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Whey-based polyether polyols as modifiers of phenol–formaldehyde resins

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The disposal of whey permeate (deproteinized whey/lactose) from the cheese industry represents a serious economic and environmental problem in the United States. The feasibility of replacing part of the phenol and formaldehyde in phenol–formaldehyde thermosetting resins by lactose/lactose derivatives in the resin formulation has been explored. Results indicate that polyols derived from lactose might be incorporated in the resin formulation without substantially affecting the wet shear strength of southern pine plywood bonded with these whey modified resins. It appears that up to 50% substitution of phenol (by weight) by the modifier in the formulation can be accomplished before significant loss of the wet-strength is observed. The modifier could also serve to reduce the amount of formaldehyde in the formulation.

INTRODUCTION

The disposal of 23×10^9 pounds of excess whey produced in the United States as a byproduct of the cheese industry represents a significant pollution problem. The newly available method of ultrafiltration/reverse osmosis may be used to remove the high molecular weight proteins in whey, thereby generating a permeate stream consisting essentially of 5% lactose and traces of salts in water. Due to the high BOD (biological oxygen demand) of lactose, the excess permeate generated exacerbates the disposal problem. In addition, the disposal of "salt-whey" presents an additional problem due to the added presence of salt.

Since the excess lactose/dry permeate produced in the United States amounts to more than 1×10^9 pounds, one has to consider its use in high volume products. The utilization of whey permeate has found some use in food-related applications, but little, if any increase in use is projected for this abundant by-product in the coming years as a food additive.

On the other hand, the area of chemical utilization of lactose as a substitute or as an intermediate for synthesis of large volume chemicals presents an excellent opportunity for the use of this abundant sugar. One such example is the production of low-density rigid polyurethane foams from whey permeate/lactose (Viswanathan *et al.*, 1984*a, b*; Viswanathan, 1988). The other is the production of formaldehyde-free whey-based adhesive resins for wood which if successful, will have a greater impact on the problem of whey utilization because of the greater raw material requirement for whey resin manufacture and the higher demand for wood adhesives (in terms of the total used in the USA). More than 2×10^9 pounds of phenol–formaldehyde resins are consumed in the USA, about half by the plywood industry (Sellers, 1982). Thus the second approach will consume more whey than could be realized otherwise.

PRIOR WORK

Formaldehyde-free resins

In this regard it has been shown (Viswanathan & Richardson, 1984, 1985; Viswanathan, 1985; Viswanathan & Gilton, 1986; Viswanathan *et al.*, 1987) that a formaldehyde-free adhesive resin may be prepared from whey permeate that can be used to prepare high-density thin particle boards that exhibit good strength and water resistance.

However, in order to stimulate industrial acceptance the resin must be made to cure faster at lower temperatures and should also be suitable for use under low pressures. Carbohydrate-based resins are known to require high temperatures for curing and high pressures are required to glue wood, due to the severe shrinkage undergone by the resin during the dehydration/polymerization reactions. Thus, carbohydrates alone under

acidic conditions are not suitable as plywood adhesives. Plywood adhesives require the mildest curing conditions (lowest temperature and pressure) and, therefore, if a glue could be formulated for binding veneers, it may be easily be adapted to bond other wood products (e.g. flakeboard, particle board etc.). Whey-based resins also suffer from the problem of excessive penetration in the wood cells of the veneers, even with the use of an excess filler, as determined by scanning electron microscopy (evidence not presented here).

Sugars as coreactants

Work is being conducted in our laboratory to overcome these problems encountered during the acidic curing process. In addition, work is also underway to utilize whey permeate/lactose in resins cured under basic conditions. Many of the problems associated with formaldehyde-free acidic cures may be overcome by the use of non-reducing sugars as coreactants during the synthesis of phenol–formaldehyde resins which are cured under basic conditions. Chang and Kononenko (1962) showed that sucrose may be incorporated in phenol–formaldehyde resins used as plywood adhesives without sacrifice in wet and dry strengths. Conner and Lorenz (1986) demonstrated that reducing sugars like glucose and xylose cannot be used to modify phenol–formaldehyde resins. They also demonstrated that when the free aldehyde group in reducing sugars is reduced to an alcohol or is converted into a methyl glucoside, it can be successfully used to modify phenol–formaldehyde resins. The variation of shear strength was unchanged by the addition of modifiers, even at very high modifier concentrations, but the wet-strength was affected by the addition of modifiers beyond 2.5 mol of sugar hydroxyls per mol of phenol. Thus, they confirmed Chang and Kononenko's observation that 0.3 mol of sucrose may be added to the formulation (containing 1 mol of phenol) without affecting the wet-shear strength. Preliminary extraction and spectroscopic analysis had indicated that part, if not all of the sugar is being covalently incorporated in the cured resin, in the form of ether linkage.

In a previous paper (Viswanathan & Toland, 1991), we demonstrated the feasibility of using preparations of N-hydroxymethyl-N'-lactosylurea (LUF) and N,N'-dilactosylurea (DLU) as modifiers of phenol–formaldehyde resins for use as adhesives for plywood. The results of these lactose/permeate derivatives as modifiers of phenol–formaldehyde indicates that other derivatives may also be incorporated.

In this paper we have explored the feasibility of using preparations of polyols (i.e. propoxylated derivatives) of lactose/permeate as modifiers of phenol–formaldehyde resin in plywood adhesives. Polyols of various molar ratios of propylene oxide and lactose were made and used in crude as well as partially purified forms for

phenol–formaldehyde modification. The resulting resins were then used to prepare three-ply Southern Pine plywood samples and subjected to standard tests for evaluation.

MATERIALS AND METHODS

Preparation of polyols

A 100 g sample of lactose or dry whey permeate (containing 80% by weight of lactose), various amounts of propylene oxide and 1 ml of 50% NaOH was reacted in a Parr reactor at 100°C until the pressure returned to zero. This crude preparation was then used directly as a modifier. Partial purification of the polyol was achieved by addition of 100 ml of methanol with 10 g of activated charcoal. The solution was then stirred and heated to boiling and was then filtered through a Celite filter aid. The filtrate was then placed in vacuum to remove the methanol. This procedure was repeated three to four times before complete clarity was obtained. This partially purified polyol was also used as a modifier.

Adhesive formulation

The partially polymerized resin formulations were prepared by combining reactants in the following order.

Phenol (solid) — 1 mol
50% NaOH   — 40 ml
Modifiers   — equal in weight to phenol
37% HCHO   — 2.5 mols

The reaction mixture was initially heated at 40°C, the temperature slowly raised (over a period of 30 min to 80°C and stirred for 150 min. The mixture was then cooled in air to room temperature. The pH and solid content were measured and the mixture was stored at room temperature. In a typical formulation, the solid content was quite high ($\sim$70%). Water was added to bring the solid content to approximately 50%. The pH of the resins varied from 10.5 to 11.0.

Preparation of boards and testing

Approximately 30 lb of solids per thousand square feet was applied between two faces of 1/6 in. veneers (cut 6 in.×6 in.) and used to make three-ply boards. The solids consisted of 70% resin, 20% filler (pecan shell flour) and 10% extender (soft wheat flour). The assembly time for the boards was 30 min (i.e. from adhesive application to hot-pressing). The boards were pressed at 180 psi on a Carver Laboratory Hot Press Model 2699-22 at a platen temperature of 170° C for 7.5 min. The boards were trimmed as per VPS PS No. 1-83 and

boiled for 2 h then cold soaked for 30 min and sheared wet.

Moisture content of veneer

The moisture contents of the veneers were determined according to VPS PS No. 1-83, and were estimated to be between 3 and 7%.

Solid content of resins

The solids content of the resins were determined by placing a sample in a moisture balance and heating at 120°C for 10–15 min.

Boil extraction study of resins

The degree of covalent incorporation of the polyol in the phenol–formaldehyde resin was determined by boil extraction. The extraction was performed as follows. An amount of resin was cured in moisture balance and then was ground into a fine powder via a ball mill grinder. First, the amount of powdered resin was weighed and the results recorded. The powder was then placed into a large beaker with 1800 ml H_2O and boiled for 4 h. The remaining solution was then filtered and the residue was dried. The weight was again recorded and the percentage retained was used as an indicator of covalent incorporation of the polyol into phenol–formaldehyde structure. The results of the boil extractions on various resins formulated with both purified and crude polyols are shown in Table 1.

Galactose Polyol   **Glucose Polyol**
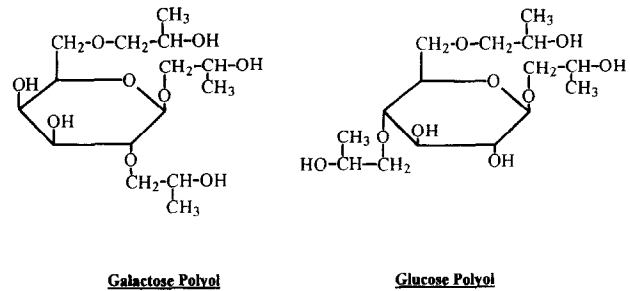
RESULTS AND DISCUSSION

Table 2 shows the strengths of three-ply plywood (after 2 h boil test) obtained using various lactose and (dry) whey permeate polyols (crude and purified) and control phenol–formaldehyde. As can be seen, good results are obtainable by using low propylene oxide:lactose (i.e. molar ratio of 2.9:1). Substantially lower molar ratios than 2.9:1 yielded mostly Maillard browning products and very little polyol. This is probably due to uneven mixing and localized heating in a Parr reactor vessel. The data also show that the purified lactose polyols and the crude whey permeate polyols gave the best results only at the molar ratio of 2.9:1.

It is easy to rationalize why polyether polyols of lactose (or any sugar for that matter) would function as efficient modifiers of phenol–formaldehyde resins. It has already been shown by us using ^{13}C-NMR (Viswanathan *et al.*, 1990) that the disaccharide is completely hydrolyzed under the basic conditions of propoxylation. The resultant product would be alkoxylated glucose and galactose with structures

Table 1. Data from boil extraction test of various polyol–phenol–formaldehyde (PF) resins

Lactose polyols Propylene oxide:lactose ratio		Weight (g)		Percent weight retained
		Start	Finish	
4.25:1	Purified	0.734	0.499	68.0%
	Crude	0.753	0.538	71.5%
3.40:1	Purified	0.765	0.573	74.9%
	Crude	0.773	0.527	68.2%
2.90:1	Purified	0.761	0.626	82.3%
	Crude	0.790	0.566	74.2%
Whey permeate polyols Propylene oxide:WP (lactose) ratio				
4.25:1	Purified	0.751	0.533	69.6%
	Crude	0.771	0.609	79.0%
3.40:1	Purified	0.775	0.592	76.4%
	Crude	0.766	0.571	74.5%
2.90:1	Purified	0.779	0.563	72.3%
	Crude	0.760	0.619	81.5%
Commercial PF resin		0.755	0.577	76.4%
Laboratory PF resin		0.773	0.697	90.2%

Table 2. Wet shear strengths of resins made by coreacting various polyols with phenol–formaldehyde (PF) (50:50 ratio of phenol:polyol by weight)

| PO:lactose or whey permeate | | Lactose polyols | | | | | | Whey permeate polyols | | | | | |
| Molar ratio | Time (min) | Purified | | | Crude | | | Purified | | | Crude | | |
		PSI	No.[a]	SD	PSI	No.	SD	PSI	No.	SD	PSI	No.	SD
5:1	7.5	121.9	5	14.6	186.4	5	8.6	236.1	5	35.9	135.1	5	17.3
	7	60.3	5	17.3	220.8	5	34.2	161.1	5	14	226.1	5	21.6
	6	193.7	5	40.1	120.7	5	9.9	100.8	2	0.73	138.7	5	16.6
	5	54.7	1	0	232.7	5	32.2	0	0	NA	220.8	2	13.7
4.25:1	7.5	163.1	5	32.4	0.0	0	NA	160.9	5	28.3	250.7	5	28.1
	7	155.4	5	30.8	98.5	3	46.7	166.1	5	9.68	134.3	5	29.8
	6	162.2	5	22.6	80.6	2	17.6	92.5	3	18.6	147.9	5	24.0
	5	141.1	5	13.7	0.0	0	NA	141.2	2	34.7	217.3	4	25.2
3.4:1	7.5	217.3	5	29.0	121.4	3	15.5	159.6	5	11.1	118.0	5	14.2
	7	186.6	5	33.1	153.0	5	22.6	210.8	5	14.6	185.2	5	16.9
	6	215.8	5	28.2	0.0	0	NA	218.3	5	11.3	167.5	4	35.7
	5	176.5	5	31.0	26.6	2	6.1	0.0	0	NA	75.5	2	0.24
2.9:1	7.5	217.2	5	32.8	147.4	5	13.4	110.9	5	10.5	243.7	4	3.77
	7	222.2	5	25.9	184.4	5	16.1	39.7	3	19.0	148.2	5	14.7
	6	222.7	5	13.5	122.7	3	18.6	151.7	5	29.4	93.5	3	18.8
	5	231.7	5	17.8	86.5	1	0.0	0.0	0	NA	188.1	5	8.48
0:1[b]	7.5	115.5	4	30.1				120.9	4	25.4			
	7	135	5	34.5				126.9	5	28.5			
	6	0	0	NA				145.0	1	0.0			
	5	0	0	NA				0.0	0	NA			
Control	7.5	207.3	5	24.2									
PF	7	116.9	5	11.6									
resin	6	171.9	5	22.4									
0:0	5	249.9	5	34.9									

SD, standard deviation of strength values.
[a]Number of replicant experiments.
[b]Unmodified lactose and whey permeate control.

shown below (note that the anomeric hydroxyl is propoxylated).

It has already been shown by us (Viswanathan & Toland, 1991) that (unmodified) lactose can be used as a modifier of phenol–formaldehyde. The apparent mechanism of curing (supported by IR) is the reaction of the hydroxyl groups on sugar with hydroxyl groups (of hydroxymethyl) phenol–formaldehydes. Extending the same reasoning, longer chains terminating in OHs on the sugar nucleus (i.e. sugar polyol) should increase the probability of cross-linking and thus yield a stronger product. This fact is borne out by the results obtained in this paper. Even the crude form of whey permeate polyol works as an efficient modifier. This is probably due to the residual proteins present in the raw material that aid during cross-linking reactions involved in final cure.

Economic considerations

Even though propylene oxide is expensive (~$0.51/lb) compared to phenol (~$0.45/lb), it can be calculated

that in the modified formulation using permeate polyol, with 2.9 mol of propylene oxide to 1 mol of lactose, as modifier (100% by weight of phenol) in phenol–formaldehyde formulation, where 2.5 mol of formaldehyde ($0.10/lb) has been added per mol of phenol, the following would be the ingredient distribution (ignoring alkali).

Whey permeate/lactose	23.5%
Propylene oxide	11.5%
Phenol	35%
Formaldehyde	30%

The ingredient cost for the above formulation based on $0.11/lb for dry permeate is ~$0.27/lb dry basis, in comparison to phenol–formaldehyde which has an ingredient cost of ~$0.32/lb dry basis (ignoring alkali). It can thus be seen that polyol modification of phenol–formaldehyde is still ecomically feasible provided the amount of propylene oxide (or ethylene oxide) is kept low. It should also be noted that there is about 20% decrease in formaldehyde and 45% decrease in phenol content in this particular formulation as compared to a

pure phenol–formaldehyde formulation (molar ratio of 2.5:1:; formaldehyde: phenol). Wood failure values have not been reported here because of the limited samples used to test the feasibility of the procedures described. Further work would involve such determinations using large number of samples to compensate for variations in veneer.

ACKNOWLEDGEMENTS

REFERENCES

Chang, C.D. & Kononenko, O.K. (1962). *Adhesive Age*, p. 36.

Conner, A.H. & Lorenz, L.F. (1986). *J. Wood Chem. Technol.*, **6**(4), 591–613.

Sellers, T., Jr (1982). *Adhesive Age*, pp. 32–35.

Viswanathan, T. (1985). *Ind. Eng. Chem., Product R and D*, **24**, 176.

Viswanathan, T. (1988). United States Patent No. 4,734,442.

Viswanathan, T., Burrington, D. & Richardson, T. (1984*a*). *J. Chem. Technol. Biotechnol.*, **34B**, 52.

Viswanathan, T., Burrington, D. & Richardson, T. (1984*b*). United States Patent No. 4,459,397.

Viswanathan, T., Burrington, D. & Richardson, T. (1986). Canadian Patent No. 1,204,739.

Viswanathan, T. & Gilton, T. (1986). *Ind. Eng. Chem., Product R and D*, **25**, 313.

Viswanathan, T. & Richardson T. (1984). *Ind. and Eng. Chem., Product R and D*, **23**, 644.

Viswanathan, T. & Richardson T. (1985). United States Patent No. 4,524,164.

Viswanathan, T., Smith, M. & Palmer, H. (1987). *J. Elast. Plast.*, **19**, 99.

Viswanathan, T. & Toland, A.D. (1991). *Carbohydr. Polym.*, **15**(1), 41–49.

Viswanathan, T., Toland, A.D., Lui, R.-Q. & Jagannathan, N.R. (1990). *J. Polym. Sci., Polym. Lett.*, **28**, 95–100.