide groups in their molecules. Therefore, they are considered to introduce three dimensionally crosslinked networks to UF resin, even if the hydrazide group has only one reactive site for formaldehyde or methylol groups. It is, however, of significance that the gelation can be attained even with such a small amount of dihydrazide compound. The hydrazide group is suggested to have multi-functions, two or three, for formaldehyde or methylol groups.

3.2 Adhesive Strength of the New Curing System

The adhesive shear strength of plywood specimens prepared by the new curing system was compared with the conventional curing with ammonium chloride as well as the curing with melamine. Table 2 shows that the new system using different compounds passed the JAS values both in the normal and water-soaking tests. The new system showed greater normal strength than the conventional curing with ammonium chloride. However, decreases of bond strength and wood failure were present after water-soaking at 60°C. This seemed to be caused by poor mixing of the dihydrazides with UF resin. Dihydrazides generally have poor solubility in water.

Table 3 shows the effects of hot press temperatures and the amount of adipoyl dihydrazide mixed with the UF resin on bond strength. The hot press temper-

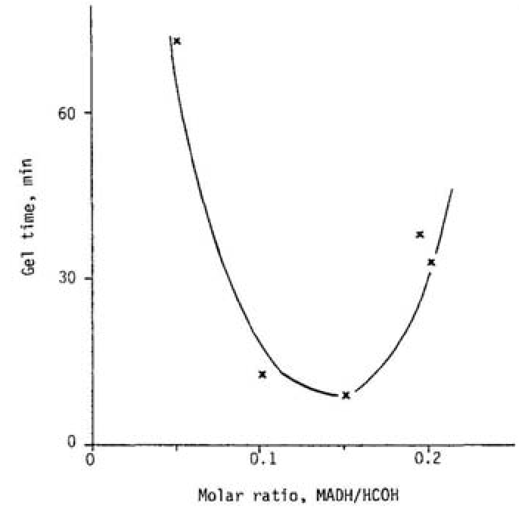

Fig. 1. Gel time vs molar ratio for malonyl dihydrazide (MADH)-UF resin system.
Note: Temperature, 60°C.

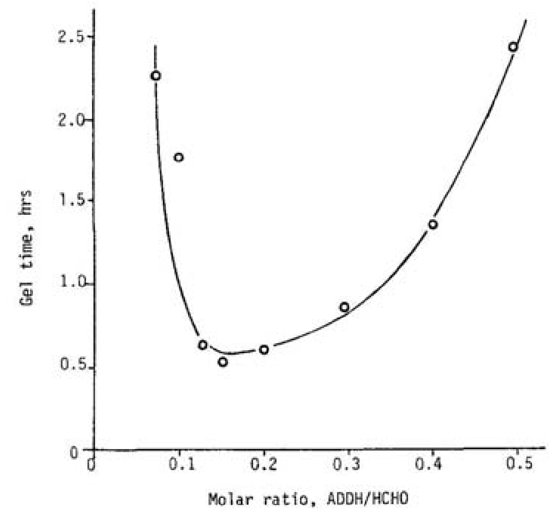

Fig. 2. Gel time vs molar ratio in adipoyl dihydrazide (ADDH)-UF resin system.
Note: Temperature, 60°C.

Table 4 shows the results of curing with the aromatic dihydrazide, isophthaloyl dihydrazide, at 135°C. Note that the bond strengths after water-soaking at 60°C were greater than in the normal test. Judging from the wood failure value, the greatest durability against water-soaking also was at the smaller amounts of dihydrazide such as 10 phr. The application of aromatic hydrazide and high curing temperatures will be emphasized in developing this new curing system for practical use.

4. CONCLUSION

The development of new curing system was investigated using a simple method to mix UF resins with poly-functional hydrazide compounds. Several dihydrazides were investigated as hardners of UF resins. The adhesive strengths of plywood made with four different of dihydrazide compounds as hardners of commercial UF resin were not inferior to that of the conventional curing by ammonium chloride, both in the normal test and in the water-soaking test at 60°C. Also, they exceeded the JAS value. Among four dihydrazides and melamine, the aromatic dihydrazides had no decreases of bond strength after water-soaking at 60°C, and superior to the conventional curing by ammonium chloride.

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