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New Curing System of Urea-Formaldehyde Resins with Polyhydrazides II.[†]

Curing with poly (methacryloyl hydrazide)*

Katsumasa MIYAKE*², Bunichiro TOMITA*³,
Chung Y. HSE*⁴ and George E. MYERS*⁵

ポリヒドラジドによるユリア樹脂の新しい硬化法 (第2報)[†]
ポリメタクロイルヒドラジドによる硬化*¹

三宅克正*², 富田文一郎*³,
チョン・シ*⁴, ジョージ・マイヤーズ*⁵

PMMAから簡単に合成できるポリメタクロイルヒドラジド (PMAH) をユリア樹脂の硬化剤とする新しい方法について検討し、次の結果を得た。

- 1) 酸性度とモル比〔ヒドラジド基量/(遊離ホルムアルデヒド量+メチロール基量)〕を変化させて、PMAH とユリア樹脂の混合系についてゲル化試験と硬化物の水抽出試験を行ったところ、この系は中性域で短時間で反応することが判明した。また、反応は2段階で進行し、2段目の反応は、比較的高温下で起こると推定された。
- 2) この方法を用いて作製したラップ試験片によって引張りせん断接着強度を測定したところ、塩化アンモニウム硬化法に遜色ない結果が得られたが、60°Cにおける水浸漬後には性能低下が認められた。合板による接着強度試験では、モル比が高くなる程、強度が低下する傾向が認められた。
- 3) この硬化法は、合板からの放散ホルムアルデヒド量を著しく低下させる。

A new curing system for urea-formaldehyde (UF) resins was investigated using poly(methacryloyl hydrazide) as the curing reagent. Results were as follows:

- 1) Gel time and the water-soluble part of cured resins were determined as function of pH and molar ratio [hydrazide group/(free formaldehyde+methylol group)]. It was found that the reaction in this system proceeds for a short time under neutral conditions, and that the reaction of hydrazide groups with UF resin involves two stages with the second stage occurring at a rather high temperature.
- 2) The adhesive shear strength of lap-joint specimens prepared under the new system was comparable to that by conventional curing with ammonium chloride, although it decreased after water-soaking at 60°C.
- 3) The adhesive strength of plywood specimens decreased as the molar ratio increased.

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*² Present address: ㈱リクルート Recruit Co. Ltd., Chiyoda-ku, Tokyo 110

*³ 東京大学農学部 Faculty of Agriculture, University of Tokyo, Tokyo 113

*⁴ 米国農務省南部林業試験場 USDA Forest Service, Southern Forest Experiment Station, Pineville, LA 71360, U.S.A.

*⁵ 米国農務省林産試験場 USDA Forest Service, Forest Products Laboratory, Madison, WI 53705, U.S.A.

- 4) A remarkable reduction of formaldehyde emission from plywood was recognized in the application of the new system.

Keywords urea-formaldehyde resin, hydrazide polymer, neutral curing, formaldehyde emission.

1. INTRODUCTION

In our previous paper,¹⁾ we reported that a new curing method for urea-formaldehyde (UF) resins had been developed, and that its practical applicability for wood adhesives was evaluated by testing the bond strength of plywood. The method is based on the simple mixing of UF resins with dihydrazide compounds under neutral conditions without using conventional curing agents such as ammonium chloride or acids. It was concluded that the hydrazide group has two or three functions against formaldehyde or the methylol group of UF resins, and that dihydrazide compounds work as curing agents (hardeners) of UF

This paper reports on the utilization of hydrazide polymer as a hardener of UF resins. Poly(methacryloyl hydrazide) (PMAH), which was synthesized easily from poly(methyl methacrylate) (PMMA), was investigated on its practical applicability as wood adhesive. The level of formaldehyde emission from the final products also was compared with the curing method with ammonium chloride.

2. EXPERIMENTS

2.1 Urea-Formaldehyde Resins

Two commercial UF resins, U1 and U2, were used as well as a commercial urea-melamine copolymer resin (UM). The free formaldehyde and methylol group contents of these resins were determined by conventional titrations, the ammonium chloride method, and iodometry. Results and other character-

Characteristics of three commercial resins.

Resin content (%)	Formaldehyde content (%)	
	methylol F + free F	free F
62.5	17.4	2.2
51.9	8.6	0.4
UM	10.7	0.6

U1: UF resin for wood working at room temperature.

U2: UF resin for making plywood.

UM: Urea-melamine copolymer resin.

istics are shown in Table 1.

2.2 Preparation of Poly (Methacryloyl Hydrazide) (PMAH)²⁾

A commercial PMMA (Wako Chemical Company, $M_n 3.29 \times 10^4$) was used. The solution of PMMA (96.5 g) in hydrazine hydrate (500 ml) was refluxed for 24 hrs. Crude PMAH was precipitated from methanol (10 l) containing 20 ml of acetic acid. The precipitate was filtered off, dissolved in 500 ml of water, and then purified by repeating reprecipitations with methanol, followed by air-drying and successive drying in a vacuum. Yield of PMAH was 60 g. Carbon 13 nuclear magnetic resonance (¹³C-NMR in D₂O): 17.5-20.0 ppm (CH₃), 43.0-47.0 (CH₂), 55.1-62 (C), 177.4-177.8 (CONHNH₂).

2.3 Gelation Time of UF-PMAH Reaction

PMAH was used as a 10% aqueous solution, and its pH was 7.8. It was mixed with UF resin at various molar ratios. The pH adjustment of the mixture of UF resin (U1) and PMAH was made with 1N NaOH and 1N CH₃COOH. Gelation time was measured at 20°C, and each value shown in the figures was based on the average of three measurements. The molar ratio of the hydrazide group to formaldehyde was based on the following equation.

$$\text{Molar ratio (CONHNH}_2\text{/HCHO)} = 3 \times 10^3 \frac{h}{(h/Mw_f)} \quad (1)$$

Here, h : weight of PMAH (g),

M : molecular weight of repeating unit of PMAH (100),

w : weight of UF resin (g), and

f : formaldehyde content determined by iodometry (%).

Gel time was measured as functions of pH and molar ratio, and was determined by the time for the mixture to solidify at 25°C.

2.4 Determination of Water-Soluble Part of Cured Resins

The mixtures of UF resins (U1) with PMAH were allowed to stand at room temperature for six or seven days. Half of the amount of each sample was treated at 110°C for 5 hrs. About 1 g of the cured sample was soaked in 10 ml of water at 60°C for 5 hrs. The

aqueous solution was evaporated to dryness and vacuum-dried.

2.5 Adhesive Shear Strength Test of Lap-Joint

Adhesives were prepared by quantitative mixing of a 30% aqueous solution of PMAH with UF resin (U1) just before using. The average solid content of the mixtures ranged from 30 to 40%. Wood specimens were Makamba (*Betula maximowicziana* Regel). The size of specimen and bonding areas were 80 mm (length) × 25 mm (width) × 5 mm (thickness) and 3.75 cm², respectively. The bonding conditions were as follows: open and closed assembly time, 0 and 3-4 days; bonding pressure, 0.98 N/mm². The hot press was applied at 110°C for 5 hrs. The adhesive strengths were evaluated both under normal conditions and after soaking in water at 60°C, and were measured with a Tensilon tensile testing machine (Toyo Baldwin Co.) with a crosshead speed of 10 mm/min.

2.6 Preparation of Plywood

Lauan veneers (*Shorea* sp.) (30 × 30 × 2 mm) was used for 3-ply plywood. Adhesives were prepared by quantitative mixing of a 15% aqueous solution of PMAH with UF resin (U2). The bonding conditions were as follows: closed assembly time, 5-10 min; spread rate, 30 g/(30 × 30) cm²; hot press temperature, 115°C; pressure, 0.98 N/mm²; hot press time, 5 min. The bond strength was measured under normal condition and after soaking in water at 60°C.

2.7 Determination of Formaldehyde Emission

Formaldehyde emission from the plywood was determined by the dessicator method of the Japanese Agricultural Standard (JAS) after aging of the plywood for one week.

3. RESULTS AND DISCUSSION

3.1 Structure of PMAH

The conversion of the methylester group to a hydrazide group was confirmed easily with a ¹³C-NMR spectroscopic comparison between the starting polymer (PMMA) and the product (PMAH). It has been reported that the methyl carbon of methylester in PMMA gives the signal at about 50 ppm, and that carbonyl carbon appears at 175.2-176.4 ppm.²¹ In the spectrum of PMAH, on the other hand, no signals corresponding to the methyl carbon of methylester could be observed at about 50 ppm, and the carbonyl carbon shifted downfield to 177.4-177.8 ppm. There-

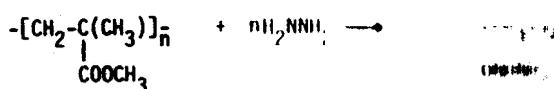


Fig. Reaction of poly(methyl methacrylate) hydrazine hydrate.

fore it was concluded that almost all the methylester groups were converted to hydrazide groups by refluxing in an excess amount of hydrazine hydrate as shown in Fig. 1. From these results the molecular weight of the repeating unit of PMAH was concluded to be 100 in Equation (1).

3.2 Reaction of PMAH with UF Resins

The molar ratio of the hydrazide group to formaldehyde (CONHNH₂/HCHO) is based on Equation (1). The total content of free formaldehyde and methylol groups, which was determined by iodometry, was used to calculate the molar ratio because they were considered to be capable of reacting with the hydrazide group as described in our previous paper.¹¹ Figures 2 and 3 show the pH dependences of the PMAH-UF resin system and the content of the water-soluble part in cured resin, respectively, at the con-

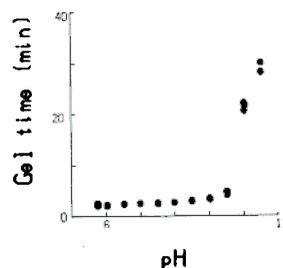


Fig. 2. Gel times vs pHs for the UF resin (U1)-PMAH system with the molar ratio of 0.25 at 25°C.

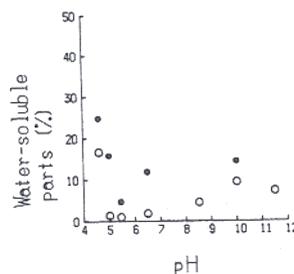


Fig. 3. Rates of water-soluble parts vs pHs for the UF resin (U1)-PMAH system with the molar ratio of 0.25.

Legend: ●, cured at room temperature; ○, cured at 110°C for 3 hrs.

stant molar ratio (CONHNH₂/HCHO) of 0.25. The new curing system has a strong reactivity in reaching the gelation point within a few minutes under a range of pH from 6 to 9.5 even at the temperature of 25°C. The water-soluble part of each sample was about 20%. By successive curing at 110°C for five hours, it decreased markedly, especially in the range of pH 5 to 8. From these results, it was confirmed that three-dimensional networks took place in this system. The effects of the molar ratio also are shown in Figs. 4 and 5, which were determined under the weakly alkaline state of pH 7.8-8.5. The gelation time was very short in the molar ratios above 0.1. It is very interesting that gelations take place soon after mixing PMAH with UF resin even with small amounts of the hydrazide group. This may be attributed to the self-crosslinking of the hydrazide polymer, where free formaldehyde in the UF resin acts as a crosslinking agent only to the hydrazide polymer. Therefore, it should be noted that this new curing system might involve two-step chemical reactions. The first step is the reaction of the hydrazide group with free formal-

dehyde to form self-crosslinkings between hydrazide polymers and to make gel at a low temperature. The second step is the reaction of the hydrazide group with methylol groups of the UF resin that produces a crosslinkage between the hydrazide polymer and UF resin. The second step seems to require a rather high temperature than the first step, partly because the water-soluble part decreases markedly by curing at 110°C as shown in Fig. 5. The highly crosslinked networks were considered to be obtained in the molar ratio of 0.5. The excess amount of hydrazide groups will cause to the consumption of reactive formaldehydes, including methylol groups, and the production of low crosslinked networks and greater amount of the water-soluble part as shown in Fig. 5.

3.3 Adhesive Strength

The adhesive shear strengths of lap-joints bonded by the new curing method were evaluated on the effects of the molar ratios and the curing conditions, and compared with those by the conventional curing (Fig. 6). The shear strength has a maximum in the molar ratios from 0.25 to 0.5 after treating at 110°C, and is not inferior to that by the conventional method using ammonium chloride. However, the shear strength of a specimen bonded at room temperature is considerably less than that at 110°C. From these evaluations, it was suggested also that the new curing involves two stages, and that a high curing temperature is required to obtain completely cured networks.

Figure 7 shows the results on the shear strength tests on plywood specimens which were prepared with three amino resins, U1, U2, and UM, at a large molar

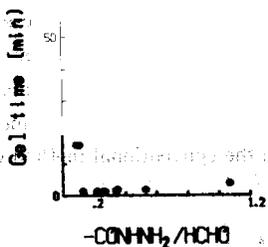


Fig. 4. Gel times vs molar ratios for the UF resin (U1)-PMAH system under pH 7.8-8.5 at 25°C.

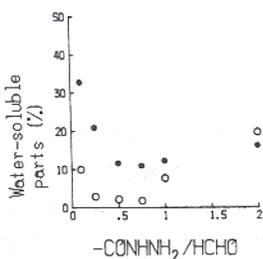


Fig. 5. Rates of water-soluble parts vs molar ratios for the UF resin (U1)-PMAH system cured at pH 7.8-8.5.

Legend: ●, cured at room temperature; ○, cured at 110°C for 3 hrs.

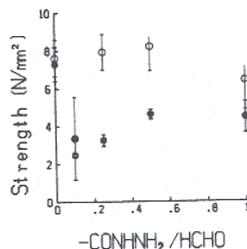
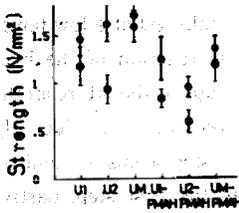


Fig. 6. Adhesive shear strengths of lap-joint specimens vs molar ratios for the UF resin (U1)-PMAH system.

Note; Plots at CONHNH₂/HCHO=0 are the results of curing by NH₄Cl.

Legend: ●, cured at room temperature; ○, cured at 110°C for 6 hrs.



Adhesive shear strengths of plywoods with adhesives U1, U2, and UM cured by NH_4Cl and adhesives U1-PMAH, U2-PMAH, and UM-PMAH with the new curing system at the molar ratio of 0.75.

Legend ○, normal test ; ●, water-soaking test (60°C).

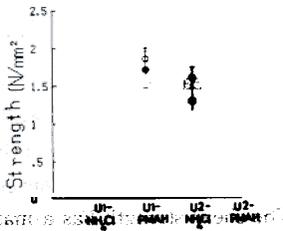


Fig. 8. Adhesive strength of plywoods with adhesives U1- NH_4Cl , U2- NH_4Cl cured by NH_4Cl and adhesives U1-PMAH and U2-PMAH with the new curing system at the molar ratio of 0.1

Legend ○, normal test ; ●, water-soaking test (60°C).

ratio of 0.75. The new curing system passed the JAS value both in the normal and water-soaking tests, but it was not superior to conventional curing. This is caused by the short gelation time resulting from the large molar ratio of 0.75. The pot-life is too short to control the spreading procedure and the assembly conditions such as wettability between adherents. On the other hand, it is shown in Fig. 8 that the shear strengths of plywood prepared at the smaller molar ratio of 0.1 are not inferior to those by the conventional curing.

Figure 9 shows the effects of the molar ratios on the bond strength of plywood specimens. The bond strength was found to decrease with increasing molar ratios. This is caused from the smaller resin contents. As PMAH was used as a 15% aqueous solution, the resin content decreased with increasing molar ratios. However, both normal and water-soaking test results exceeded the JAS requirements at the molar ratios between 0.1 and 0.3.

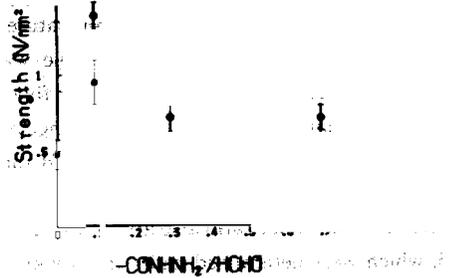


Fig. 9. Adhesive strength of plywoods prepared at various molar ratios.

Note Plots at $\text{CONHNH}_2/\text{HCHO}=0$ are the results of curing by NH_4Cl .

Legend ○, normal test ; ●, water-soaking test (60°C).

3.4 Formaldehyde Emission

The preliminary data of formaldehyde emissions from the plywoods prepared at various molar ratios are shown in Fig. 10. A remarkable reduction of formaldehyde emission is observed in the application of the new curing system compared with the conventional curing method using ammonium chloride. However, the amount of UF resin decreased inevitably as the molar ratio increased, since the spreading ratio was constant. The corrected values in Fig. 10 mean the emission levels when the same amounts of UF resin as in the conventional method were applied

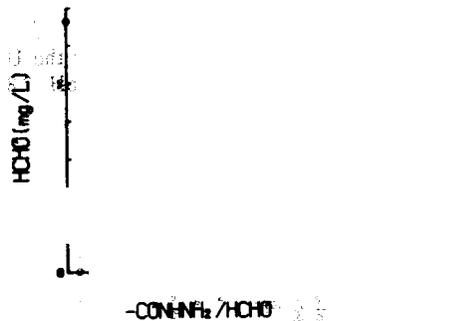


Fig. 10. Determination of formaldehyde emission from plywood prepared under the new curing system at various molar ratios.

Note Plots at $\text{CONHNH}_2/\text{HCHO}=0$ are the results of curing by NH_4Cl .

Legend ●, original data ; X, corrected data assuming the same amount of UF resin as in $\text{CONHNH}_2/\text{HCHO}=0$ was used.

under the new curing method at every molar ratio. A remarkable reduction also was recognized after the corrections. Therefore, it was concluded that the hydrazide polymer has a strong capability to act not only as hardner of the UF resins but also as a formaldehyde scavenger. From the aspect of the reduction of formaldehyde emission, the practical utilization of hydrazide compounds and polymers will be emphasized.

4. CONCLUSIONS

A new curing system of UF resins was investigated using the hydrazide polymer, poly(methacryloyl hydrazide), as a hardner. It was found that this system has not only comparable adhesive strengths with the conventional curing by ammonium chloride, but also reduces formaldehyde emission from the final product of plywood. It also was suggested that the reaction of hydrazide polymers with UF resin involves two stages. The first stage is the reaction of hydrazide groups with free formaldehyde which makes hydrazide polymers self-condense through methylene linkage to result in the initial gelation. The second stage at a higher temperature is the co-condensation of hydrazide groups with methylol groups of UF resins, which gives the crosslinking

networks between UF resins and hydrazide polymers.

From the practical point of view, the new curing system has the great advantage of reducing formaldehyde emissions from the final products. There is, however, a difficulty to be solved in this system. The extremely short pot-life will make practical use difficult. Further work on practical application, such as using a separate spreading method, will be emphasized in developing this system.

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