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Characteristics of Urea-formaldehyde Resins as Related to Glue Bond Quality of Southern Pine Particleboard[*1]

Chung-Yun HSE[*2]

サウザンパイン・パーティクルボードの材質におよぼすユリア・ホルムアルデヒド樹脂特性の影響[*1]

Chung-Yun HSE[*2]

ユリアに対するホルムアルデヒドのモル比（5水準），反応時の濃度（3水準），反応温度（3水準）の3要因の組合わせで，生成樹脂によるボード材質を検討した。その結果，フリーのホルムアルデヒド量は，ボードの諸強度（はく離強さ，曲げ強さ，曲げヤング率，木ねじ保持力）と直線的かつ正に相関した。またメチロール量も，曲げ強さを除く諸強度と正に相関した。硬化の過程に生じた樹脂の収縮は，ボード諸強度と負に相関し，収縮の最も大きな樹脂が最も弱い接着力を示した。

Forty-five urea resins were formulated and replicated by factorial arrangement of three variables: molar ratio of formaldehyde to urea (1.5, 1.7, 1.9, 2.1, and 2.3), reactant concentration (35, 42.5, and 50 %), and reaction temperature (75°, 85°, and 95°C).

In the range of the 90 batches of resins, free formaldehyde content (1.3 to 6.7 %) was linearly and positively correlated with strength of internal bond (IB), modulus of rupture (MOR), modulus of elasticity (MOE), and screw withdrawal forces (SW). Methylol content (3.2 to 10.3 %) was also positively correlated with IB, MOE, and SW, but not with MOR. Resin shrinkage (24 to 36 %) during cure was, in general, negatively correlated with IB, MOR, MOE, and SW; *i.e.*, resins with most shrinkage yielded the poorest bond.

1. INTRODUCTION

Technology for formulating urea-formaldehyde (UF) resin adhesives for plywood and particleboard manufacture has for the most part been developed empirically. This situation has resulted mainly from two factors: (a) the immediate requirements of industry have been satisfied without a great deal of fundamental research; (b) the complexity and instability of the resin system make complete chemical analysis extremely difficult. Recently, however, as resin technology has developed and applications have become specialized, research laboratories have become more concerned with the factors controlling mode of formation and speed of cure, and effect of additives.

Several workers[1)~4)] have studied the preparation, properties, and adhesive characteristics of UF resins. Almost all these studies have been concerned with resins as adhesives for plywood.

By contrast, the study reported here was part of a sequence of investigations aimed at developing UF resin systems for further improvement of southern pine particleboard.

The present paper considers the effect of formulation variables on resin properties and relates these properties to glue bond quality of particleboard. Subsequent articles will discuss the effect of reaction pH and type of catalyst on board properties.

2. PROCEDURE

Resin preparation and characterization

All urea-formaldehyde resins were prepared in the laboratory, formulation variables being as follows:

Five molar ratios of formaldehyde to urea (CH_2O/urea): 1.5, 1.7, 1.9, 2.1, and 2.3.

*1 Received Dec. 24, 1973.
*2 Southern Forest Experiment Station, Forest Service, U. S. Department of Agriculture, Pineville, Louisiana

Three reaction temperatures: 75°, 85°, and 95°C.

Three reactant concentrations: 35, 42.5, and 50 % by weight.

Thus, 45 resins were formulated; as each was replicated, 90 batches were prepared.

In preparing each resin, the pH was adjusted initially to 8 with a mixed solution of caustic and ammonium hydroxide. The mixture was then quickly heated and maintained at reaction temperature. After an initial period of 50 minutes, pH was adjusted to 5.0 with acetic acid solution to promote condensation. When viscosity reached 40 CPS, the reaction was terminated by rapidly cooling the mixture and adjusting the pH to 7.5.

Specific gravity: Specific gravity of the fresh resin was determined with a Hubbard-type pycnometer according to ASTM Method D 1963. To determine specific gravity after curing, resin was spread thinly on a watch glass and put in an oven held at 110°C. The resulting flake was weighed to the nearest 0.1 mg and its volume determined on a volumeter.

Surface tension: The surface tension of each resin was measured with a Du Nouy ring mounted on an Instron testing machine set at maximum sensitivity (10 g full scale); the method has been described previously.[7]

Free formaldehyde: A slightly modified sodium sulfite mothod[8] was used for determination of free CH_2O. Fifty ml of a molar solution of sodium sulfite and three drops of thymolphthalein indicator solution were placed in a 250-ml Erlenmeyer flask and carefully neutralized by titration with normal hydrochloric acid until the blue color of the indicator disappeared. An accurately measured and substantially neutral resin sample was then added to the sodium sulfite; temperature was kept at 4°C to minimize hydrolysis of the resin. The resulting mixture was titrated with the standard acid to complete decoloration and the percent of free CH_2O was determined as:

$$\frac{\text{(acid titer)(normality of acid)(3.003)}}{\text{weight of sample}}$$

Methylol formaldehyde: The same sodium sulfite method was used for this determination, except that the solution was kept for 1 hour at 80°C in a water bath before titration. Methylol formaldehyde was then calculated as the difference between the values for total CH_2O at 80°C and the sum of the values for free CH_2O.

Board preparation

Board specification: All boards were prepared in the laboratory.

Specifications were:

Size: 36 by 36 cm

Thickness: 1.59 cm

Density: 0.7

Resin level: 7 % (on basis of ovendry wood)

Wax level: 0.5 % (on basis of ovendry wood)

Particle preparation: The dried southern pi[ne] wood particles (6 % moisture content) were obtain[ed] at a particleboard plant in Louisiana and used witho[ut] additional preparation. Sieve analysis of particl[es] was:

	+ 4 mesh:	1.2 %
− 4 mesh,	+ 8 mesh:	20.5 %
− 8 mesh,	+20 mesh:	55.9 %
−20 mesh,	+32 mesh:	12.1 %
−32 mesh,	+48 mesh:	4.9 %
	−48 mesh:	5.4 %

Blending: To prepare a board, wood furnish w[as] weighed out and placed in a rotating cement mix[er]. Amounts of resin and wax were then weighed a[nd] applied separately to the wood particles by air-atom[iz]ing nozzles. Moisture content of the particles af[ter] spraying was adjusted to 10 to 12 %.

Forming the mat: The blended particles we[re] carefully felted into the final mat with a forming b[ox] 36 cm². The mat mas prepressed at 10.5 kg/cm² f[or] 1 minute.

Hot pressing: The prepressed mat was transferr[ed] immediately to a 50 cm² single-opening hot pr[ess] heated at 160°C. Pressure was sufficient——usua[lly] 28 to 40 kg/cm²——to bring the press down to t[he] 1.59-cm stops in approximately 1 minute. Total pr[ess] time was 6 minutes.

Sampling and testing

As soon as the boards were cool enough to hand[le] they were trimmed to 30 cm² and weighed. Th[ey] were then stored in a chamber controlled at 30 relative humidity and 27°C until equilibrium w[as] reached, whereupon board volumes were determin[ed]. Board density was computed from volume and weig[ht] immediately after trimming, *i.e.*, at about 10 % M[C].

When conditioned, each board was cut to yie[ld] specimens for determination of modulus of elastic[ity] (MOE), modulus of rupture (MOR), screw withdraw[al] force (SW), and internal bond strength (IB). The tests were performed in accordance with ASTM Stan[d]ard D 1037-64.

3. RESULTS AND DISCUSSION

Resin properties

As expected, the 45 resins exhibited a wi[de] range of physical and chemical properties (Tab[le] 1). Ranges for all 90 batches were: free CH_2[O], 1.3 to 6.7 %; methylol content, 3.2 to 10.3 %; specific gravity of uncured resin, 1.0878 [to] 1.1580; specific gravity of cured resin, 1.43[..] to 1.5095; and surface tension, 70.9 to 8[.] dynes/cm.

Table 1. Physico-chemical properties of resins and strength properties of particleboard

Concentration	Temperature	Free CH_2O content	Methylol content	Specific gravity: Uncured resin	Specific gravity: Adjusted	Specific gravity: Cured resin	Cure shrinkage	Surface tension	IB	MOR	MOE	SW
%	°C	%		Gm/cm³			%	dyne/cm³	kg/cm²			kg
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)
1.5 Mole of CH_2O/mole urea												
35	75	2.60	4.40	1.119	1.119	1.495	33.4	78.4	7.73	88.9	14694	175
35	85	2.50	3.45	1.106	1.106	1.494	35.4	81.4	6.47	78.8	14905	155
35	95	2.00	3.75	1.117	1.117	1.509	35.3	77.9	8.37	103.8	17176	169
42.5	75	1.60	5.70	1.137	1.110	1.471	32.5	80.4	7.87	88.3	15102	174
42.5	85	2.05	4.95	1.138	1.111	1.471	32.5	80.9	8.15	89.4	14976	173
42.5	95	1.80	4.70	1.112	1.091	1.467	34.5	79.9	7.24	95.5	16122	151
50	75	1.90	6.10	1.154	1.103	1.459	32.3	80.4	7.80	84.9	14730	167
50	85	1.50	5.50	1.154	1.105	1.466	32.6	80.4	8.99	92.2	15278	188
50	95	1.90	4.95	1.149	1.101	1.465	33.1	80.9	8.57	100.6	16965	195
1.7 Mole of CH_2O/mole urea												
35	75	3.60	4.35	1.110	1.110	1.459	31.4	78.9	10.12	94.5	15594	193
35	85	2.50	4.05	1.112	1.112	1.464	31.6	80.4	10.05	103.4	17858	183
35	95	2.70	4.05	1.114	1.114	1.482	33.0	81.4	11.18	101.8	16452	191
42.5	75	3.70	6.30	1.124	1.100	1.461	32.9	81.4	9.42	102.3	17472	191
42.5	85	2.85	5.35	1.128	1.103	1.472	33.4	79.4	9.49	91.5	15489	193
42.5	95	1.90	5.25	1.130	1.104	1.465	32.7	81.9	10.41	108.2	17929	199
50	75	2.15	6.95	1.149	1.105	1.465	32.6	80.9	9.49	94.5	16171	198
50	85	2.35	6.35	1.139	1.095	1.451	32.3	81.4	8.99	110.4	17401	202
50	95	2.00	6.30	1.150	1.101	1.463	32.9	77.9	11.46	135.3	20024	232
1.9 Mole of CH_2O/mole urea												
35	75	3.80	6.00	1.106	1.106	1.477	32.6	81.4	9.00	100.0	19089	176
35	85	3.75	4.60	1.100	1.100	1.449	31.7	80.4	9.70	106.5	17753	201
35	95	3.35	4.10	1.110	1.110	1.473	32.7	79.4	9.84	102.0	16909	216
42.5	75	4.00	6.40	1.131	1.106	1.464	32.4	79.4	8.58	92.2	15981	183
42.5	85	4.05	5.45	1.121	1.097	1.454	32.5	80.4	9.77	97.4	15981	215
42.5	95	4.15	5.25	1.132	1.103	1.454	31.9	80.4	9.42	110.6	17507	194
50	75	3.90	7.75	1.153	1.102	1.439	30.6	81.4	11.25	107.5	17739	211
50	85	4.45	7.20	1.149	1.102	1.459	32.7	79.4	8.86	91.2	16944	178
50	95	4.80	6.85	1.148	1.099	1.455	32.3	77.9	10.19	116.2	18210	219
2.1 Mole of CH_2O/mole urea												
35	75	4.70	6.00	1.112	1.112	1.477	32.9	81.9	9.84	103.8	18301	198
35	85	4.80	5.15	1.107	1.107	1.449	31.0	79.9	8.51	98.4	16241	174
35	95	5.15	4.40	1.106	1.106	1.459	31.9	80.4	9.42	103.8	16733	213
42.5	75	4.75	6.60	1.130	1.103	1.465	32.6	78.4	8.58	93.6	18055	183
42.5	85	5.30	5.85	1.117	1.098	1.455	32.4	79.4	10.83	101.6	18020	210
42.5	95	5.30	5.60	1.129	1.106	1.458	31.9	81.4	11.39	108.3	17071	210
50	75	5.20	8.80	1.148	1.092	1.446	32.4	80.4	9.28	102.8	19757	174
50	85	5.65	7.85	1.150	1.100	1.452	31.9	80.9	12.23	127.4	21057	205
50	95	5.80	6.90	1.143	1.096	1.453	32.6	79.9	10.62	120.2	17950	206
2.3 Mole of CH_2O/mole urea												
35	75	4.95	6.50	1.100	1.100	1.457	32.6	80.4	9.07	91.9	16944	183
35	85	4.95	5.90	1.096	1.096	1.456	32.8	80.9	8.01	95.9	17493	185
35	95	5.45	4.70	1.104	1.104	1.472	33.3	81.4	9.84	119.2	19953	188
42.5	75	5.20	7.90	1.128	1.103	1.458	32.2	80.9	10.76	110.1	18969	197
42.5	85	5.10	7.50	1.131	1.104	1.453	31.6	81.4	9.70	104.5	17612	197
42.5	95	5.60	5.75	1.131	1.105	1.446	30.9	80.9	10.69	119.9	18618	202
50	75	6.25	9.45	1.152	1.102	1.445	31.1	79.9	13.08	118.3	20621	222
50	85	5.90	8.50	1.144	1.100	1.442	31.1	79.4	10.26	99.0	17577	200
50	95	6.10	7.10	1.147	1.099	1.444	31.4	79.4	10.55	108.8	17507	226

The effect of formulation variables on resin properties were evaluated by analysis of variance. Testing was at the 95 % level of probability, and all curves drawn are sigificant at that level.

Free formaldehyde content: Variance analysis indicated that free CH_2O differed significantly with change in CH_2O/urea ratio. The interactions of this ratio with reactant concentration and reaction temperature proved significant.

On average, free CH_2O increased with an increase in the ratio:

CH_2O/urea ratio	Free CH_2O content %
1.5	1.96
1.7	2.64
1.9	4.03
2.1	5.16
2.3	5.50

Between ratios of 1.7 and 1.9, the increase was more than twice as large as between 1.5 and 1.7. The sharp increase is important to the problem of odor; *i.e.*, a small increase in the ratio may bring the free CH_2O to an unacceptable level.

At ratios of 1.5 and 1.7, the free CH_2O decreased with reactant concentration and with increased reaction temperature (Fig. 1). At ratios of 1.9, 2.1, and 2.3, however, free CH_2O increased with both concentration and temperature (except at 85°C with ratio of 2.3).

Table 2. Effects of reactant concentration, CH_2O/urea ratio, and reaction temperature on methylol content of the resin

		Methylol content %
Reactant concentration (percent)	35	4.76
	42.5	5.87
	50	7.10
CH_2O/urea ratios	1.5	4.83
	1.7	5.44
	1.9	5.98
	2.1	6.35
	2.3	6.97
Reaction temperature, °C	75	6.61
	85	5.84
	95	5.31

Methylol content: Methylol content differ significantly with change in all three prima variables. As Table 2 shows, methylol creased as concentration and ratio increas and as reaction temperature decreased.

Significant interactions are charted in Fig. The lower and higher ratios differed in t rate at which methylol content increased wi reactant cocentration. At ratios of 1.5 and 1 methylol increased sharply with concentrati from 35 to 42.5 %. For higher ratios the fast increase occurred between concentrations 42.5 to 50 %.

At all ratios, methylol content consisten decreased as reaction temperatures rose (Fig. 2

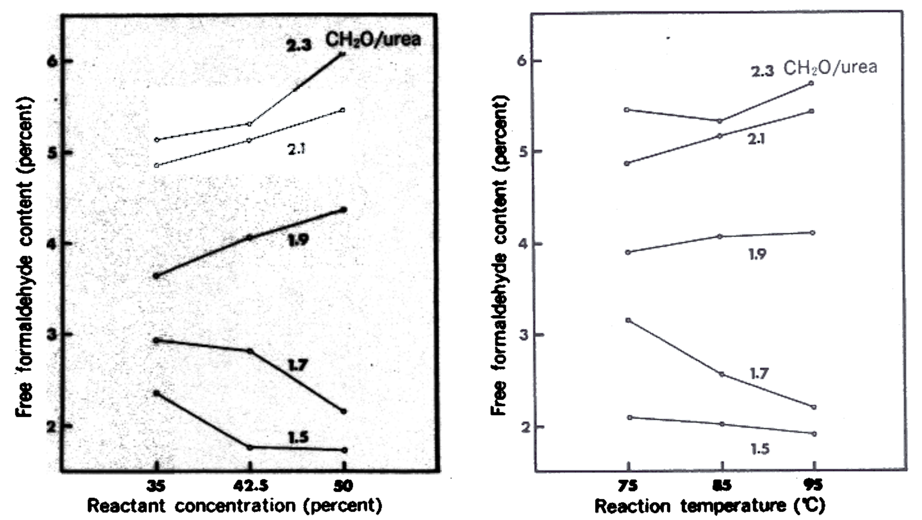

Fig. 1. Free formaldehyde content of the resin as affected by interactions of CH_2O/urea ratio with reactant concentration (left) and reaction temperature (right).

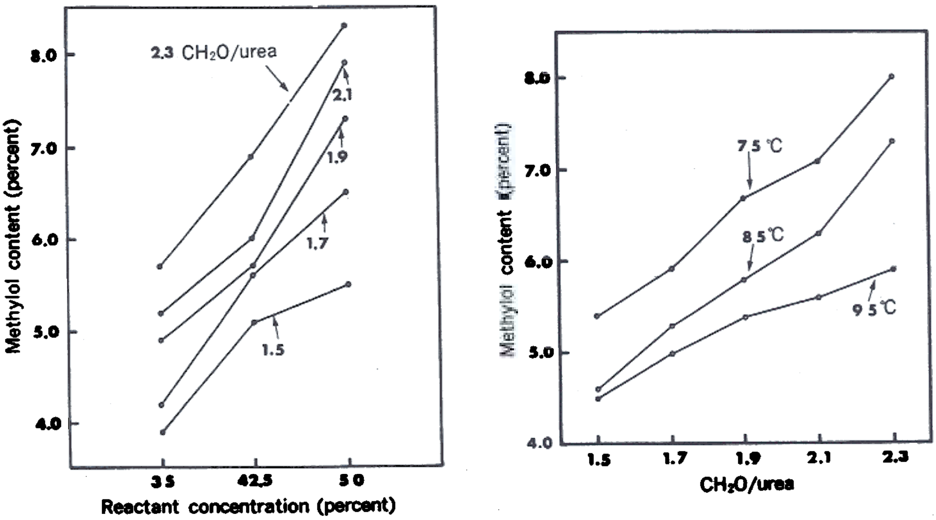

Fig. 2. Methylol content of the resin as affected by interactions of CH_2O/urea ratio with reactant concentration (left) and reaction temperature (right).

Because free CH_2O did not differ with change in temperature, the lower methylol content may signify a greater condensation reaction at high temperature.

Specific gravity: Density of the liquid resins increased substantially as concentration increased. This was to be expected, largely because water is less dense than resin. An attempt was therefore made to calculate specific gravities by adjusting the water content to an equal basis, as follows:

Letting d_0 equal the specific gravity of liquid resin with concentration of C_0, and d equal the specific gravity after adjustment to C, where $C_0>C$, then,

$$C_0W_0=CW \qquad (1)$$

where W_0 and W are weight of the liquid resins before and after adjustment.

Hence, the amount of water (*i. e.*, weight W_a or volume V_a) required for changing concentration is:

$$W_a=W-W_0 \qquad (2)$$

$$\text{or} \quad V_a=V-V_0 \text{ and } V_a=W_a \qquad (3)$$

where V is volume of the liquid resin after adjusting concentration.

V_0 is the volume of the liquid resin of weight W_0.

The adjusted specific gravity of liquid resin can, therefore, be stated as:

$$d=\frac{W}{V}=\frac{W_0+W_a}{V_0+V_a}=\frac{W_0+W_a}{V_0+W_a} \qquad (4)$$

By combining equations 1, 2, and 4:

$$d=\frac{C_0W_0}{CV_0+(C_0-C)W_0} \qquad (5)$$

In equation 5, W_0 and V_0 were determined experimentally; reactant concentration was used directly as C_0; and 35 percent by weight was chosen as the level of adjusted concentration C. The results of this computation are given in column 6 of Table 1.

For both fresh and cured resin, specific gravity decreased with an increase in ratio and concentration (Table 3).

Surface tension: Resin surface tension differed with changes in CH_2O/urea ratio and reactant concentration but not with changes in

Table 3. Effects of reactant concentration and CH_2O/urea ratio on specific gravity and surface tension.

		Specific gravity		
		Adjusted uncured resin	Cured resin	Surface tension
		Gm/cc		dynes/cm
Reactant concentration (%)	35	1.108	1.471	76.
	42.5	1.103	1.461	75.
	50	1.099	1.453	73.
CH_2O/urea ratio	1.5	1.107	1.477	76.
	1.7	1.105	1.464	76.
	1.9	1.103	1.457	75.
	2.1	1.102	1.456	74.
	2.3	1.101	1.453	73.

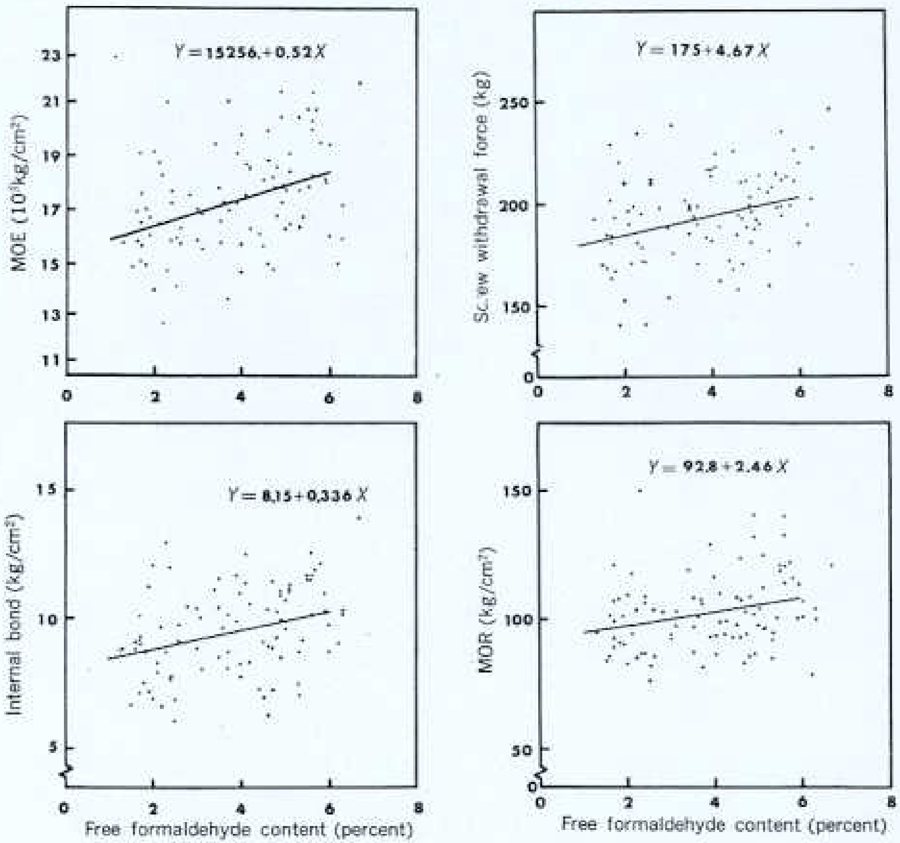

Fig. 3. Relationships between free formaldehyde content and board strength properties.

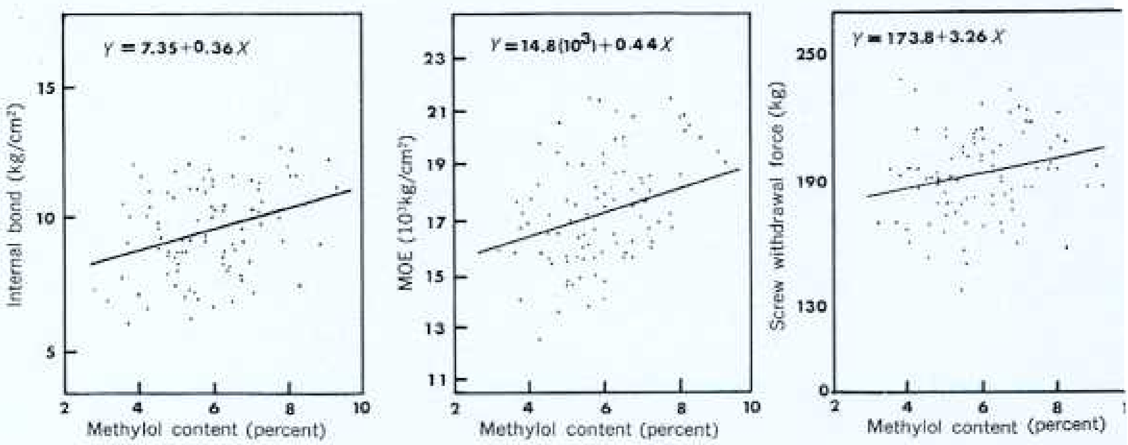

Fig. 4. Relationships between methylol content and strength properties.

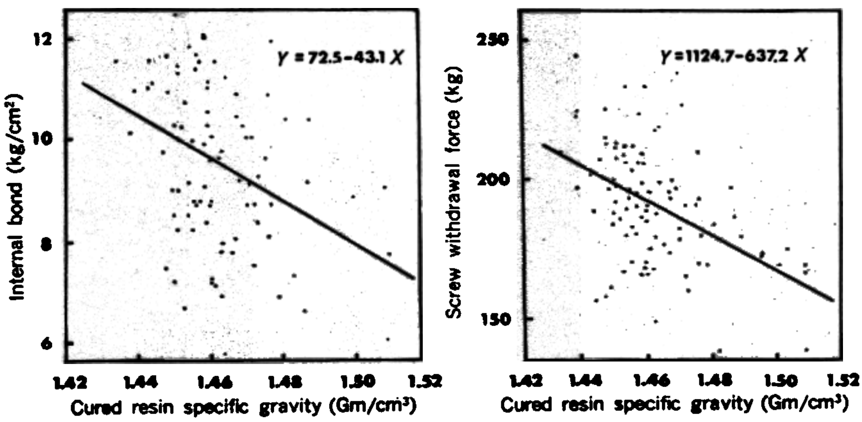

Fig. 5. Relationships of internal bond and screw withdrawal force to specific gravity of cured resin.

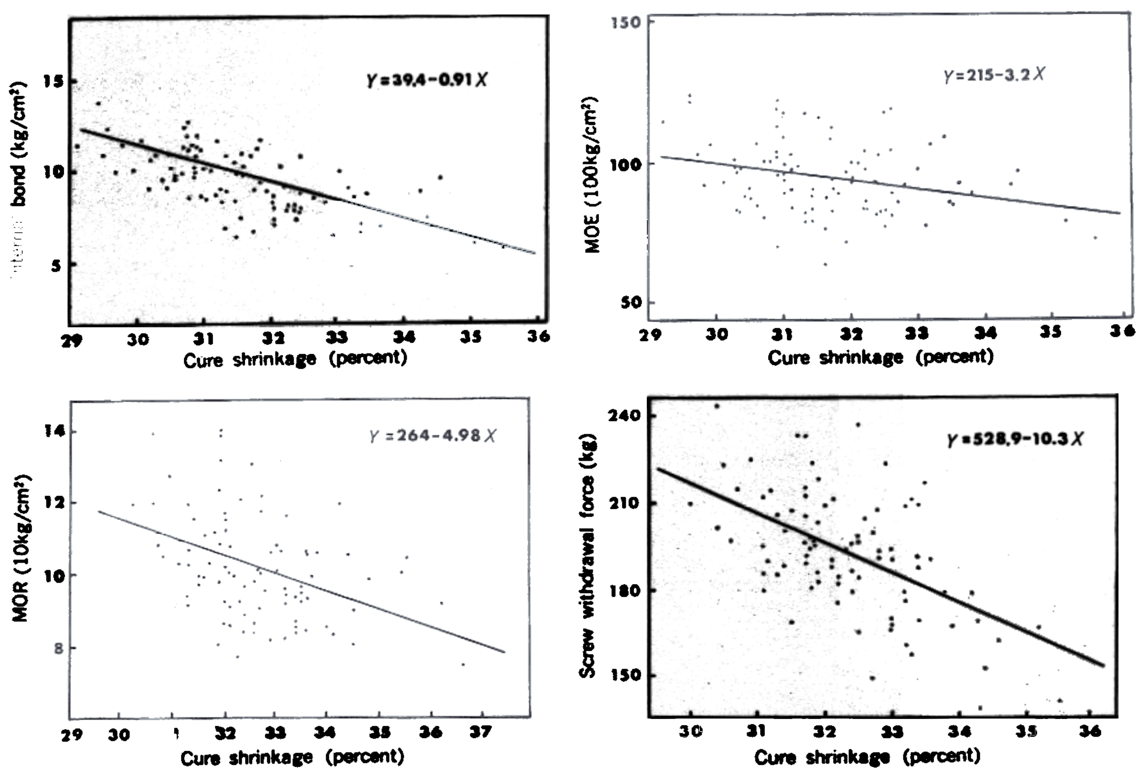

Fig. 6. Relationships between cure shrinkage and strength properties.

reaction temperature.

Surface tension increased slightly (from 76.0 to 76.3 dynes/cm) with a change of ratio from 1.5 to 1.7; thereafter it decreased consistently (from 76.3 to 73.7 dynes/cm) with a change of ratio from 1.7 to 2.3 (Table 3).

Table 3 shows that surface tension decreased as reactant concentration increased. The decrease between reactant concentration of 35 to 42.5 % was substantially less than that between 42.5 to 50 %.

Resin properties related to particleboard strength

Relationship between resin properties and board strength were evaluated by regression analysis at the 95 % level of probability. All equations were of the form: $y=a+bX$.

Free formaldehyde content: In the range of the 90 batches of resins, free CH_2O was linearly and positively correlated with all four strength properties (Fig. 3). The explanation probably is that free formaldehyde, under the heat and pressure applied during resin curing, reacts with the catalyst to liberate an acid to act as an additional polymerization catalyst. Hence, low free CH_2O may cause insufficient liberation of acid and retard the cure rate to the extent that a poor bond results.

Methylol content: The methylol content was positively correlated with IB, MOE, and SW (Fig. 4), but not with MOR. The methylol provides primary functional groups for cross-linking of the resin, and also furnishes active sites for molecular interaction at the resin-wood interface.

Specific gravity: The adjusted specific gravity of liquid resin appeared to exert no effect on board properties. The specific gravity of cured resin, however, proved negatively correlated with IB and SW (Fig. 5).

Cure shrinkage: Primarily because of shrinkage during curing, specific gravity was consistently higher in the cured than in the fresh resins. The difference, expressed as a percentage of the adjusted specific gravity, was therefo used as an indicator of cure shrinkage (Tab 1).

All four strength properties decreased as cu shrinkage of resin increased (Fig. 6). Shrinka causes internal stresses; several studies ha shown that such stresses weaken bonds[9)~11)].

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