

New Aspects in Cationization of Lignocellulose Materials. IX. Flame Retardancy Effect of Modification with Nitrogen and Sulfur Containing Groups

IVAN ŠIMKOVIC, JAN PASTÝR, and MIROSLAV ANTAL,
Institute of Chemistry, Slovak Academy of Sciences, 84238 Bratislava, Czechoslovakia, KAROL BALOG and ŠTEFAN KOŠIK, *Fire Research Laboratory, 82104 Bratislava, Czechoslovakia,* and JAN PLAČEK, *Polymer Institute, Slovak Academy of Sciences, 84236 Bratislava, Czechoslovakia*

Synopsis

Lignocellulose materials were modified with 3-chlor-2-hydroxypropyltrimethylammoniumchloride, 1,3-bis(3-chlor-2-hydroxypropyl)imidazoliumhydrogensulphate, and 2-chlorethylsodiumsulphonate and the flame-retardant properties of materials obtained were studied. The flame-retardant effect was proved using the limited oxygen index (LOI) method and values up to 32.8 vol % of oxygen were determined. The LOI values were higher when the modification was done without using NaOH for activation, but in that case the alkylating groups were not chemically bonded to the material. The NaOH activation was necessary to obtain material with flame-retardant properties stable against washing. No synergistic effects were observed when the material was modified with both nitrogen- and sulfur-containing groups.

INTRODUCTION

Flame retardants used for modification of lignocellulose materials are mostly inorganic salts combined with pH regulators, colloids, and chelating compounds.¹ Several sulfur- and nitrogen-containing groups have been used to study flame retardation of cotton.²⁻⁵ 2-Chlorethanesulfonic acid and its sodium salt were used previously for modification to improve resistance to burning.⁶ All the mentioned compounds affect the thermal degradation acting as crosslinking, oxidizing, dehydrating, and hydrolyzing agents.

In the present paper we have examined the flammability of lignocellulosic materials modified with nitrogen- and sulfur-containing groups using the limiting oxygen index (LOI) test, elemental analysis, ESR, and infrared (IR) spectroscopy. We chose ion exchange groups for modification to find out how they act as flame-retardant agents.

EXPERIMENTAL

Materials. Beech or spruce boards (80 × 10 × 4 mm) and chromatographic paper (Whatman 1, 85 g/m²) were used as lignocellulose materials. Solutions containing from 3 to 50% of 3-chlor-2-hydroxypropyltrimethylammoniumchloride (CHMAC), 1,3-bis(3-chlor-2-hydroxypropyl)imidazolium-

TABLE I
Conditions of Individual Experiments and LOI Values
of Modified Materials

| Expt no. | Material | Activation | Alkylating agent | Conditions | Washing | LOI ^a |
|----------|-------------------|-----------------------|----------------------|------------|------------------|------------------|
| 1 | Paper | 5% NaOH | — ^b | RT | — | 27.8 |
| 2 | Paper | — | CHMAC ^c | 16 h/105°C | H ₂ O | 18.6 |
| 3 | Paper | 5% NaOH ^d | CHMAC ^c | 16 h/105°C | H ₂ O | 19.4 |
| 4 | Paper | — | BCHPIHS ^c | 16 h/105°C | — | 19.9 |
| 5 | Paper | 5% NaOH | BCHPIHS ^c | 16 h/105°C | H ₂ O | 19.2 |
| 6 | Wood | — | CHMAC ^c | 20 h/105°C | H ₂ O | 27.2 |
| 7 | Wood | 5% NaOH | CHMAC ^c | 20 h/105°C | H ₂ O | 25.0 |
| 8 | Wood | — | BCHPIHS ^c | 20 h/105°C | — | 32.8 |
| 9 | Wood | — | BCHPIHS ^e | 300 h/RT | — | 27.7 |
| 10 | Wood | — | BCHPIHS ^f | 20 h/105°C | — | 27.0 |
| 11 | Wood | — | BCHPIHS ^f | 300 h/RT | — | 24.2 |
| 12 | Wood | — | BCHPIHS ^f | 300 h/RT | H ₂ O | 22.4 |
| 13 | Wood | 10% NaOH ^d | BCHPIHS ^e | 24 h/105°C | H ₂ O | 31.5 |
| 14 | Wood | — | CES ^f | 24 h/105°C | — | 24.6 |
| 15 | Wood | — | CES ^c | 240 h/RT | — | 25.6 |
| 16 | Wood | — | CES ^c | 360 h/RT | — | 31.2 |
| 17 | Wood ^g | — | CES ^f | 240 h/RT | — | 28.2 |
| 18 | Wood ^h | — | BCHPIHS ^c | 240 h/RT | — | 23.3 |
| 19 | Wood | 10% NaOH | CES ⁱ | 3 h/80°C | H ₂ O | 25.5 |
| 20 | Wood | 20% NaOH | CES ⁱ | 3 h/80°C | H ₂ O | 30.4 |
| 21 | Wood | 30% NaOH | CES ⁱ | 3 h/80°C | H ₂ O | 33.5 |
| 22 | Wood | 17.5% NaOH | CHMAC ^j | 240 h/RT | H ₂ O | 25.1 |

^aVol% of oxygen.

^bDried at room temperature (RT) to constant weight.

^c50% w/w solution.

^dNaOH was added simultaneously with alkylating agent.

^e30% w/w solution.

^f5% w/w solution.

^gSample from expt 9 was used as substrate.

^hSample from expt 15 was used as substrate.

ⁱ3% w/w solution.

^jSample from expt 21 was used as substrate.

hydrogensulphate (BCHPIHS), and 2-chlorethylsodiumsulphonate (CES) were used as alkylating agents.

Preparation of Samples. The materials were activated for 30 min prior to modification with excess of 5–30% NaOH solution at room temperature. In some cases no activation was done. The samples were then immersed in the solution of alkylating agent in a steel autoclave. Table I summarizes details of the experimental conditions.

Methods. The LOI test was performed according to ASTM D-2863-1977. The ESR spectra were recorded on a Varian E-4 X-band spectrometer at 1 mW microwave power, 0.2 mT modulation amplitude, 0.3 s time constant, 337.7 mT field set, 9.51 GHz microwave frequency, 10 mT scan range, and 240 s scan time. The values of *g* factors were determined on a Bruker ER 200D SRC X-band spectrometer using 2,2,6,6-tetramethylpiperidine-*N*-oxide as an internal standard. The surface layer of burned wood boards were

isolated by using the 0.2 mm metal sieve. The IR spectra were measured in the form of KBr pellets on Perkin-Elmer 983 spectrometer. Elemental analysis was done on a Perkin-Elmer elemental analyzer (Model 240).

RESULTS AND DISCUSSION

Table I lists LOI values of materials studied. The unmodified paper, beech, and spruce boards gave LOI values 18.4, 23.1, and 23.5 vol % of oxygen, respectively. As can be seen in Table I, NaOH alone is a good flame-retarding agent. Paper activated with 5% NaOH solution and dried at room temperature gave LOI = 27.8 vol % of oxygen. When the sample was modified with CHMAC without activation with NaOH and washed with water, the LOI (18.6 vol% of oxygen) was low. The highest value of LOI obtained with CHMAC was observed when the solid NaOH was added to the solution of alkylating agent (Table I, experiment 3). When BCHPIHS was used for modification without activation with NaOH, the obtained LOI was 19.9 vol% of oxygen. In this case the sample was not washed with water after modification. In the presence of NaOH (activation, experiment 5) the LOI was 19.2 vol% of oxygen.

When wood boards were used as starting material, much higher values of LOI were obtained, probably because a higher quantity of alkylating agent was able to diffuse into the sample. The boards were tempered in excess of CHMAC (Table I) without activation with NaOH and washing with water. A LOI equal to 27.2 vol% of oxygen was obtained. In experiment 7 the sample was activated with NaOH, modified, and washed with water. The LOI value was lower, but the alkylating agent was chemically bonded and could not be washed out. The bifunctional agent (BCHPIHS) modified the material more effectively (expt 8) than CHMAC (expt 6). With decreasing temperature and time of modification the effect was decreased (expts 9–11). Experiments 8–11 were done without activation with NaOH and washing (LOI values from 24.0 to 32.8 vol% of oxygen). In expt 12 the material was washed with water after modification and the obtained LOI value was lower than for the unmodified material. When NaOH was added simultaneously with BCHPIHS, modified, and washed, a product with satisfactory flame-retardant properties resulted.

The use of CES for paper modification was not suitable because the product was soluble in water. When the boards were modified without activation with NaOH, the flame retardancy effect was dependent upon concentration of CES and diffusion time (expts 14–16). In expt 17 the material modified with BCHPIHS was used as substrate. The LOI value was slightly increased. When the product from expt 15 was used as substrate in expt 18 and modified with BCHPIHS, the LOI of product decreased to the value of unmodified material. The activation with NaOH increased the LOI values with increasing NaOH concentration. The alkylating agent was chemically bound to the wood and could not be washed out with water. In the last experiment, we used as a substrate the material produced in expt 21. After activation, modification, and washing with water, the LOI value decreased to 25.1 vol% of oxygen. We suppose that the synergistic effect was not observed because the alkylating agent was hydrolyzed with NaOH, and also interaction between cations and anions of functional groups occurred.

The yields of material obtained after modification were from 90 to 130% of the starting material, but no relation was observed between them and LOI values. When paper materials were modified, the yields were higher in comparison to modified wood. More material could be eluted during the modification of wood than from paper.

When we analyzed the surface layer of burned residue by IR spectrometry, the formation of known groups was confirmed: C=C (1600 and 1400 cm^{-1}) and C=O (1700 cm^{-1}).^{3,4} The bands of C—O at 900 cm^{-1} and of OH at 3500 cm^{-1} disappeared. This confirms the degradation of material to polycyclic aromatic char structures.⁷ Another band present in IR spectra was at 1160 cm^{-1} (COC stretching). We ascribe this band to oxygen remaining or buildup in the char structure. The presence of sulfur and nitrogen could not be proved in this way.

On the basis of elemental analysis of surface layer of burned residue of wood material (C = 55–82%, H = 1.9–3%, N = 0.2–3%, S = 0.7–3.5%), we suppose that nitrogen and sulfur were included in the polycyclic system. When paper was used as the substrate, the highest concentration of nitrogen in modified material (Table I, expt 4) was 2.9%, and the same concentration of this element was found in burned residue. During the burning of the paper the carbon content increased from 41 to 82% and hydrogen concentration decreased from 5.9 to 1.9%. It is known that the modification of cellulose with quaternary groups influences its thermal degradation mechanism toward increased char production and lowers the temperature at which thermal degradation starts.^{8,9} We believe that in this case nitrogen and sulfur reacted with the free radicals and became a part of the charcoal residue.

The concentration of free radicals in the residue after LOI measurements of unmodified wood was 6.26×10^{18} spins per gram. This value could not be determined in burned paper because the unmodified ash-free paper burns without forming a residue. Modified papers contained from 3 to 5×10^{18} of unpaired electrons per gram of residue. The residue from modified wood boards exhibited only slightly higher content of spins per gram ($8\text{--}12 \times 10^{18}$). The values of g factor were the same for unmodified and modified materials (from 2.0030 to 2.0032). From these results it could be concluded that the free radical concentration in burned residues was not affected by the modification. We believe this is due to secondary free radicals in residues which were formed by thermooxidation of the burned residues.

The advantage of lignocellulosic materials prepared by chemical modification with ion exchange groups is their stability against washing with water. We believe that this is a better way for preparation of materials with flame-retardant properties than the use of inorganic additives.¹⁰

CONCLUSIONS

Lignocellulosics modified with nitrogen- and sulfur-containing groups exhibited satisfactory flame-retardant properties. The alkylating groups were chemically bonded to the material when NaOH was used for activation. When alkylating groups diffused only into the material and samples were not activated, these groups could be washed out with water. The burned residues of modified lignocellulose materials consisted of condensed polycyclic aromatic

char containing nitrogen and sulfur. The content of free radicals in burned residues from LOI tests was not affected by the modification. The modification of the material with nitrogen- and sulfur-containing groups was not accompanied by synergistic effects.

References

1. *Am. Dyestuff Rep.*, **74**, 13 (1985).
2. L. H. Chance, *J. Appl. Polym. Sci.*, **26**, 2959 (1981).
3. N. Inagaki and K. Katsuoka, *J. Polym. Sci., Polym. Chem. Ed.*, **18**, 441 (1980).
4. K. Katsuoka and N. Inagaki, *J. Appl. Polym. Sci.*, **22**, 679 (1978).
5. N. Inagaki and K. Katsuoka, *J. Polym. Sci., Polym. Chem. Ed.*, **16**, 2771 (1978).
6. J. D. Guthrie, L. H. Chance, and C. L. Hoffpauir, U.S. Pat. 2,681,846 (1954).
7. Y. Sekiguchi and F. Shafizadeh, *J. Appl. Polym. Sci.*, **29**, 1267 (1984).
8. I. Šimkovic, M. Antal, V. Mihálov, J. Königstein, and M. M. Micko, *J. Appl. Polym. Sci.*, **30**, 4707 (1985).
9. I. Šimkovic, M. Antal, K. Balog, Š. Košík, and J. Plaček, *J. Appl. Polym. Sci.*, **30**, 4713 (1985).
10. S. L. LeVan, in *The Chemistry of Solid Wood*, R. M. Rowell, Ed., Am. Chem. Soc., Washington, DC, 1984, Chap. 14.

Received November 18, 1986

Accepted January 20, 1987