THE EFFECT OF SOY PROTEIN ADDITIONS ON THE REACTIVITY AND FORMALDEHYDE EMISSIONS OF UREA-FORMALDEHYDE ADHESIVE RESINS

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ABSTRACT

Urea-formaldehyde (UF) resins were modified with soy protein, hydrolyzed soy protein, soy flour, or casein, at 1.5 to 50 percent of UF solids, to determine if modifying the resins would reduce formaldehyde emissions. Differential scanning calorimetry was used to determine the reactivity of the modified UF resins compared with unmodified UF resin. The reactivity was reduced as the added protein modifier increased, but up to 30 percent protein modifier could be added to the UF resin before the reactivity was reduced significantly. Formaldehyde emissions from cured UF resins were not decreased as the amount of protein modifier added to the resin was increased.

Urea-formaldehyde (UF) adhesives are excellent adhesives for bonding wood and are considerably less costly than other adhesives. However, modified UF adhesives are needed that will significantly reduce the formaldehyde emission problem associated with this adhesive system. Many materials have been shown to reduce formaldehyde emissions from UF resins, including powdered glass, inorganic salts, amines, and amine hydrochlorides (7,8). Soybean products and casein have been reported to reduce formaldehyde emissions from UF resins (1-4,6,11). The studies with soybean and casein modifiers used UF resins with a high formaldehyde-to-urea molar ratio (F/U) and high free-formaldehyde contents. The reported lower formaldehyde emissions would not meet current standards. Because soybean protein is a readily available material, the addition of soy protein to a UF resin with a low F/U molar ratio needed to be investigated. To determine the chemical and physical nature of the addition of soy protein to UF resins, experiments were conducted and are reported here that assessed 1) the amount of soy protein that could be added to a commercial UF resin; 2) the reactivity, as determined by differential scanning calorimetry (DSC), of the soy-protein-modified and unmodified UF resins; and 3) the formaldehyde emissions of the modified and unmodified UF resins after curing.

EXPERIMENTAL

MATERIALS

The commercial UF resin used was GP 3342 particleboard resin from Georgia-Pacific Resins, Inc., Decatur, Ga. The resin has 66 percent nonvolatiles, less than 0.65 percent free formaldehyde, a pH of 7.9, and an F/U of 1.25.

Soy protein (SP) was an isolate (Ardex FR) obtained from Archer Daniels Midland Company, Decatur, Ill. The protein content is 90 percent, and 90 percent passes through a No. 100 mesh screen (150-µm sieve opening). The pH of a 1:10 dispersion in water is 6.4 to 7.0.

Soy flour (SF, toasted) was also obtained from the Archer Daniels Midland Company.

Casein (CA, lactic, JO-8) was obtained from National Casein Company, Chicago, Ill. The protein content is 83 to 86 percent, and 95 percent passes through a 70-mesh (210-µm) screen. The pH is 4.0 to 5.0.

Dispersed soy protein (DSP) was prepared by adjusting a 10 percent aqueous solution of SP to pH 9.5 with 50 percent sodium hydroxide and stirring for 10 to 15 minutes (5). Sulfuric acid (0.5 *M*) was then added to reduce the pH to 8, so the DSP could be added to the UF resin without neutralizing the acid catalyst.

Hydrolyzed soy protein (HSP) was prepared by adding sodium carbonate (6 g) to 100 g of a 15 percent aqueous solution of SP to adjust the pH to 11 and

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TABLE 1. — *Data from differential scanning calorimetry of unmodified and modified commercial urea-formaldehyde (UF) resins.* [a]

Protein	Catalyst $(NH_4)_2SO_4$	Total solids	Peak temperature	ΔH (UF basis)
	(%)		(°C)	(J/g)
Unmodified				
0	0.6	65	84	190
0	1.2	65	85	192
0	1	65	84	193
0	5	65	85	173
0 (diluted[b])	5	25	91	140
Soy protein				
10	1	67	94	182
20	1	69	100	176
30	1	72	109	150
40	1	24	112	107
50	1	29	124	21
20	5	68	94	180
30	5	72	98	128
Dispersed soy protein				
10	5	40	96	148
20	5	38	102	129
30	5	24	114	76
40	5	24	117	67
soy flour				
1.5	1	65	84	186
10	1	67	92	172
30	1	72	104	160
Hydrolyzed soy protein				
3	1	60	88	170
10	1	51	95	174
Casein				
10	1	67	87	170
20	1	69	89	148
30	1	72	91	148

[a] Based on previous replications, an approximate value for the standard deviation of the ΔH values is 3.94. An approximate standard deviation for the temperature values is 0.56.
[b] Water was added to reduce the total solids to 25 percent.

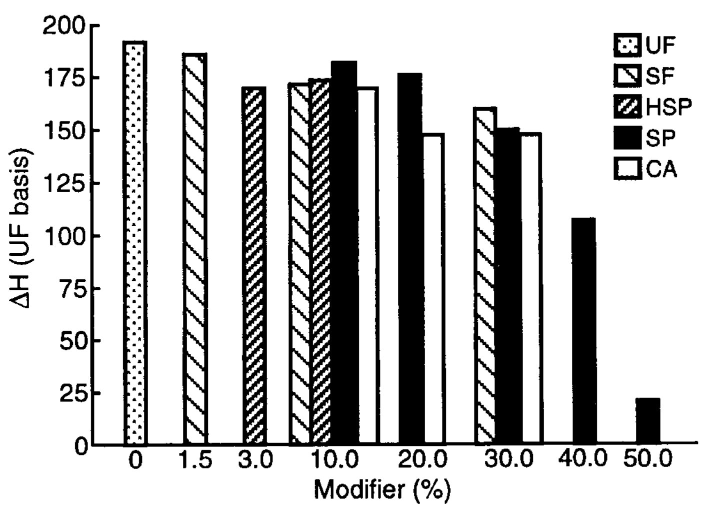

Figure 1. — Exothermic heat of cure (ΔH) values for modified UF resins at 1 percent catalyst and unmodified resin (UF) at 1.2 percent catalyst; SF = soy flour; HSP = hydrolyzed soy protein; SP = soy protein; CA = casein.

heating the mixture at 95°C for 20 hours. The pH was adjusted to 8 with sulfuric acid (0.5 *M*) so the HSP could be added to the UF resin without neutralizing the acid catalyst.

FORMULATION OF RESINS

Modified UF resins were formulated by adding SP, SF, CA, DSP, or HSP to the UF resin, calculating the percentage on the basis of total UF plus protein solids. For example, the resin designated as UF + 30 percent SP contains 70 percent UF solids and 30 percent SP solids by weight. Ammonium sulfate (as a percentage based on UF solids) was added as a catalyst to cure the resin. The SP, SF, and CA were added as dry powders directly to the UF resin and stirred until it was well mixed. The DSP and HSP were added as aqueous solutions. The amount of water in the resins for DSC scans was kept to a minimum to ensure that sufficient resin solids were present in the capsule to allow for detection of the curing reactions.

METHODS

Differential scanning calorimetry. — The instrument used was a Model DSC 7 from Perkin-Elmer Corporation, Norwalk, Conn. Approximately 10- to 30-mg samples were weighed into stainless steel large volume capsules (LVCs, from Perkin-Elmer), which were sealed by o-rings to 2.4 MPa to prevent spurious thermal events caused by moisture escape. Weights were measured on an electrobalance. The heating rate was 10°C/minute. The DSC measures the amount of heat evolved or absorbed as a sample is heated at a constant rate. The temperature at which heat output reaches a maximum, the peak temperature, is frequently used as a simple indication of the hot-press temperature needed to cure an adhesive in a reasonably short time. The amount of heat released during the curing reaction (ΔH) was calculated by dividing the area under the DSC peak by the weight of the UF solids in the sample (considered the minimum reactive component).

Formaldehyde emissions. — Formaldehyde emissions from small samples of unmodified UF resin and UF resin modified by SP, SF, HSP, or CA were determined by the chromotropic acid procedure from the formaldehyde test method FTM 1-1983 (9,10). Resin samples were cured for 10 minutes in shallow covered nonstick-coated stainless steel pans heated between press platens. The cured samples were ground to 40 mesh (0.420 µm), and 10 mg of each resin was weighed into a small stoppered weighing bottle. A small x-shaped glass rod was placed in the bottom of the weighing bottle to raise a small beaker above the sample. A small beaker containing 5 mL of 40 percent sulfuric acid was placed on the glass rod to absorb the formaldehyde emitted from the sample and to maintain the relative humidity in the weighing bottle at 60 percent. The weighing bottles were kept in a constant temperature room at 26°C. The beakers were replaced at 1, 4, 7, 10, and 14 days with beakers containing fresh 40 percent sulfuric acid, and aliquots were analyzed for formaldehyde by the chromotropic acid procedure. In this procedure, 0.10 mL of a 1 percent solution of chromotropic acid (4,5-dihydroxynaphthalene-2,7-disulfonic acid, disodium salt dihydrate) and 6 mL of concentrated sulfuric acid are added to 4 mL of the solution being analyzed. The absorbance of the resulting solution is measured at 580 nm with a UV-VIS spectrophotometer. The milligrams of formaldehyde in the acid solution are calculated from a calibration curve constructed from the absorbances of known formaldehyde standards.

TABLE 2. —Formaldehyde emissions of unmodified and modified commercial urea-formaldehyde (UF) resins.

Protein	Solids	Cure temperature	Total formaldehyde[a]
----------(%)----------		(°C)	(µg F/10 mg UF solids)
Unmodified			
0	35	110	224,236
0	45	110	228, 142, 310, 338, 307
0	45	120	234
0	45	130	78, 52
0	55	120	59, 230
0	65	110	72, 115, 106, 90, 62
0	65	130	24, 51
Soy protein			
10	35	120	24, 15
10	45	120	88, 152, 96
10	55	110	74, 68
10	55	120	62, 67
10	55	130	20, 26
10	55	140	12, 13
10	65	120	66, 48, 90
20	45	110	104, 88
20	45	130	88, 102, 54
20	55	120	56, 58
20	65	110	72, 85
20	65	130	60, 31, 33
30	55	120	82, 69
Soy flour			
10	45	120	74
10	65	120	56
Casein			
10	45	110	246
10	65	110	90, 46
20	65	110	57
30	65	115	107

[a] Each number in this column represents a separate determination of two duplicate samples. The formaldehyde samples were collected for a total of 14 days. The underlined numbers were produced by a modified 2^3 factorial experiment. The paired numbers are the paired conditions in the design as described in the text.

RESULTS AND DISCUSSION

DIFFERENTIAL SCANNING CALORIMETRY

The UF resin samples catalyzed by ammonium sulfate $(NH_4)_2SO_4$, at 0.6 to 5 percent of UF solids by weight, were compared by DSC **(Table 1).** As the amount of ammonium sulfate increased from 0.6 to 1.2 percent, the peak temperatures and ΔH values held constant within experimental error. The peak temperature increased and the ΔH value of the exotherm decreased at 5 percent catalyst compared with 0.6 or 1.2 percent. This indicates that 0.6 percent ammonium sulfate is equivalent to 1.2 percent in curing the UF resin.

The UF + 20 percent SP and UF + 30 percent SP resins with 1 or 5 percent ammonium sulfate added as a catalyst were analyzed by DSC to determine the effect of the amount of catalyst on the curing reaction of the modified UF resins **(Table 1).** The peak temperatures increased and ΔH values (based on UF solids) decreased as the SP increased from 20 to 30 percent. As the amount of catalyst increased, the peak temperatures decreased. The ΔH values increased at 20 percent SP but decreased at 30 percent SP, as the amount of catalyst increased. These results suggest that there is an optimum amount of catalyst needed to cure the resin, depending on how much modifier is in the resin.

The peak temperatures of the UF resin samples with 40 or 50 percent SP were much higher and the ΔH values (based on UF solids) were much lower than those of the other UF + SP resins. The lower ΔH values may have resulted in part because the total solids contents of UF resins with 40 or 50 percent SP were lower than those of the other resins since more water was required to suspend the SP and reduce the viscosity. To determine the effect of adding water, an unmodified UF resin (shown as “diluted” in **Table 1)** was diluted to approximately the same total solids content as the UF + 40 or 50 percent SP resins. The added water increased the peak temperature and decreased the ΔH value but not to the same extent as adding 40 or 50 percent SP. Also, the added water increased the peak temperature less than adding 20 percent SP to the UF resin, while decreasing the ΔH value more.

In general, DSC analysis shows that changes in the peak temperature and ΔH for the cure of UF resins with similar contents of other proteinaceous modifiers parallels the changes observed with SP-modified UF resins **(Table 1). Figure 1** shows ΔH values for the modified UF resins, except those modified with DSP at 1 percent catalyst and the unmodified UF at 1.2 percent catalyst. For the UF resin samples with added modifier (SP, HSP, or SF), the peak temperatures increased and the ΔH values (based on UF solids) decreased as the amount of modifier increased, both indicating lower reactivity.

The UF resins with added DSP had much lower ΔH values and slightly higher peak temperatures compared with UF resins with SP added at the same concentrations. This may be because these resins were formulated with a lower solids content and a higher catalyst content than the SP-modified UF resins. The DSP was tested as a modifier because traditional soybean adhesives are prepared by dispersing the SP with alkaline materials, and using DSP might enhance the adhesive properties of the UF resin (5). However, based on our data, it does not appear that DSP has any advantages over SP as a modifier for UF resins.

The UF resins with added HSP had increased peak temperatures and essentially unchanged ΔH values as the amount of HSP increased. For the resin samples with added CA, the peak temperatures increased and the ΔH values decreased as the amount of CA increased. Casein was included as a protein modifier for comparison with SP.

Adding a modifier tends to increase the peak temperature and decrease the ΔH value of the UF resin. These results suggest that proteinaceous modifiers interfere with the cure of UF resin, raising the cure temperature and reducing the amount of heat in the curing reaction.

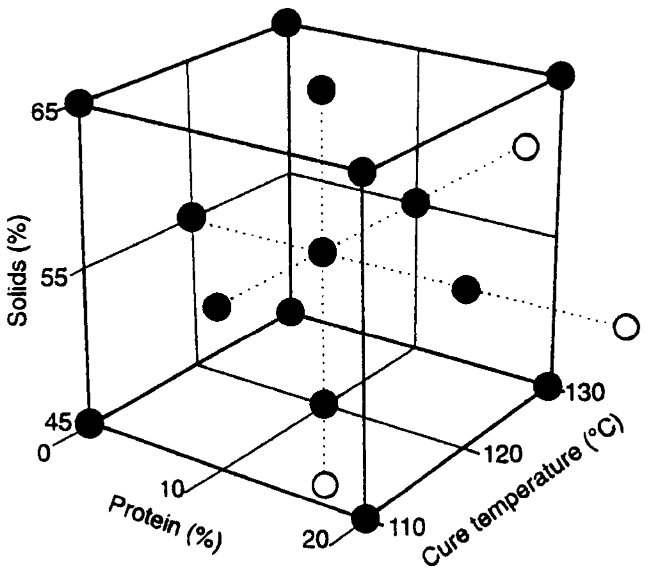

Figure 2. —Experimental design used to determine the relationship between resin cure temperature, resin solids content, amount of protein added to the resin, and formaldehyde emissions of the cured resin. The solid and open circles represent the conditions at which modified resins were prepared and formaldehyde emissions determined. The three open circles represent points beyond the bounds of the cube.

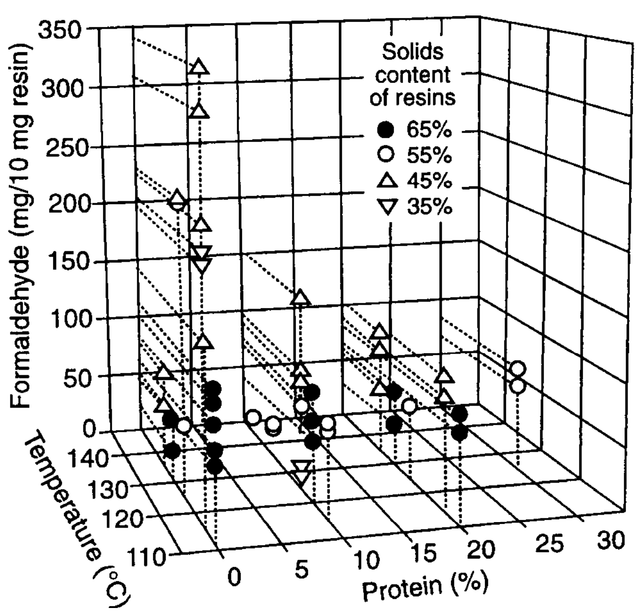

Figure 3. — Formaldehyde emissions from UF resins and UF resins modified with 10, 20, or 30 percent soy protein, measured at 60 percent relative humidity and 26°C for 14 days. The total solids contents of the resins before cure were 65, 55, 45, and 35 percent.

FORMALDEHYDE EMISSIONS

Two methods were investigated for using SP to reduce formaldehyde emissions from cured UF resins. The first method was to modify commercial UF resins by adding various amounts of SP The problem with this method was that the viscosity of the modified resin increases dramatically as the amount of SP increases. Additional water can be added to the resin to overcome this increase in viscosity, but this lowers the resin solids content and could lead to adhesion problems with the resin. Because of the increase in viscosity, the practical limit for the addition of SP appears to be about 30 percent.

The second method was to modify commercial UF resins with an SP hydrolyzate, which partly overcomes the problem of the viscosity increase. A potential problem with this method is the need for controlling the extent of hydrolysis to produce consistent resin formulations.

Modified urea-formaldehyde resins.— Formaldehyde emissions from small samples of unmodified UF resin and UF resin modified with SP, SF, HSP, or CA were determined after curing. **Table 2** shows the results of several experiments on formaldehyde emissions from UF and modified UF resins. In these experiments, 10, 20, or 30 percent SP, SF, or CA was added to the UF resin. The total solids content was 35, 45, 55, or 65 percent, and the samples were cured at 110°, 115°, 120°, 130°, or 140°C.

Formaldehyde emissions data for UF resins with and without added SP are presented in **Table 2.** The underlined formaldehyde emission values were obtained from a modified 2^3 factorial experiment. The statistical design can be represented by a cube **(Fig.** 2) having sides formed from: 1) percentage protein added to the resin (0 to 20%); 2) percentage resin solids (45 to 65%); and 3) cure temperature (110° to 130°C). Samples of modified resin were prepared at the conditions dictated by the corners, the centers of the faces, and the center point inside the cube. Three points of excursion beyond the bounds of the cube from the center point were also examined at 30 percent protein, at a resin solids content of 35 percent, and at a cure temperature of 140°C as indicated by the open circles in **Figure 2.** Additional measurements were made on the unmodified resin (0% protein) at 35 percent solids and 110°C and at 45 percent solids and 120°C. The additional measurements are not underlined in **Table 2.**

The formaldehyde emission data from the experiment **(Table 2)** were evaluated to determine whether and how formaldehyde emissions were related to the cure temperature, the resin solids, and the SP content of the modified resin. The high formaldehyde emission values for the unmodified UF resins compared with the low formaldehyde emission values of the modified resins appear to suggest that the addition of soy protein to UF resins reduces formaldehyde emissions. However, those resins with high formaldehyde emissions were generally resins cured at low temperatures (110” and 120°C) and with low solids content (35% and 45%). As demonstrated previously by DSC data, reactivity of UF resins tends to decrease with a decrease in solids content. Thus, those resins with the higher formaldehyde emissions were probably not completely cured.

Statistical analysis of the formaldehyde emissions data obtained from the modified 2^3 factorial experiment **(Table 2)** leads to the following conclusions:

1. There is good statistical evidence that formaldehyde emissions significantly decrease as the cure temperature for the resin increases. In 9 of 10 paired conditions in the design (2 cubes; 4 pairs of corners and 1 pair of opposite faces per cube), formaldehyde emissions decreased as the temperature increased from 110° to 130°C. If there were no temperature effect, the probability of seeing an event this extreme would be 0.021.

2. There is strong statistical evidence that formaldehyde emissions decrease as the percentage of solids increases. In 10 of 10 paired conditions in the design, formaldehyde emissions decreased as the percentage of solids increased from 45 to 65 percent. If there were no solids effect, the probability of seeing an event this extreme would be 0.002.

3. There is no statistically significant indication that formaldehyde emissions decrease as the percentage of SP used to modify the resins increases.

The nonunderlined emissions data in **Table 2,** although not included in the statistical analysis, would not change the conclusion that there is no statistically significant indication that formaldehyde emissions decrease as the percentage of SP used to modify the UF resin increases.

Figure 3 shows the amount of formaldehyde emitted as a function of SP content and the temperature used to cure the resin **(Table 2).** To simplify **Figure 3,** the data on UF resins modified by SF or CA are not included. **Figure 3** clearly shows that, except for several unmodified UF resins cured at lower solids content and lower temperature resulting in emissions 200 mg formaldehyde per 10 mg resin, the formaldehyde emission levels for the remaining resins are, within experimental error, essentially constant with respect to SP content. The resins with the highest formaldehyde emissions were probably not fully cured due to the low curing temperature and the high amounts of water, conditions dictated by the statistical design **(Fig.** 2). Thus, the data suggest that the addition of SP as a modifier to UF resins does not reduce formaldehyde emissions.

The formaldehyde emissions of UF resins modified with SF and CA are similar to the emissions of UF resins modified with SP, except for one of the CA samples that had a lower total solids content and was probably not cured sufficiently at 110°C.

Hydrolyzed soy protein. — The UF resins with added HSP **(Table 3)** differ from those just discussed in that the SP was hydrolyzed with sodium carbonate and then neutralized prior to addition to the UF resin. Hydrolyzed soy protein (3%, 10%, or 50% based on UF solids) was added to the UF resin. Except for the resin modified with 3 percent HSP, formaldehyde emissions from the modified UF resins were higher than the emissions from the unmodified UF resins. Moreover, formaldehyde emissions for HSP-modified UF resins were collected for only 4 days compared with the formaldehyde emissions in **Table 2,** which were collected for 14 days.

TABLE 3. — Formaldehyde emissions of commercial urea-formaldehyde (UF) resins unmodified and modified with hydrolyzed soy protein (HSP).

Modifier	Protein	Cure temperature	Total formaldehyde[a]
	(%)	(°C)	(μg F/10 mg UF solids)
None	0	110	49, 74, 75, 72
HSP	3	120	48
	10	120	88
	50	120	165

[a] Each number in this column represents a separate determination of two duplicate samples, The formaldehyde samples were collected for a total of 4 days.

CONCLUSIONS

1. Soy protein can be added to UF resin in amounts up to at least 50 percent of total solids, but the reactivity is reduced as the amount of SP is increased.

2. Other protein modifiers (DSP, HSP, SF, and CA) also reduce the reactivity of UF resin at concentrations similar to those of SP.

3. Formaldehyde emissions of UF or UF modified by SP, DSP, HSP, SF, or CA decreased as the cure temperature and the percentage of solids increased. However, formaldehyde emissions were not decreased as the percentage of protein used to modify the resins increased.

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