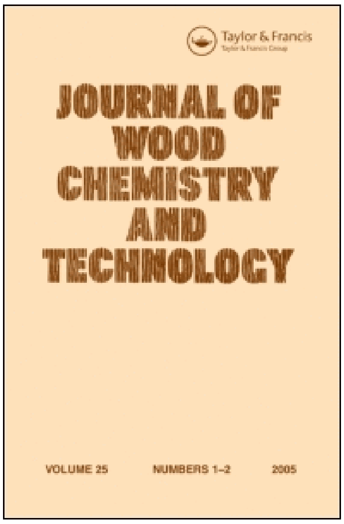

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APPLICATION OF MODIFIED LIGNOSULFONATES IN ADHESIVES FOR INSULATION BOARD MANUFACTURE BASED ON MINERAL WOOL

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Keywords: Lignosulfonates (SL), Ultrafiltration, Phenol-formaldehyde resins, Adhesives, Insulation boards, Mineral wool

ABSTRACT

Extensive laboratory investigations and mill scale trials confirmed the applicability of ultrafiltrated high molecular weight Ca-lignosulfonates in adhesive composition with phenolic resin for insulation board manufacture based on mineral wool. Insulation materials produced with adhesive components with a formulation of lignosulfonate/PF resin between 10/90 and 30/70 have appropriate technical and commercial properties.

INTRODUCTION

Relatively expensive phenol-formaldehyde (PF) resins have been used as binders in insulation board manufacture, for example in mineral wool products. The resin content in mineral fiber mats is between 1 - 5 %, mostly 3 % and it represents a considerable material cost. For this reason, many attempts have been made to replace a part of the PF resin with cheaper lignosulfonates.

Lignosulfonates are possible substitutes for conventional resins in wood adhesives. As a polyphenol, lignin contains reactive sites capable of condensation reactions with formaldehyde or methylol groups of phenol resols and intramolecular reactions leading to cross-linked structures. Owing to the ortho- and para positions of the aromatic rings, occupied to a large extent by $-OCH_3$ groups or propane side chains, its reactivity is reduced[1].

A comprehensive review of lignin applicability as coreactant in PF adhesives for wood composites production is given by Nimz[2], Ayla et al[3], Coughlin et al[4]. The influence of the molecular weight of lignins to the adhesive properties in PF/lignin mixtures has been reported by Lange et al[5]. According to Forss and Fuhrmann[6,7], the size of the lignin macromolecule is very important for the efficiency of lignin copolimerization with PF resins. The greater effectiveness of high molecular weight lignin is due to a higher level of crosslinking, which requires less phenol-formaldehyde for the formation of an insoluble copolymer than do low molecular weight lignin molecules. Condensates between smaller lignin molecules and phenol-formaldehyde cannot contribute to the three-dimensional network. A commercial resin based on this research - Karatex - has recently been marketed.

Lignin utilization in PF adhesives for insulation materials is also known. The procedure for alkali lignin application in adhesives for mineral wool is described by Sarjeant[8]. Commercial products based on urea modified alkali lignins, e.g., Reax[9], are already known. According to the procedure described by Zellar and Strauss[10], the binder composition for glass fiber wool comprises, in addition to a phenolic resol resin, animal bone glue, dicyandiamide, also a sulfite spent liquor.

In this paper, our experiences are presented of the application of ultrafiltrated high molecular weight Ca-lignosulfonates in *adhesives for mineral wool of eruptive stones origin. After investigations the condensation ability of different lignosulfonates with PF resin the binding properties of adhesive mixtures prepared on a laboratory scale were tested. The results were confirmed by industrial trials on insulation board production.*

EXPERIMENTAL

Materials and Methods

High molecular weight lignosulfonates (UFCaSL) were separated from Ca-bisulfite liquor by ultrafiltration techniques. The DDS UF system with membranes having a nominal molecular weight cutoff of 20.000 was used. The molecular weight distributions of the lignosulfonates were evaluated by gel permeation chromatography using Sephadex G-75 gel column (1,5 cm diam., 90 cm length) with 0,75 M NaCl as eluant at the flow rate 21 ml/h. Ca-lignosulfonates were transformed into sodium and ammonium lignosulfonates by treating spent sulfite liquor with Na_2SO_4 *and* $(NH_4)_2SO_4$*, respectively. According to the Westwaco procedure for alkali lignin[9] with urea modified calcium and ammonium lignosulfonates (*$UFCaSL_{mod.}$*,* $UFNH_4SL_{mod.}$*) were also prepared.*

A standard commercial PF resin adjusted for insulation materials based on mineral wool was used.

The adhesive mixtures were prepared by a simple blending of the PF resin with lignosulfonates. The pH value of the lignosulfonates was previously adjusted to 8,5 using NH_3*.*

Condensation abilities were determined by a modified Roffael's method[11]. The principle of this method is that reactive phenol resols are transformed by means of heating, into water insoluble condensates with crosslinked structures. The water solubility, detected by UV spectroscopy at 280 nm before and after thermal treatment, is a measure of the crosslinking or curing level.

The adhesive quality was quantified using a laboratory testing method based on the determination of the bonding properties of model specimens prepared from quartz sand impregnated with adhesive. After curing, the bending strength in the dry and wet state was me-

assured. The spraying of an adhesive onto mineral fibers is only possible in the phase of fibers formation from the melt at high temperature. A laboratory method is therefore recommended for an estimation of whether the adhesive quality justifies direct mill scale trials.

Industrial trials of insulation board manufacture

The insulation boards were produced from mineral wool obtained from the melts of eruptive stones, e.g., diabase. Thin fibers were formed from molten material on rotating spinning wheels by the cascade principle. The adhesives were prepared by homogenization of components in a reactor and, after dilution to the correct dry solids content, were sprayed onto the fibers in the phase of their formation. The adhesives were hardened in a blowing chamber at a temperature of 220 - 240°C. Boards of different densities and with various amounts of bonding agent were produced.

The insulation boards were tested according to DIN 18 165 standard requirements for delamination in the dry and wet state. A statistical analysis was used for delamination test results to determine if any statistically significant differences existed among the PF control and the adhesive mixtures data. The parametric analysis of variance which tests equality of mean values was performed[12].

RESULTS AND DISCUSSION

Properties of adhesive components and their mixtures

The molecular weight distribution of lignosulfonates is shown in Figure 1 and Table 1. It can be seen that about 67 % of ultrafiltrated lignosulfonates (UFNaSL) have a molecular mass greater than 5000.

One of the most important variables affecting the performance of board composites is the degree of adhesive cure. A resin with a high degree of cure forms a highly cross-linked structures with low water solubility. The condensation ability of adhesives is inversely correlated to their water solubility after thermal treatment.

TABLE 1: Molecular Weight Distribution of UFNaSL as Measured on a Sephadex G 75 Column

Proportion of UFNaSL with molecular weight % (w/w)	M_w
67 %	> 5.000
50 %	> 10.000
34 %	> 20.000
25 %	> 30.000
20 %	> 40.000

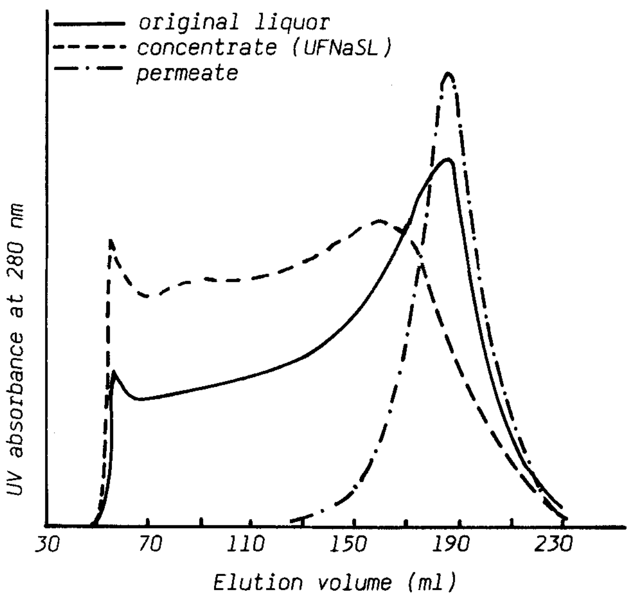

FIGURE 1 Sephadex G-75 gel chromatograms of lignosulfonates using 0,75 M NaCL as eluant.

The results of testing the condensation ability of pure PF resin and its mixtures with different weight proportions of UFNaSL as measured by water solubility at different pressing temperatures are shown in Fig. 2. We can state that the reaction temperature and the amount of UFNaSL significantly influence the solubility of cured adhesives. Higher addition of UFNaSL increases the water solubility of the copolymer, especially at a lower curing temperature. In view of these results, we decided to prepare and test the quality of adhesive mixtures with 20 % to maximal 65 % lignosulfonate.

According to the literature data[13], the curing properties depend to some extent on the spent sulphite liquor cooking base. The ammonium lignosulfonates (NH_4SL) in combination with an alkaline PF resin posses adhesive characteristics superior to those based on sodium (NaSL)-PF or calcium (CaSL)-PF resins. The higher reactivity of NH_4SL toward PF is assumed to be related to the ammonium lignosulfonate functionality itself. At temperatures above 170°C NH_4SL decomposes into lignosulfonic acid and ammonia gas, whereafter the lignosulfonic acid condenses and polymerizes, whereas CaSL and NaSL do not decompose and polymerize in the presence of lignocellulosic materials. In our investigation we compared adhesive mixtures using sodium, calcium and ammonium lignosulfonates. The adhesive properties are given in Table 2. The adhesive mixtures demonstrate infinite water dilutability. In order to ensure compatibility with lignosulfonates and to achieve good mixture stability, infinite water dilutability of the PF resin is required. The mixtures of PF resin with lignosulfonates display shorter curing times, especially those which include urea. The addition of UFCaSL at different pH values does not essentially lower the pH value of the mixture. A considerable lowering of the pH value of the mixture with $UFNH_4SL$ is characteristic. The latter is a consequence of the reaction between the ammonia ion and free formaldehyde present in the mixture and simultaneously liberation lignosulfonic acid[14].

The condensation abilities and bonding properties of adhesive mixtures (bending strength of model specimens) were evaluated in comparison with commercial PF resin and its mixture with lignin based product Reax. It can be seen from Fig. 3 that small additions

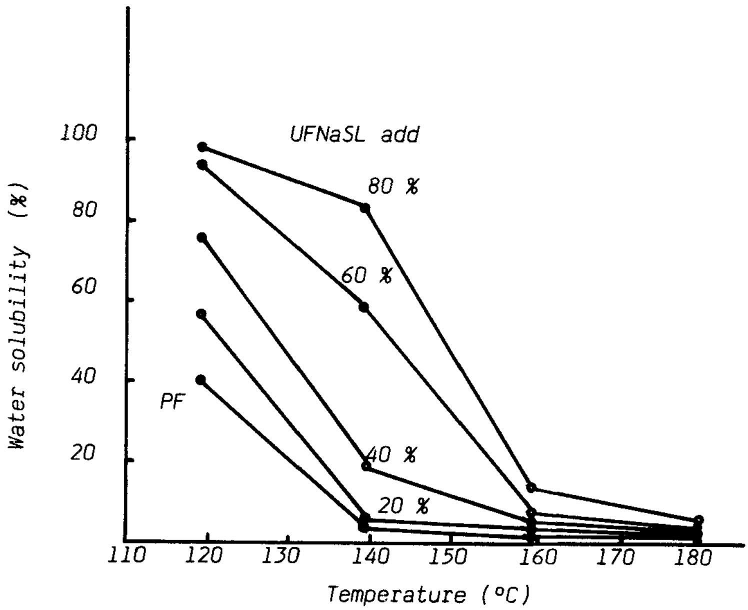

FIGURE 2 Condensation abilities of adhesive mixtures as measured by water solubility with different UFNaSL / PF resin ratios at different temperatures.

of UFCaSL and $UFNH_4SL$ as well as their urea modificates, have no major influence on the bending properties compared with the pure PF resin. Higher additions of lignosulfonates enhance water solubility and decrease the bending strength. At the same lignosulfonate to PF resin weight ratios (65 : 35) the urea modified lignosulfonates yielded bending strengths not distinctly different from those of the Reax, but nevertheless they did not reach the values obtained with pure PF resin.

The laboratory testing of the adhesive mixtures showed no significant differences in the application of different lignosulfonates. Small specimen laboratory tests were sometimes found to lack sufficient reality to commercial application. For this reason the

TABLE 2: Properties of Adhesive Mixtures at 40 % Solids

SL	pH	Weight ratio PF : SL : U	Mixture pH	"B" time at 130°C sec.
-	-	100	8,5	522
UFNaSL	9	80 : 20	8,3	-
UFCaSL	8,8	80 : 20	8,3	315
	8,5	60 : 40	8,0	136
	8,5	70 : 20 : 10	8,3	211
	2,8	80 : 20	8,3	313
	2,8	70 : 20 : 10	8,3	290
$UFCaSL_{mod.}$	3,6	80 : 20	8,4	228
	8,5	80 : 20	8,5	286
$UFNH_4SL$	9,0	80 : 20	4,9	476

SL = lignosulfonate

U = urea

Note: Water dilutability of the adhesives mixtures was infinite

TABLE 3: **Results of Industrial Insulation Boards Manufacture**

Density	Adhesive addition	Weight ratio	"B" time at 130°C	Delamination test			
				Dry	t-test	Wet	t-test
kg/m^3	%	PF : UFCaSL:U	sec	N/m^2	results	N/m^2	results
130	3	100	600	4200		4200	
130	3	90 : 10	370	4170	S	4180	S
130	3,5	100		4450		4430	
130	3,5	80 : 20	325	4330	S	4300	S_1
150	2,9	100		7250		7200	
150	2,9	70 : 30	310	6830	D	6440	D
180	3,5	100		10560		10500	
180	3,5	80 : 10 : 10	445	10360	S	10170	D
150	3	100		7250		7170	
150	3	70 : 20 : 10	310	7130	S	6950	D
180	3	100		11010		10450	
180	3	60 : 30 : 10	250	8890	D	8170	D

S = no significant differences at 0,05,

S_1 = no significant differences at 0,01

D = significant differences at 0,05

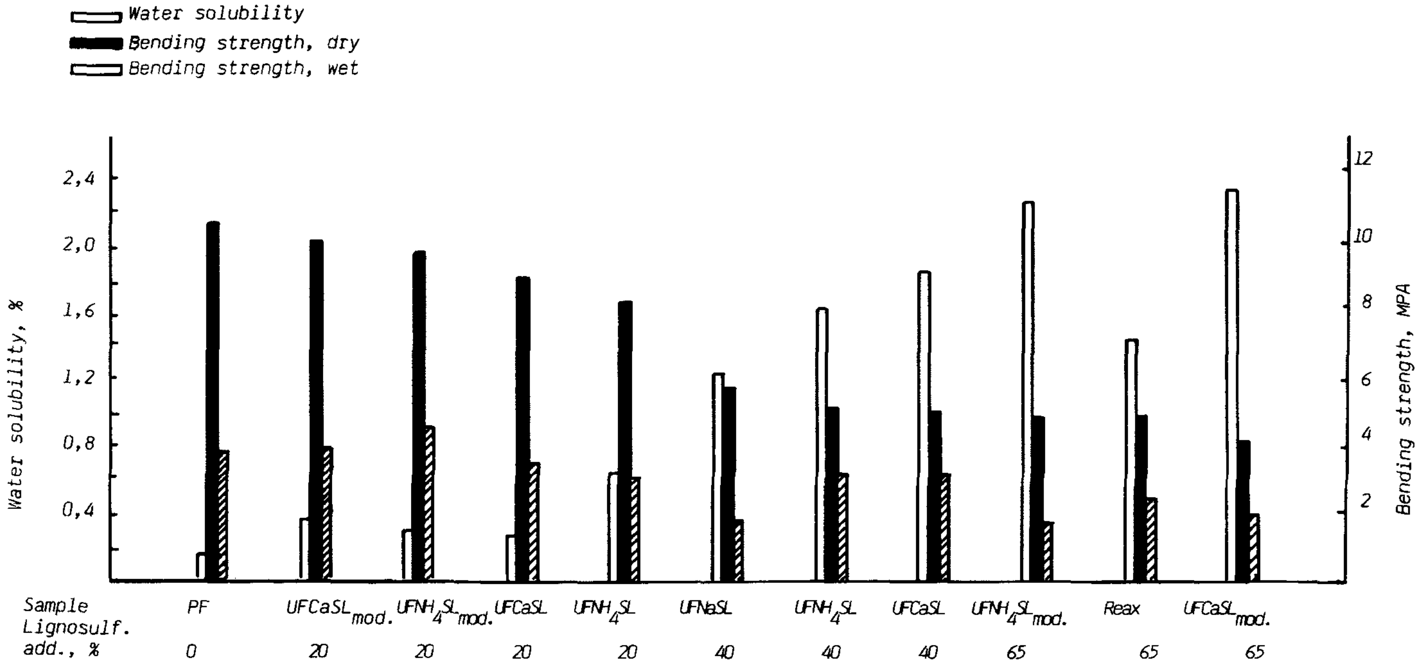

FIGURE 3 Bending strength and water solubility of adhesive mixtures with different lignosulfonates at different lignosulfonate / PF resin ratios.

industrial trials of insulation board manufacture with lignin based resins were performed. Ultrafiltrated calcium lignosulfonates which are most appropriate from the economic point of view were used.

The properties of industrial boards prepared with different PF : UFCaSL ratios in adhesive mixtures were compared with those manufactured with pure PF resin. In normal board production the urea as free - formaldehyde scavenger in amount about 10 parts by weight is added to the adhesive. Therefore some experiments using urea in adhesive formulation were included. The results in Table 3 show that at 20 % replacement of PF resin with UFCaSL board properties were equal to those made with pure resin, while at 30 % replacement, the quality obtained was slightly lower. These results, were quantified with a series of modified t-tests at 0,05 and 0,01 confidence levels respectively. The dry delamination values of adhesives with 10 % and 20 % UFCaSL were not significantly different in comparison with control PF resin. The wet delamination values of the adhesive with 20 % UFCaSL and control PF resin were significantly different at 0,05 level, but they were not different at 0,01 level. The adhesive with 30 % UFCaSL provided significantly lower delamination values in the dry and wet state. They nevertheless met the DIN standard requirements. The same is true of boards produced with urea included in the adhesive.

CONCLUSIONS

From these investigations it can be concluded that ultrafiltrated high molecular weight calcium lignosulfonates can be used as a component in mineral wool adhesives. Up to 30 % lignosulfonates may be included successfully in these adhesives. The experiments demonstrated that in spite of the shorter curing times of adhesive mixtures with lignosulfonates, their application in insulation materials production under conventional conditions is possible.

Full scale industrial application of 25 % UFCaSL in adhesive has been applied for more than two years in one of our insulation board mills.

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