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Cottonseed and Peanut Meal Glues. Resistance of Plywood Bonds to Chemical Reagents¹

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THE preparation and strength properties (4, 6), viscosity (1, 2, 5, 8), and resistance to accelerated service tests (7) of cottonseed and peanut meal glues have been described in previous reports from this laboratory. It was indicated that cottonseed and peanut meal glues prepared from solvent-extracted meals compare favorably with commercial casein glues in static strength properties and that cottonseed meal glue is superior to peanut meal glue and compares favorably with commercial casein glue on an interior test basis for 5 cycles, the strength of the casein bond changing from 384 to 283 pounds per square inch and of the cottonseed meal bond changing from 375 to 264 pounds per square inch.

The purpose of this report is to present data on the resistance of cottonseed and peanut meal plywood glue bonds to chemical reagents and to suggest fundamental interpretations of these data relative to the chemical factors affecting adhesion of cottonseed and peanut protein to wood.

Experimental

Glue formulation. Cottonseed meal glue, consisting of 100 parts of hexane-extracted meal, 4 parts of sodium hydroxide, 15 parts of sodium silicate, 15 parts of calcium hydroxide, and 3 parts of carbon disulfide-carbon tetrachloride, was prepared as previously described (6). Peanut meal glue was prepared from solvent-extracted peanut meal in a similar manner (4). The casein glue was a commercially available glue mix which required only the addition of water.

Plywood preparation. The method used was similar to that described in other reports (4, 6). Each glue mix was prepared and applied to birch veneer to form 3-ply panels as recommended to give maximum shear strengths. These recommended conditions were selected in order that each glue could be compared under its optimum utilization. The cottonseed meal glue was applied at a rate of 21 pounds of glue (dry basis) per 1,000 square feet of glue line, cold pressed at 80°F. and 200 p.s.i. for 1,440 minutes, and followed by hot pressing at 237°F. and 200 p.s.i. for 10 minutes. The peanut meal glue was applied at a rate of 28 pounds of glue (dry basis) per 1,000 square feet of glue line and cold pressed at 80°F. and 200

p.s.i. for 1,440 minutes. The commercial casein glue was applied at a rate of 26 pounds of glue (dry basis) per 1,000 square feet of glue line, cold pressed at 80°F. and 200 p.s.i. for 10 minutes. The press opening during these operations was five $\frac{3}{16}$ -inch panels. Test pieces, $\frac{3}{16}$ inch, $3\frac{3}{4}$ inches by 1 inch, cross-slotted to give a center section of 1 square inch, were cut from the plywood panels; then they were conditioned at 77°F. and 32% relative humidity for 6 days (3).

Method of testing. The method of testing the chemical resistance of cottonseed and peanut meal glue

TABLE I
Effects of Organic Reagents on Tensile Shear Strengths of Birch Veneer Bonded with Cottonseed Meal, Peanut Meal, and Casein Glues

Reagent	Number of Days Immersed	Tensile Shear Strengths - Wood Failure (lbs./in. ² - %)		
		Cottonseed Meal Glue	Peanut Meal Glue	Casein Glue
Carbon Tetrachloride	0	343 - 55	321 - 65	368 - 90
	1	152 - 30	175 - 60	182 - 30
	2	180 - 25	188 - 25
	4	168 - 30	202 - 40	195 - 35
	8	176 - 35	206 - 40
	10	206 - 35
	12	178 - 25	210 - 40
Benzene	1	184 - 35	165 - 50	224 - 45
	2	189 - 25	171 - 55	214 - 40
	4	201 - 20	180 - 35
	8	194 - 35	217 - 30
	10	205 - 25
	12	185 - 40	215 - 30
	14	195 - 30	183 - 45	221 - 35
Acetone	1	141 - 30	126 - 40	194 - 30
	2	153 - 25	131 - 40	197 - 40
	4	160 - 20	141 - 35	206 - 45
	8	169 - 20	148 - 30	212 - 25
	10	157 - 35
	12	175 - 30	224 - 40
	14	174 - 25	166 - 30	241 - 35
Ethanol 95%	1	159 - 25	146 - 40	205 - 30
	2	172 - 30	157 - 45	203 - 30
	4	171 - 25	154 - 35	201 - 35
	8	163 - 35	160 - 30	204 - 30
	10	173 - 15
	12	174 - 30	197 - 25
	14	155 - 20	159 - 50	209 - 30
Ethanol 50%	1	143 - 25	114 - 15	192 - 40
	2	139 - 5	113 - 10	174 - 20
	4	114 - 0	101 - 0	155 - 15
	8	81 - 0	68 - 0	101 - 0
(Water)	1	144 - 25	129 - 10	181 - 30
	2	131 - 20	105 - 0	153 - 30
	4	75 - 0	50 - 0	124 - 20
Methanol	1	126 - 30	117 - 25	137 - 40
	4	134 - 35	126 - 30	145 - 35
	10	142 - 30	136 - 30	140 - 30
	14	135 - 25	142 - 25	151 - 30

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TABLE II

Effects of Inorganic Reagents on Tensile Shear Strengths of Birch Veneer Bonded with Cottonseed Meal, Peanut Meal, and Casein Glues

Reagent	Number of Days Immersed	Tensile Shear Strengths - Wood Failure (lbs./in. ² - %)		
		Cottonseed Meal Glue	Peanut Meal Glue	Casein Glue
Sulfuric Acid 3%	0	343 - 55	321 - 65	368 - 90
	1	109 - 10	101 - 0	137 - 20
	2	69 - 0	63 - 0	87 - 10
	3	38 - 0	36 - 0	51 - 0
	4	22 - 0	20 - 0	24 - 0
Sulfuric Acid 30%	1	91 - 15	83 - 0	111 - 15
	2	44 - 0	41 - 0	57 - 0
	3	23 - 0	20 - 0	31 - 0
Sodium Hydroxide 1%	1	68 - 5	61 - 10	80 - 20
	2	53 - 0	47 - 0	58 - 10
	3	37 - 0	31 - 0	41 - 0
	4	27 - 0	27 - 0
Sodium Hydroxide 10%	1	30 - 0	25 - 0	59 - 0
	2	23 - 0
Nitric Acid 10%	1	63 - 0	58 - 0	81 - 25
	2	40 - 0	35 - 0	52 - 5
	3	29 - 0	23 - 0	37 - 0
Hydrochloric Acid 10%	1	70 - 0	57 - 0	84 - 0
	2	52 - 0	40 - 0	59 - 0
	3	27 - 0	22 - 0	36 - 0
Sodium Chloride 10%	1	56 - 0	51 - 0	91 - 15
	2	47 - 0	42 - 0	61 - 0
	3	28 - 0	23 - 0	37 - 0
Sodium Sulfate 10%	1	65 - 0	65 - 0	115 - 10
	2	51 - 0	52 - 0	78 - 0
	3	34 - 0	37 - 0	53 - 0

bonds consisted of totally immersing the conditioned test pieces in a reagent for a specified period of time and, on removing 20 of the pieces from the reagent, immediately determining their tensile shear strengths. Then the remaining unbroken pieces, which were still immersed in the reagent, were removed at a specified time, and their strengths were determined in a similar manner. The tests were similar to A.S.T.M. Designation D896-46T and D906-49 methods for testing adhesives (3).

Shear strengths reported are averages of at least 20 values. The coefficients of variation of these averages were 10-20%. Wood failure, which was evaluated by visual observation, was reported, and the percentage of the total number of pieces tested showing wood failure was calculated.

Results

The effects of organic reagents (carbon tetrachloride, benzene, acetone, ethanol 95 and 50%, methanol, and water) and inorganic reagents (sulfuric acid 3 and 30%, sodium hydroxide 1 and 10%, nitric acid 10%, hydrochloric acid 10%, sodium chloride 10%, and sodium sulfate 10%) on the strength properties of plywood glue joints are shown in Tables I and II. These reagents were selected from the lists of standard and supplementary reagents of A.S.T.M. Designation D896-46T (3).

From these data it is observed that on immersion of the test pieces in carbon tetrachloride and acetone solvents there was an initial decrease in the tensile strengths of the bonds followed by an increase in their strengths. On immersion of the test pieces in aqueous ethanol, methanol, and water, the tensile strengths of the bonds decreased with increasing time in contact with the solvents until a minimum value was reached. On immersion of the test pieces in benzene, an initial decrease in tensile strength of the bonds was noted; then there was no significant change

in the strengths of the bonds for periods of immersion ranging from 1 to 14 days.

It is also observed that the resistance of the bonds to inorganic reagents was low. The effects of salts, acids, or bases on the tensile strengths of the bonds were about equal.

Discussion

There are probably four classes of forces involved in the adhesive bond, a) ionic or valence resulting from the polar groups, b) hydrogen bonding, c) van der Waal attractions, and d) dipolar interactions depending on the orientation of the protein molecules in the bond.

The strength of the bond corresponds to the weakest attractive force. For the moment neglecting the chemical nature of the adhesive forces, there are probably three bonds involved: a) the cohesion of the glue bond, b) the cohesion of the wood veneer, and c) the adhesion between the glue bond and the veneer. When the forces of adhesion and of cohesion of the glue bond are greater than the forces of cohesion of the wood, wood failure results during testing.

The data presented in Table III indicate that the tensile strengths of the bonds, determined after they have reached a reasonably constant value during immersion in the reagents, vary inversely as the dielectric constant of the reagents in which the test pieces were immersed.

TABLE III

Effects of the Dielectric Constants of the Reagents on Tensile Shear Strengths of Glue Bonded Birch Veneer

Reagent	Dielectric Constant ¹ (20°C.)	Tensile Shear Strengths ² (lbs./in. ²)		
		Cottonseed Meal Glue	Peanut Meal Glue	Casein Glue
Carbon Tetrachloride.....	2.24	183	225	231
Benzene.....	2.28	195	183	221
Acetone.....	21.4	174	166	241
Ethanol, 95%.....	25.7 ³	155	159	209
Methanol.....	33.7	135	142	151
Ethanol, 50%.....	114	101	155
Water.....	80.0	75	50	124
Inorganic, aqueous.....	20-30	20-40	20-60

¹From "International Critical Tables of Numerical Data, Physics, Chemistry, and Technology," Natl. Res. Council of the U.S.A., McGraw-Hill Book Co. Inc., New York, 1933

²Pieces immersed for 14 days except for 50% ethanol and water which were immersed for 4 days before testing.

³Value for absolute alcohol.

This may be interpreted to indicate that ionic or valence forces are the primary attractive forces involved in the bond.

The chemical nature of the dielectric medium as well as its dielectric constant must also be considered in evaluating the effect of reagents on the bonds. The effect of benzene is to decrease the strengths of the bonds to a constant value in about 24 hours. On the other hand, immersion in carbon tetrachloride and acetone results in a decrease in strength in 24 hours below that caused by immersion in benzene. On continued immersion there is an increase in the strengths until the values obtained after 14 days of immersion are about equal to those obtained after immersion in benzene. One possible explanation is that new attractive forces are introduced by the reaction of carbon tetrachloride and acetone with the protein. To support further the concept of reaction when test pieces, which are removed from these reagents after 14 days, are reconditioned and tested, the

wet strengths of the bonds are significantly increased. This possibility of modifying the glue bonds to increase their wet strengths, i.e., to increase the forces of adhesion by substituting other attractive forces for ionic forces, is the subject of another investigation.

Summary

The resistance of cottonseed and peanut meal and casein birch plywood glue bonds to organic and inorganic reagents for periods ranging from 1 to 14 days was determined. It was suggested that the principal attractive forces involved in the protein bonds were ionic or valence forces and that differences observed in the resistance of the glues to chemical reagents

were probably due to variations in the amino acid constitution of the proteins.

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Fatty Acid Amides. IV.¹ Reaction of Fats With Ammonia and Amines²

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FATTY acid amides have a well-established industrial position, and their use is widespread and increasing (7, 11). In the commercial preparation of fatty acid amides, fatty acids, rather than fats, are treated with ammonia or amines. The main reason for this is probably the availability of inexpensive, purified fatty acids, notably from vegetable oil foots and inedible animal fats. A large increase in the demand for amides, coupled with the need for utilizing fatty acids in other applications, would probably require that fats themselves be employed as starting materials. The direct conversion of fats to amides and glycerol by reaction with ammonia or amines appears to be an attractive reaction because of its apparent simplicity and the ready availability and low cost of the starting materials. Numerous studies of this reaction have been published in the patent literature, but only a few reports have appeared in technical journals describing systematic investigations (1, 7, 8, 11).

Study of the published reports reveals considerable difference of opinion regarding the best techniques for quantitative conversions of fats to amides and glycerol. The points in question are the time and temperature of reaction, the desirability of operating under anhydrous or aqueous conditions, the need for catalysts, such as ammonium chloride and other salts, and the quantity of ammonia or amines required. Furthermore the basis for assuming that high yields have been obtained is not clear from much of the published work and, in some cases, is open to serious question. In most patents the assertion that quantitative yields are obtained is usually unsubstantiated by actual experimental data.

As part of a systematic investigation of the preparation and characteristics of nitrogen-containing fatty materials in progress in our laboratory (12, 13, 14, 15, 17), it was considered desirable to study the direct conversion of some selected fats to amides and glycerol to define conditions for obtaining quantitative yields

of products. A major portion of the present investigation was devoted to a study of the direct conversion of beef fat (in this study, oleo oil) to amides and glycerol since the most plentiful inexpensive domestic industrial fats are of animal origin. To demonstrate the generality of this work and to extend its utility, olive, castor, and tobacco seed oils were included. The direct preparation of N-(*n*-dodecyl)- and N-(2-hydroxyethyl)- as well as unsubstituted amides was also studied.

An additional line of work investigated, after conditions had been developed for quantitative conversion of fats to amides and glycerol, was the fractionation of amides by crystallization techniques in an attempt to prepare purified fatty acid amides. These could presumably then be readily converted to fatty acids by hydrolysis or employed in applications where their specialized properties made them valuable. The reasons for employing amides for the preparation of purified fatty acids, particularly the unsaturated ones, were that they are among the highest melting fatty acid derivatives, and their solubility in organic solvents is usually so low that they can be conveniently crystallized at or above 0°C. In general, crystallization for purification of unsaturated acids requires temperatures in the range of -40° to -80°C. (7, 11), and it would be a considerable advantage to be able to conduct the purifications at higher temperatures. With the exception of ricinoleamide from castor oil, oleamide from olive oil, and perhaps N-(2-hydroxyethyl) oleamide from oleo oil, amides of high purity (above 90%) were not obtained, presumably because the solubility of all the components of the mixtures were considerably reduced and, more important, the differences in solubility of the various amide types (based on degree of unsaturation) were probably too small for efficient fractionation. Some degree of fractionation was achieved however in all cases.

Experimental

All reactions with amines were conducted in an atmosphere of nitrogen; those with ammonia in an ammonia atmosphere.

¹ The previous paper in this series is reference 14.

² Presented at the Fall Meeting of the American Oil Chemists' Society, Chicago, Ill., Oct. 8-10, 1951.

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