

Flame Retardancy Effect of Crosslinking of Lignocellulose Materials

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Synopsis

Dynamic and isothermal thermogravimetry (TG) was used for the study of flame retardancy effects caused by crosslinking of lignocellulose materials. This effect was also checked with the limited oxygen index (LOI) method. It was found that dynamic TG measurements run to 400°C could indicate the decrease of flame retardancy effect when lower residues are observed for samples measured in oxidative in comparison to inert environments. The isothermal TG data of initial reactions are not suitable for the prediction of flame retardancy effects. Epichlorhydrin (E) is a suitable chemical for the flame retardancy of wood. The addition of polyethyleneimine (PEI) decreases the flame retardancy of wood. On the other hand xylan crosslinked with E gives lower LOI values than the xylan crosslinked in the presence of PEI.

INTRODUCTION

In our previous study we showed the evident difference in behavior of wood during the thermal degradation in a nitrogen and oxygen environment.¹ In the present work we have used wood and xylan and their crosslinked derivatives to find out how they act in the presence of oxygen during thermolysis. We have again used dynamic and isothermal TG measurements for these purposes. Additionally, limiting oxygen index (LOI) values of the same samples were measured to find out how the TG results relate with flame retardancy.

EXPERIMENTAL

Materials. Beech sawdust, (4-*O*-methyl-*D*-glucurono)-*D*-xylan in H⁺ and Na⁺ forms were characterized previously.^{2,3}

Methods. Thermogravimetric measurements were performed on a TGS-1 (Perkin-Elmer) device in static nitrogen or oxygen atmosphere as described previously.⁴ The LOI tests were performed on Stanton-Redcroft apparatus at 23°C modified with horizontal adapter and a 15 × 1 cm holder. The samples were conditioned for 24 h at 23°C at 60% humidity prior to the LOI measurements. Each sample was freely poured on the horizontal holder where it formed a 8-mm thin layer. The material was switched on with a heating spiral tempered

TABLE I
Results of Dynamic TG Measurements (wt. %) and LOI Values of Lignocellulose Materials

Sample	Atmosphere	Temperature (°C)								LOI ^a
		105	250	275	300	325	350	375	400	
XH ⁺ (1)	Nitrogen	96.6	84.4	58.0	34.9	27.1	21.4	17.7	14.3	
	Oxygen	96.0	82.7	56.1	36.0	28.2	23.0	19.6	16.2	
XNa ⁺ (2)	Nitrogen	96.3	91.4	75.3	48.6	37.6	33.8	31.1	29.1	22.9
	Oxygen	96.1	91.2	76.4	48.8	38.1	34.4	32.0	29.7	
X-E (3)	Nitrogen	95.5	92.0	85.7	71.5	57.0	45.4	38.0	33.0	22.4
	Oxygen	98.2	65.3	61.4	53.1	44.0	35.8	30.0	26.5	
X-E-PEI (4)	Nitrogen	92.4	79.6	67.9	60.2	55.1	50.2	46.7	44.0	30.5
	Oxygen	94.3	80.3	68.5	60.7	56.0	51.1	47.6	44.7	
BS-E (5)	Nitrogen	94.6	87.4	81.8	73.4	63.7	55.6	50.3	46.7	35.8
	Oxygen	93.5	84.6	77.6	69.4	60.1	53.8	50.4	48.7	
BS-E-PEI (6)	Nitrogen	95.3	91.2	86.4	74.8	61.8	53.3	48.6	45.1	24.7
	Oxygen	95.9	90.8	85.4	73.2	60.5	52.3	47.8	44.1	

^a Vol. % of oxygen. XH⁺—(4-*O*-methyl-*D*-glucurono)-*D*-xylan in H⁺ form. XNa⁺—(4-*O*-methyl-*D*-glucurono)-*D*-xylan in Na⁺ form. X-E—(4-*O*-methyl-*D*-glucurono)-*D*-xylan crosslinked with epichlorhydrin. X-E-PEI—(4-*O*-methyl-*D*-glucurono)-*D*-xylan crosslinked with epichlorhydrin in the presence of polyethyleneimine. BS-E beech sawdust crosslinked with epichlorhydrin. BS-E-PEI—beech sawdust crosslinked with epichlorhydrin in the presence of polyethyleneimine.

to 950–1000°C. The Ni-Cr-Ni thermocouples were used for measuring the temperatures of burning. All the other methods were described previously.²

Preparation of samples. (4-*O*-Methyl-*D*-glucurono)-*D*-xylan in Na⁺ form (sample 2, 1.8 g) was mixed with water (7.2 mL), epichlorhydrin (7.2 mL, Fluka), and 2.3 g of NaOH and stirred for 4 h at 20°C. The sample was then diluted with water, neutralized with 6 *M* acetic acid overnight, and dewatered in acetone overnight. The sample was dried at 20°C and subsequently at 105°C for 8 h. The weight of product was 3.7 g (sample 3, 2.0% of ash).

Sample 4 was prepared as described previously.⁵ Thus, 2 g of polyethyleneimine (50% water solution, Fluka) was mixed with 7 mL of water and stirred until a homogeneous solution formed. Then 2 g of sample 2 was added, and after stirring NaOH (8 mL, 25% conc.) and epichlorhydrin (8 mL) were added. The solution was stirred for 1 h at 50°C and subsequently washed with water and dried (3 g of sample; 8.5% nitrogen; 0.24% of ash).

Beech sawdust (6.7 g) was mixed with 27 mL of water, 8.6 g NaOH, and 27 mL of epichlorhydrin. The sample was stirred for 4 h at 20°C. After washing with water till neutral reaction on phenolphthalein and oven drying (8 h/105°C) we obtained sample 5 (8.4 g, 8.1% of ash).

Beech sawdust (sample 6, 3.1 g) was mixed with polyethyleneimine (50% water solution, 3.1 g) and 7 mL of water. Then 8 mL of 25% water solution of NaOH (319.5 g/L) and 8 mL of epichlorhydrin was added. The sample was stirred for 1 h at 50°C. The sample was then washed with water, acetone, and oven-dried (8 h/105°C; 6.2 g of 6; 5.4% nitrogen; 0.45% ash).

RESULTS AND DISCUSSION

The results of dynamic TG measurements run on xylans and modified lignocellulose materials are listed in Table I. (4-*O*-Methyl-*D*-glucurono)-*D*-xylan

in H^+ form (sample 1) was degraded much quicker in the inert atmosphere in comparison to reduced xylan.⁶ Also the Na^+ form of (4-*O*-methyl-*D*-glucurono)-*D*-xylan (sample 2) was degraded faster than the reduced xylan. This is because of the presence of hemiacetal group in samples 1 and 2, which is probably the most reactive one in these samples. The greater weights of residues of the Na^+ form (sample 2) in comparison to H^+ form (sample 1) could be due to the elimination of the autohydrolysis effect on sample 2. The crosslinked (4-*O*-methyl-*D*-glucurono)-*D*-xylan (sample 3) is more stable in nitrogen atmosphere than samples 1 and 2 as well as the reduced (4-*O*-methyl-*D*-glucurono)-*D*-xylan. This could be interpreted with the theory that the crosslinked polysaccharide contains less hydroxyl groups that could undergo dehydration. The xylan crosslinked in the presence of polyethyleneimine (PEI) with epichlorhydrin (sample 4) is less thermally stable in the inert atmosphere than sample 3. This is probably caused by the fact that in sample 4 less polysaccharide is crosslinked together, and instead some xylan molecules are bounded through epichlorhydrin with polyethyleneimine. The synthetic polymer is probably less stable than (4-*O*-methyl-*D*-glucurono)-*D*-xylan. The beech sawdust run dynamically in inert atmosphere is thermally more stable to 325°C than sample 5 crosslinked with epichlorhydrin.¹ It could be due to the fact that the material was modified only on the surface and not homogeneously through the whole sample. The beech sawdust crosslinked with epichlorhydrin in the presence of PEI (sample 6) exhibited a similar course of dynamic TG curve in nitrogen environment than sample 5.

The results of dynamic TG measurements in oxygen atmosphere (Table I) show that the effect of oxygen on the course of degradation of samples 1 and 2 is negligible. While the thermooxidative effect on beech sawdust was evident,¹ the xylan samples (1 and 2) are stable against thermooxidation and exhibit the same cause of dynamic TG curves in inert and oxidative environments. It could be expected that the native hemicelluloses are more thermally labile than the isolated ones and also that the wood components trapped in the cell wall act differently than the isolated ones. So it is hard to conclude if the thermooxidation of wood lignocellulose material is caused by the hemicellulose component. The epichlorhydrin-crosslinked xylan (sample 3) exhibits a strong thermooxidative effect at 250°C (26.7% of difference between the residues obtained in inert and oxidative atmospheres). This effect decreases gradually to 6.5% to 400°C. The other xylan sample (4) crosslinked with epichlorhydrin in the presence of PEI is more stable against thermooxidation than sample 3. The same thing holds also for the crosslinked sawdust samples 5 and 6. They are exhibiting higher residues in oxygen atmosphere at temperatures higher than 300°C than TMAHP-sawdust in $H_2PO_4^-$ form, the most stable sample against thermooxidation from all analyzed cycles.¹

The results of isothermal TG measurements are listed in Table II. All the rate constants fit the first order with regression coefficients $R = 0.95-0.99$. They are considered as the overall rate constants of the initial reactions taking place in the material. The rate constants for (4-*O*-methyl-*D*-glucurono)-*D*-xylan in H^+ form (sample 1) were the highest ones measured in the inert environment. Both forms of xylan (samples 1 and 2) exhibited higher rate constants than reduced xylan.⁶ While the initial rate of degradation of sample 3 is higher than that of sample 2 but lower than sample 1, its course of dynamic

TABLE II
 Values of Rate Constants (min^{-1}) and Activation Energies (kJ/mol) of Thermolysis and
 Thermooxidation of Lignocellulose Materials

Sample	Atmosphere	Temperature ($^{\circ}\text{C}$)					Activation energy
		260	270	280	290	300	
XH ⁺ (1)	Nitrogen	0.1519	0.2435	0.4189	0.7690	0.9798	124.0
	Oxygen	0.2438	0.3460	0.6168	0.8885	1.1485	102.8
XNa ⁺ (2)	Nitrogen	0.0043	0.0790	0.1938	0.2181	0.5900	159.0
	Oxygen	0.0395	0.1347	0.2147	0.4427	2.1577	232.9
X-E (3)	Nitrogen	0.0174	0.0249	0.0542	0.0704	0.1018	116.4
	Oxygen	0.0277	0.0458	0.0677	0.0894	0.1721	109.7
X-E-PEI (4)	Nitrogen	0.0048	0.1514	0.2741	0.4470	0.7590	137.7
	Oxygen	0.0670	0.1224	0.2913	0.4058	0.8669	160.5
BS-E (5)	Nitrogen	0.0034	0.0121	0.0302	0.1452	0.2633	285.9
	Oxygen	0.0395	0.0661	0.1265	0.2448	0.3178	139.3
BS-E-PEI (6)	Nitrogen	0.0139	0.0293	0.0576	0.1597	0.2217	183.8
	Oxygen	0.0188	0.0312	0.0841	0.1310	0.2052	158.1

TG curve in the inert environment exhibits greater residue during the whole temperature interval than those of samples 1 and 2. The activation energy of the degradation process of sample 3 is the lowest one from all obtained thermolysis values. Sample 4 has higher rate constants than 3 as well as the value of the activation energy. The degradation of xylan crosslinked with epichlorhydrin (sample 3) seems to be more complex than that of samples 1 and 2. The xylan crosslinked with epichlorhydrin in the presence of PEI (sample 4) has lower rate constants and higher activation energies of thermolysis than sample 3. According to the rate constants, crosslinked sawdust is thermolyzed with higher initial rate than unmodified sawdust.¹ This could be because E and PEI could not penetrate through the wood cell wall material in the same way as for xylan. The increased activation energy could be due to modification of lignin. The thermal stability of the samples increases with the sequence: 3 < 1 < 4 < 2 < 6 < 5. The rate constants obtained in an oxygen environment are higher while the activation energies lower than it was observed in the inert atmosphere. The exception is sample 2, which gave the greatest value of activation energy for thermooxidation. The difference between the values obtained in inert and oxidative conditions is smallest for the sample that is most stable against thermooxidation. From the values of activation energy the thermooxidative stability increases in the sequence: 5 < 6 < 4 < 1 < 3 < 2.

The complexity of the process is confirmed when we compare the obtained results with LOI values. (4-*O*-Methyl-*D*-glucurono)-*D*-xylan in H⁺ form (sample 1) gives the lowest LOI value of 17.6 vol. % of oxygen. This is lower than the value obtained for the cellulose sheet of paper.⁷ The Na⁺ form of xylan (sample 2) has a higher value of LOI (22.9 vol. % of oxygen) because of the presence of inorganic elements. After the crosslinking with epichlorhydrin the LOI drops slightly (22.4 vol. % of oxygen for sample 3). It is concluded that no retardancy effect was observed after crosslinking modification of xylan. A much better result was obtained with xylan crosslinked in the presence of PEI (4, LOI = 30.5 vol. % of oxygen). The effect of crosslinking on flame

retardancy observed on beech sawdust was opposite to that of samples 3 and 4. Sawdust sample crosslinked with epichlorhydrin (sample 5) had LOI = 35.8 vol. % of oxygen while the BS-E-PEI sample (6) had LOI = 24.7 vol. % of oxygen. The LOI of unmodified beech boards is 23.1% of oxygen.⁷ The lower LOI value of 6 in comparison to 5 is probably again because the more bulky PEI could not diffuse into the wood material while epichlorhydrin could be more effective because the smaller dimensions of this molecule. So we can make the following sequence of samples according to their increasing LOI: $1 < 3 < 2 < 6 < 4 < 5$.

When we compare the TG results with the LOI values (Table I), we can say that while the dynamic TG is giving small indications about the flame retardancy effect, the isothermal TG is unsuitable for this purpose. It could be because the initial reactions of the thermal degradation are taking place at much lower temperatures and are not the determining ones for the flame retardancy effect. The temperature of the flames of studied samples were in the range 400–1100°C. It is problematical to use the isothermal TG for the study of lignocellulose materials at this temperature interval.

CONCLUSIONS

The results of dynamic TG measurements measured to 400°C in inert and oxidative environments could indicate the possible flame retardancy effect. On the other hand the isothermal TG data for the initial processes could not be used for the prediction of flame retardancy properties of lignocellulose materials. This is because the temperature of these is much lower in comparison to the temperatures of the flames (400–1100°C). PEI is not a suitable flame retardancy component for wood material but could be effective when crosslinked with xylan. On the other hand epichlorhydrin could work as an effective flame retardant for wood.

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