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Modification of Lignins. I. Reaction of Lignins with Chlorophosphazenes

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ABSTRACT

Lignin is a potential raw material for several applications. The immediate future should result in the development of lignin modifications yielding new polymers with special properties such as flame and/or thermal resistance. In this report a new reaction of lignins with chlorophosphazenes is discussed. The effect of different types of lignin and chlorophosphazene oligomers on the properties of the reaction product was investigated. The reactions were found to result in products with flame as well as with a base and acid hydrolitic resistance.

Lignin is a potential raw material for several applications [1-5]. Lignin modifications are likely to be developed in the near future, resulting in new polymers with special properties such as a thermal or flame resistance. These new materials will meet the need for thermal and flame-resistant polymeric materials for special applications [1, 6, 7].

Using the aliphatic and phenolic hydroxyl groups of lignin as a basic lignin, modifications can be developed mainly by the condensation process [1, 3-5]. The reaction of lignin with phosphorus halides has resulted in the formation of biologically active and flame-resistant lignin derivatives [1, 8].

This report is part of lignin modification studies concerned with the reaction of lignins and chlorophosphazenes and the structure and properties of the products obtained.

EXPERIMENTAL

Materials

Commercial kraft lignin (Indulin AT, Westvaco Co., N. Charleston, South Carolina) and sodium ligninosulfonate (type Ultra B002, Rauma-Repola OY, Rauma, Finland) were used in the investigation. Phosnic 390 (hexachlorocyclotriphosphazene donated by IK Inabate Co., Nippon Fine Chemical Co., Japan, mp 112-113.5°C, IR P=N 1220 cm^{-1}, ^{31}P NMR -19.47) and a mixture of cyclic oligomers of chlorophosphazene [9] (mp 87-91°C, IR P=N 1295 cm^{-1}, 1218 cm^{-1}, ^{31}P NMR -19.57, +6.86) were used for reactions with lignins. Reagent grade dioxane was used as both the solvent and inert dispersion medium. Reagent grade n-propanol (n_D^{20} = 1.3850) and diethylamine (n_D^{20} = 1.3860) were used for modification of the standard products.

Methods for Reaction of Lignins with Chlorophosphazenes

Reaction of Kraft Lignin with Chlorophosphazenes

Method A$_1$. Kraft lignin (1.0 g) was dissolved in dioxane (100 mL) and a corresponding amount of pyridine was introduced as a hydrogen chloride acceptor. Chlorophosphazenes dissolved in dioxane (25 mL) were added dropwise during continuous agitation at 80°C for 15 min. The mixture was allowed to react at the boiling point for 3 h. The reaction mixture was then poured into ice water. The solid product was washed several times in 5% sodium dicarbonate solution and water to obtain a neutral reaction. It was centrifuged at 66.6 rps for 15 min. The residual product was dried at 60°C under reduced pressure.

Method B$_1$. Kraft lignin (1.0 g) was dissolved in dioxane (100 mL) under continuous agitation, and chlorophosphazenes oligomers (0.706 g, 6.086 × 10^{-3} mol) were added at 80°C. Pyridine (0.98 mL, 1.21 × 10^{-2} mol) dissolved in dioxane (25 mL) was then added dropwise at 80°C for 15 min. Then the temperature was increased to the boiling point and the mixture was allowed to react for 3 h. The reaction product was purified in the same way as in Method A_1 (Sample 9).

Reaction of Sodium Ligninosulfonate with Chlorophosphazenes

Method A_2. Sodium ligninosulfonate (1.0 g) was dispersed in dioxane (100 mL) and a corresponding amount of pyridine was introduced as a hydrogen chloride acceptor. Chlorophosphazenes dissolved in dioxane (25 mL) were added dropwise at 80°C during continuous agitation for 15 min. The mixture was allowed to react at the boiling point for 3 h. The reaction mixture was then poured into ice water. The solid product was washed several times in water and centrifuged at 66.6 rps for 15 min. The residual product was dried at 60°C under reduced pressure.

Method B_2. Sodium ligninosulfonate (1.0 g) was dispersed in dioxane (100 mL) under continuous agitation, and chlorophosphazene oligomers (0.498 g, 4.293×10^{-3} mol) were added at 80°C. Pyridine (0.69 mL, 8.53×10^{-3} mol) dissolved in dioxane (25 mL) was then added dropwise at 80°C for 15 min. The temperature was then raised to the boiling point and the mixture was allowed to react for 3 h. The reaction product was purified in the same way as in Method A_2 (Sample 10).

The reaction conditions used in these studies are shown in Table 1.

Modification of the Kraft Lignin-Chlorophosphazenes Reaction Product

Kraft lignin (1.0 g) was dissolved in dioxane (100 mL) and pyridine (1.96 mL, 2.42×10^{-2} mol) was introduced. Chlorophosphazene oligomers (1.412 g, 1.22×10^{-2} mol) dissolved in dioxane (25 mL) were added under continuous agitation at 80°C for 3 h. The reaction mixture was cooled to 60°C and pyridine (0.18 mL, 2.23×10^{-3} mol) was added for modification by n-propanol. After this, n-propanol (1.595 mL, 2.13×10^{-2} mol) or diethylamine (15.05 mL, 0.145 mol) dissolved in dioxane (25 mL) was added dropwise at 60°C for 15 min. The mixture was allowed to react at 60°C for 3 h. The solid reaction product was washed several times in dioxane and 5% sodium dicarbonate solution and water to obtain a neutral reaction. It was centrifuged at 66.6 rps for 15 min. The residual product was dried at 60°C under reduced pressure (Sample 11, a product modified by n-propanol; Sample 12, a product modified by diethylamine).

The phosphorus content of the lignin-chlorophosphazene reaction products was determined by the Püschell method and the chlorine content according to the Schëning method.

The products obtained and the raw materials were examined by infrared spectroscopy with a Specord 71IR using the KBr technique.

X-ray diffractograms were obtained by using an x-ray diffractometer of Drom-1 with a registration velocity of 2°/min.

The flammability of the reaction products was tested qualitatively

TABLE 1. The Conditions of Reaction between Lignins and Chlorophosphazenes[a]

Symbol of		Type of		Amount of	
Sample	Reaction system	Lignin	Chlorophosphazenes	Chlorophosphazenes $(\text{mol} \times 10^3)$	Pyridine $(\text{mol} \times 10^3)$
		Used in reaction			
1	A_1	Kraft	Mixture	3.052	6.091
2	A_1	Kraft	Mixture	6.104	12.182
3	A_1	Kraft	Mixture	12.208	24.364
4	A_2	Ligninosulfonate	Mixture	2.146	4.848
5	A_2	Ligninosulfonate	Mixture	4.292	9.696
6	A_2	Ligninosulfonate	Mixture	8.584	19.392
7	A_1	Kraft	Trimer	3.052	6.091
8	A_2	Ligninosulfonate	Trimer	2.146	4.848

[a] All reactions were carried out on kraft lignin or sodium ligninosulfonate (1.0 g).

by holding powdered material (50 mg) in a Bunsen flame for 5 s on a spatula.

The hydrolitic resistance of the product was investigated quantitatively in 0.4 N potassium hydroxide and 0.5 N sulfuric acid solutions by mixing powdered material (40 mg) in a suitable solution (20 mL) at 50 ± 0.1°C for 24 h. The hydrolitic resistance was determined by a titration method using sky-blue bromothymol.

RESULTS AND DISCUSSION

Modification of lignins by chlorophosphazenes seems to be a promising way of making new types of flame-resistant material with adequate thermostability.

Referring to data presented in Table 2, it should be noted that the substitution of chlorine in chlorophosphazene cycles was not complete

TABLE 2. Properties of the Products of Reaction between Lignins and Chlorophosphazenes

Symbol of sample	Yield of product[a] (g)	Color of solid product	Content of (%)		Infrared frequency of units (cm^{-1})	
			P	Cl	P=N	P–O–C
1	0.6043	Light brown	2.51	-	1275, 1225	1150[s], 1035
2	0.6452	Dark brown	2.27	-	1270, 1220	1160[s], 1035
3	1.0330	Gray-brown	6.76	1.38	1260, 1225[s]	1158, 1030
4	0.0718	Brown	0.80	1.31	1265, 1210	1158, 1030
5	0.5800	Brown	2.33	-	1260, 1200	1160[s], 1030
6	1.0032	Brown	2.55	0.44	1260, 1210	1155[s], 1030
7	0.6006	Black	1.20	-	1210	1025
8	0.0350	Light brown	1.01	-	1212	1165, 1030
9	1.4327	Gray-brown	2.12	0.67	1265, 1210	1150[s], 1030
10	0.0770	Brown	1.58	0.93	1260[s], 1210[s]	1030[s]
11	1.0970	Dark brown	5.82	1.22	1255, 1210	1160, 1030
12[b,c]	0.6120	Dark brown	7.42	1.00	1260, 1210	1150, 1035

[a] All reactions were carried out on kraft lignin or sodium ligninosulfonate (1 g).
[b] The absorption band at a frequency of 935 cm^{-1} is related to P–N–C.
[c] The nitrogen concentration was 5.27%.
[s] Slight.

TABLE 3. Flame Resistance of the Product of Reaction between Lignins and Chlorophosphazenes[a]

Symbol of sample	Flame resistance	Glow resistance
2	NF	NG
3	NF	NG
5	NF	SG
6	NF	NG
11	NF	NG
12	NF	NG
Kraft lignin	F	G
Sodium ligninosulfonate	NF+	G+

[a] F = flammable, NF = nonflammable, G = glowing, NG = nonglowing, SG = slight glowing, +sample burned by intensive glowing .

for the product formed in the reaction between lignins and chlorophosphazenes. After modification by n-propanol and diethylamine, somewhat higher substitution was observed. On the basis of the data in Table 2, it can also be stated that the increase in chlorophosphazenes concentration in the reaction environment resulted in an increase in the phosphorus content of the product formed. The highest content of phosphorus was obtained with the product (# 3) of the reaction between kraft lignin and chlorophosphazene oligomers. A suitable lower phosphorus content was obtained in the product derived from the reaction with sodium ligninosulfonate. This phenomenon is probably related, among other, to the type of reaction medium and the lower reactivity of sodium ligninosulfonate under varying conditions compared with kraft lignin dissolved in dioxane. Based on the results of the experiments, it can be concluded that the reactivity of kraft lignin and sodium ligninosulfonate was somewhat lower with reaction method B than with method A.

The results in Table 2, referring to a product formed in a reaction with hexachlorocyclotriphosphazene, show a lower reactivity for this type of oligomer compared with a mixture of cyclic oligomers. This phenomenon is confirmed by previous findings [10, 11].

Low chlorine concentration in a product may indicate incomplete substitution of chlorine in the phosphazene cycles. Modification by diethylamine was found to result in the highest phosphorus content. This phenomenon is probably related to the substitution of chlorine

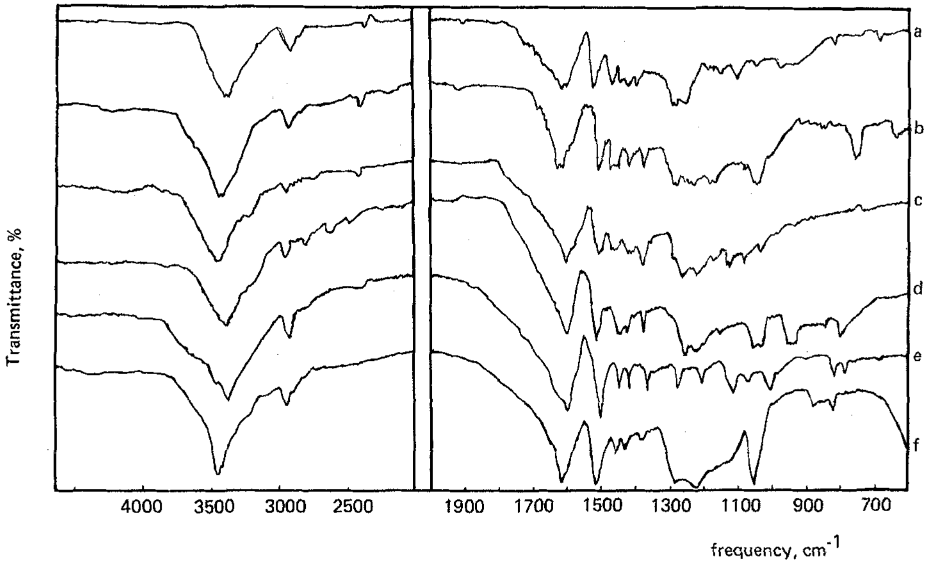

FIG. 1. Infrared spectra of the reaction product of: (a) kraft lignin with chlorophosphazene oligomers (#3), (b) sodium ligninosulfonate with chlorophosphazene oligomers (#6), and (c) kraft lignin-chlorophosphazene oligomers reaction product modified by n-propanol (#11), (d) kraft lignin-chlorophosphazene oligomers reaction product modified by diethylamine (#12), as well as of (e) kraft lignin and (f) sodium ligninosulfonate.

by diethylamine and the protection of phosphazene cycles against hydrolysis at the time of purification. The unmodified product was probably influenced by faster hydrolysis at the time of its purification, especially in the case of lower substitution [12].

Phosphazenylated lignins did not dissolve in typical solvents such as tetrahydrofurane, dioxane, benzene, and ethanol. Some swelling in dimethylsulfoxide was, however, observed. The ligninlike products modified by n-propanol and diethylamine were the same. These observations are consistent with the conclusion that the reaction products were cross-linked.

Table 3 contains a summary of quantitive tests of fire resistance. Pure kraft lignin ignited very easily and sustained a flame whereas a modified kraft lignin did not ignite under the same conditions. On the other hand, a pure sodium ligninosulfonate glowed very fast in these conditions, whereas a modified sodium ligninosulfonate was flame resistant and did not glow completely.

Infrared studies of the products formed in the reaction of lignins with chlorophosphazenes showed a small displacement at higher

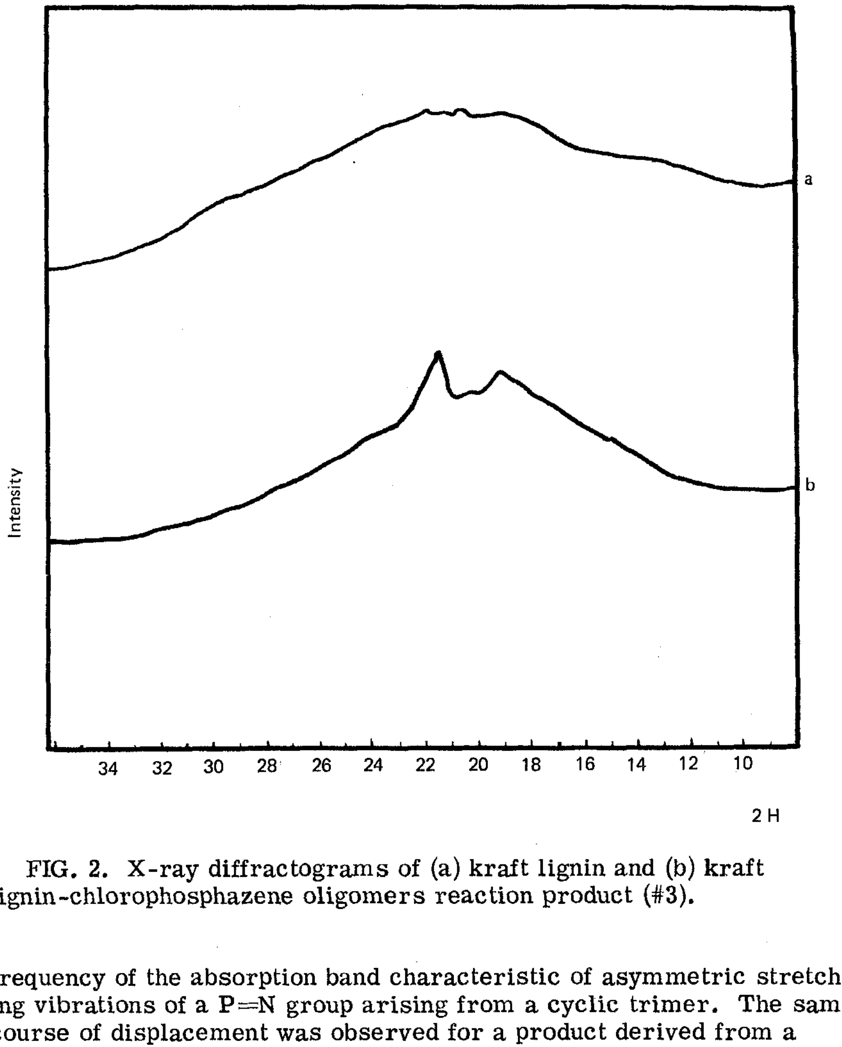

FIG. 2. X-ray diffractograms of (a) kraft lignin and (b) kraft lignin-chlorophosphazene oligomers reaction product (#3).

frequency of the absorption band characteristic of asymmetric stretching vibrations of a P=N group arising from a cyclic trimer. The same course of displacement was observed for a product derived from a mixture of cyclic oligomers of chlorophosphazene (Table 2, Fig. 1). Infrared spectra also showed a low intensity absorption band typical for the stretching vibrations of $P-O-C_{arom}$ in the frequency range 1165-1150 cm^{-1} and for $P-O-C_{aliph}$ in the range 1035-1030 cm^{-1}.

The x-ray diffractograms of the product from the reaction of kraft lignin with chlorophosphazenes showed a crystalline pattern, whereas the original kraft lignin showed a typical amorphous pattern. The difference in x-ray patterns between the raw material and the product

TABLE 4. Hydrolitic Resistance of the Lignin-Chlorophosphazene Reaction Products

Symbol of sample	Amount of potassium hydroxide (g) consumed by 1 g of a reaction product ($\times 10^3$)[a]
3	92.5
6	75.0
11	85.0
Kraft lignin	85.0
Sodium ligninosulfonate	85.0

[a] The investigations were made for 24 h at 50°C in 0.4 N potassium hydroxide solution.

derived from it is probably due to the formation of an initial crystalline structure in the product discussed (Fig. 2).

The hydrolytic resistance of modified lignins is an important property, especially for their utilization. The data concerned with the resistance of the lignin-chlorophosphazene reaction product expressed in terms of the amount of potassium hydroxide (g) consumed per 1 g of product in the hydrolysis process are presented in Table 4. The lignin's raw materials were also investigated.

Based on the results of 24 h experiments at 50°C, it can be concluded that products derived from the reaction of a kraft lignin and a sodium ligninosulfonate have roughly the same base resistance which also corresponded to this parameter characteristic for the lignins as raw materials used for the reaction discussed.

Analogous results were obtained for acid resistance. No difference was observed between the acid resistance of raw materials and the product derived from them.

The investigations in this report deal with new products with flame resistance and base and acid hydrolitic resistance formed in the reaction of lignins with chlorophosphazenes. Interesting thermal properties of the lignin-chlorophosphazene reaction products will be presented in the next report.

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