*Carbohydrate Polymers* **15** (1991) 41–49

# Whey Modified Phenol–Formaldehyde Resins as Plywood Adhesives

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(Received 12 January 1990; accepted 7 February 1990)

## *ABSTRACT*

*The disposal of whey permeate (deproteinized whey/lactose) from the cheese industry represents a serious economic and environmental problem in the USA. 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 dilactosylurea and N-hydroxymethyl-N′-lactosylurea 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% (by weight) substitution of phenol by the modifier in the formulation can be accomplished before significant loss of the wet strength is observed.*

## INTRODUCTION

The disposal of $23 \times 10^9$ pounds of excess whey produced in the USA as a by-product of the cheese industry represents a significant problem of a national stature. The newly available method of ultrafiltration may be used to remove the high-molecular-weight proteins in whey, thereby generating a permeate stream consisting essentially of lactose and traces of salts. Due to the high BOD 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 USA amounts to more than a billion pounds, one has to consider its use in products used in high volumes. The utilization of this dairy by-product has found some use in food-related applications but little, if any, increase is projected for this abundant sugar 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 cheese by-product. One such example is the production of low-density rigid polyurethane foams from whey permeate/lactose (Viswanathan *et al.*, 1984*a*, 1984*b*, 1986; 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 amount used in the USA). More than 2 billion pounds of phenol–formaldehyde resins is 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 process. It is for this reason that whey-based resins produced by the thermal degradation/polymerization of lactose under acidic conditions cannot be used as a suitable plywood adhesive. 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 adapted to bond other wood products (e.g. flakeboard, particleboard, etc.). Whey resins also suffer from the problem of excessive penetration in the wood cells of the veneers even with the use of an excess of filler, as determined by scanning electron microscopy (evidence not presented here).

## Sugars as coreactants

Work is being done in our laboratory to overcome these problems encountered during the acidic curing process. 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, and cured under basic conditions. Chang and Kononenko (1962) showed that sucrose may be incorporated in phenol–formaldehyde resins and used as plywood adhesives without sacrifice in wet and dry strengths. Conner and Lorenz (1986) demonstrated that reducing sugars cannot be used to modify phenol–formaldehyde resins. They also demonstrated that when the free aldehydic group in reducing sugars is blocked by conversion into a methyl glycoside or converted into an alcohol by reduction, it can be successfully used to modify phenol–formaldehyde resins. They concluded that non-reducing sugars function partially as reactants and partly as fillers. The variation of shear strengths with varying amounts of modifier showed that dry-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 moles of sugar hydroxyls per mole of phenol. Thus they confirmed Chang and Kononenko's observation that 0·3 moles of sucrose may be added to the formulation (containing 1 mole 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.

## Use of reducing sugars

Conner *et al.* (1989) demonstrated that reducing sugars can be incorporated into phenol–formaldehyde resins under neutral conditions. In another article by Christiansen and Gillespie (1986) the feasibility of using reducing sugars as modifiers for exterior quality phenol–formaldehyde resins is discussed. In it they had explored the patents by Gibbons and Wondolowski (1977, 1980) on carbohydrate–phenol-based condensation resins incorporating *N*-containing compounds. In their process the conditions used to react the monosaccharide (glucose) with urea included the addition of sulfuric acid and heating to very high temperatures (150°C). The reaction was carried out in the presence of phenol which functioned as an inert solvent in the absence of water. Such conditions are conducive to degradation of sugars, such as dehydration and formation of Maillard browning reaction products. The formation of any appreciable quantities of glycosyl or diglycosylurea may be ruled out due to the lack of water and the very high temperatures used to carry out the reaction (Osipov, 1962). On the other hand, under conditions of high acidity and temperature, glycosylurea formed would undergo hydrolysis back to the starting materials (Benn & Jones, 1960). In addition any amino sugar formed would readily undergo decomposition to yield Maillard products, including a host of colored compounds with a wide range of molecular weights. A complete analysis of the products formed has been frustrating because of the complexity of the reaction mixture. Spectroscopic analysis of the fusible resole resin, by Christiansen and Gillespie using FTIR and NMR revealed an extremely complex system, without any appreciable quantities of 5-hydroxymethyl-2-furfuraldehyde (HMF) being detected. The mechanism of the reaction thus remained obscure.

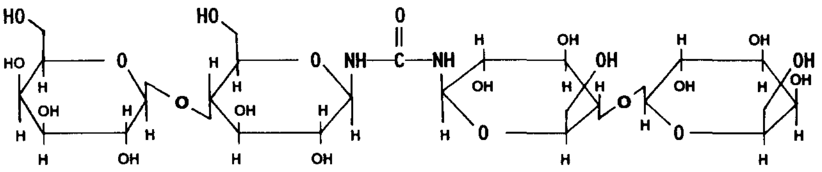
In this paper we have explored the feasibility of using whey-permeate/lactose (reducing sugars), and crude as well as partially purified preparations of *N*-hydroxymethyl-*N*′-lactosylurea (LUF) and *N*,*N*′-dilactosylurea (DLU) as modifiers of phenol–formaldehyde resins for use as adhesives for plywood. Figure 1 shows the structures of the lactose derivatives used as modifiers.

## EXPERIMENTAL METHODOLOGY

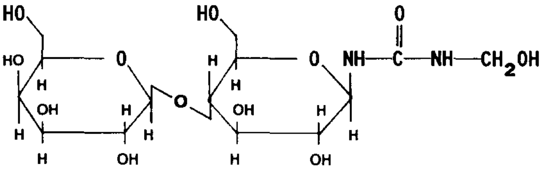
### Adhesive formulation

The partially polymerized resin formulations were prepared by combining reactants in the following order: phenol (solid), 1 mole; 50% NaOH, 40 ml; modifiers, equal in weight to phenol; and 37% HCHO, 2·5 moles. The reaction mixture was initially heated at 40°C for 30 min. The temperature was then slowly raised to 75°C and stirred for 75 min. The reaction mixture was then cooled. The pH and solid content was measured and the mixture was stored at room temperature. In case of formulations containing a modifier, the solid contents were quite high (~70%). Water was added to reduce the solid content between 55% and 65%.

In the case of the synthesis of lactose-modified phenol–formaldehyde resin, 35·25 g (0·375 moles) phenol was mixed with 42·07 g (0·375 moles) lactose monohydrate in 30 ml $H_2O$. Then 5 ml of 12·5 M NaOH were added and the mixture stirred at room temperature until all the lactose went into solution. Then 70 ml of 37% HCHO and 10 ml of 12·5 M NaOH were added slowly over a 2-h period (temperature was



DLU



LUF

**Fig. 1.** Dilactosylurea (DLU) and *N*-hydroxymethyl-*N*′-lactosylurea (LUF).

kept around 40°C). Then the mixture was heated at 65°C for 1 h. The final pH was 10·39 and the solid content was 63·5%.

## Preparation of DLU

Dry whey permeate (213·95 g) (containing 80% by weight of lactose) and 15 g urea were mixed with 50 ml $H_2O$ and either conc. $H_2SO_4$ or conc. $H_3PO_4$ (85%) were aded to bring down the pH to 2·2. The thick slurry was then stirred with a mechanical device and heated at 70°C for 8 h. Small amounts of water were added at intervals when the reaction mixture turned unmanageably viscous. The mixture was cooled and neutralized with 50% NaOH. This was then used directly as a modifier. Partial purification involved washing the crude with 100 ml methanol. Colored impurities were removed during this process.

## Preparation of LUF

Lactose monohydrate (180 g, 0·5 moles) and urea (30 g, 0·5 moles) were mixed with 50 ml $H_2O$ and 2·75 ml conc. $H_2SO_4$. The mixture was stirred and heated at 110°C for 2 h in a Parr reactor. The reaction mixture was cooled and 200 ml ethanol was mixed and the mixture was filtered. The residue was then dried and powdered. A 100-g sample of the powder was stirred with 52 ml of 37% HCHO and 3·5 ml of 12·5 M NaOH was added (final pH 10·0) and the mixture stirred at 35–40°C overnight. This mixture was then used directly as a modifier.

## Preparation of boards and testing

Approximately 30 lb solids/1000 $ft^2$ 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 170°C for 7·5 min. The boards were trimmed according to VPS PS # 1-83, boiled for 2 h and sheared wet.

## Moisture content of veneers

The moisture content of the veneers was determined according to VPS PS # 1-83, and was estimated to be between 3% and 7%.

## Solid content of resins

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

## RESULTS AND DISCUSSION

Figure 2 shows the strengths of three-ply plywood (after 2-h water boil and tested wet) obtained for the different modified formulations and control phenol–formaldehyde. From the data it can be seen that lactose/ whey permeate and lactose derivatives (DLU and LUF) can be used to modify phenol–formaldehyde resins that show good water resistance after curing. Even though lactose alone can be used to modify phenol–formaldehyde, the lower water-resistance and strength obtained is indicative of the undesirable role of a reducing group during the curing process. However the somewhat decent strength obtained with the use of a reducing sugar is somewhat surprising.

This may be due to the fact that, under alkaline conditions and low temperature, lactose is known to undergo epimerization to lactulose (Fig. 3) (Montgomery, 1962). The additional hydroxymethyl group in lactose may participate in the formation of an ether linkage with hydroxymethyl phenol, during synthesis of the resin before further degradation can take place. This is in view of the fact that sugar primary hydroxyls are more reactive (lower pka values) than secondary hydroxyls.

Evidence of better performance by the conversion of an aldehydic group to a non-reducing form to modify phenol–formaldehyde is seen by

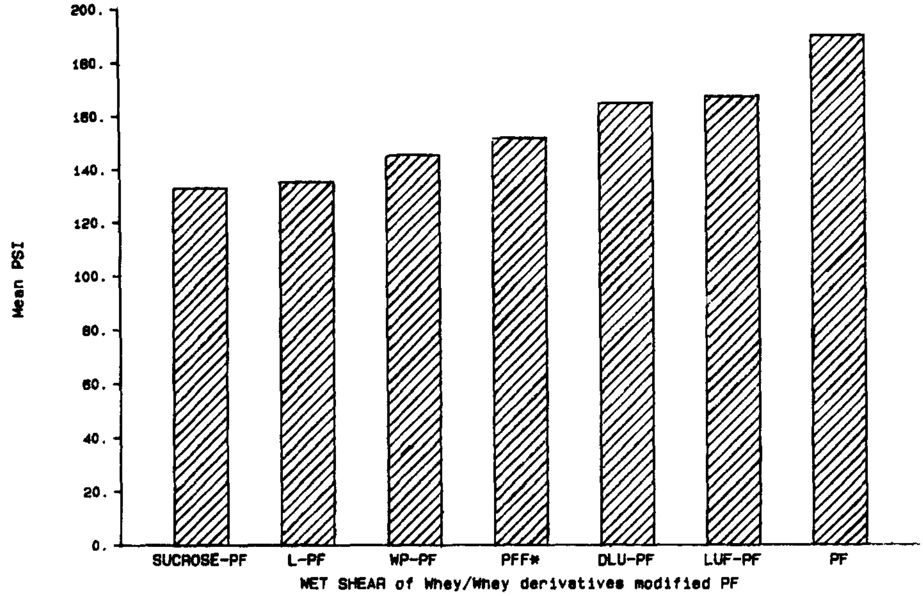


**Fig. 2.** Shear strength after 2 h boil test. *, The amount of modifier is replaced by the same amount of filler.

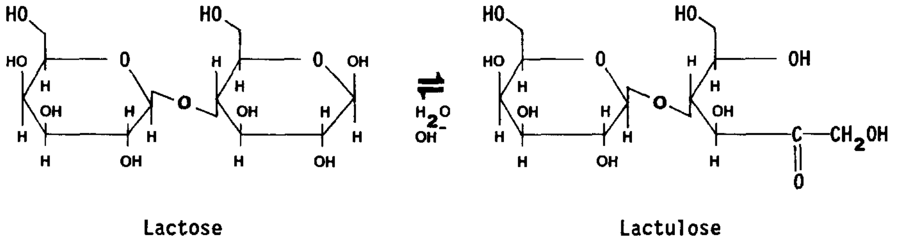


**Fig. 3.** Conversion of lactose to lactulose.

the better performance of DLU- and LUF-modified phenol-formaldehyde resins under identical conditions of curing, such as those used for lactose-modified resins. Also, lactosylurea (LU) alone is not as suitable a modifier as lactose, because the unreacted end of the urea would degrade upon basic conditions and heat, to yield lactosylamine, $CO_2$ and $NH_3$. The amine would then decompose readily, more so than lactose alone. Also the evolution of $CO_2$ and $NH_3$ might be detrimental during the curing process in between veneers. In our laboratory, boards prepared using LU-modified phenol-formaldehyde do not show good water resistance. However, blocking the amine end of the LU molecule by a reaction with formaldehyde, prior to using it as a coreactant renders the molecule highly suitable for phenol-formaldehyde modification.

## ECONOMIC CONSIDERATIONS

Most substitutes for formaldehyde-based resins have the disadvantage of being economically impractical. Others suffer from lack of adequate supplies (e.g. tannins) or extensive preparation (e.g. lignin) before they can be coreacted with phenol and formaldehyde.

Diglycosylurea (McNeff, 1972; Smith & McAllan, 1978) and LUF (Sachetto *et al.*, 1979) on the other hand are known to be excellent cattle feeds (non-protein nitrogen sources), because $NH_3$ is released from them less than from urea. Urea alone is toxic to animals for this reason. Thus we have an opportunity for multi-use for this abundant sugar. This potential dual outlet for the lactose derivatives would stimulate the dairy industry to consider the manufacture of these derivatives on a large scale, which should consequently bring the price down. Since no purification of DLU/LUF prepared using whey permeate or whey is required, and since the proteins present in the crude may render further cross-linking of the phenol–formaldehyde-resin, the product will be very cheap and will be available in plenty. Also, these derivatives should be cheaper than sucrose, whose price is controlled internationally.

## CRITICAL APPRAISAL OF THE PROCESS

The preparation of lactose derivatives DLU and LUF involve straightforward procedures using very cheap reactants. DLU and LUF are prepared by reacting the reducing sugar with the appropriate amount of urea in the presence of an acid. The urea derivatives used as cattle feed are made by reacting the ingredients in the presence of $H_2SO_4$ or $H_3PO_4$. We have tried using both the acids and find that the use of the latter yields a better modifier probably because of higher yields of the urea derivatives. Also no purification of the product is required when whey permeate is directly used as the source of lactose. We have found no advantage of purification and in some instances there is a small loss of strength on using purified materials, probably due to the removal of proteins and salts that enhance cross-linking reactions during phenol–formaldehyde cure. It would therefore be prudent to use whey permeate instead of pure lactose due to the much lower cost of the former. 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 a large number of samples to compensate for variations in veneer.

## ACKNOWLEDGMENTS

The authors would like to thank the Wisconsin Milk Marketing Board for funds to pursue the research work. We also wish to thank the Office of Research in Science and Technology, UALR, in the typing of this manuscript.

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