THERMOGRAVIMETRIC ANALYSIS OF FIRE RETARDANT TREATED PARTICLEBOARDS

P. S. Karastergiou - J. L. Philippou

Abstract

In this work the thermogravimetric analysis (TGA) of particleboards treated with fire retardants (waterglass, ammonium sulfate, ammonium hydrogen phosphate and a mixture of chemicals containing ammonium sulfate, ammonium hydrogen phosphate, borax and boric acid) was studied. The TGA showed that fire retardants altered the reaction of thermal decomposition of particleboards. More specifically, retardant chemicals altered the pyrolysis of particleboards, increasing the amount of char residuals and reducing the amount of volatile, combustible vapors. In the fire retardant treated particleboards thermal decomposition started at lower temperatures. The type of fire retardant and the level of the application affected thermal decomposition.

Key words: fire-retardants, particleboard, thermogravimetric analysis

Introduction and Survey of Literature

Thermal degradation and burning of wood and wood products is the result of the various chemical reactions of its components [6, 7, 9,13, 15, 17]. Wood burns primarily because the cellulose and hemicellulose polymers undergo pyrolytic and oxidative reactions with increasing temperature, giving off flammable gases. The lignin component, being more thermally stable, contributes more to char formation than does cellulose and hemicellulose. Increased char formation reduces flammable gas formation and helps insulate wood from further thermal degradation [7, 9, 11, 13, 15, 17]. The main pyrolysis of wood would start at temperatures above 250 °C and finish below 500 °C. Cellulose, the main component of wood, generates volatiles in the temperature range from 310 to 380 °C [11, 13, 14, 17].

To increase its resistance to fire wood is treated with fire retardant chemicals. These chemicals according to the 'chemical theory' [7, 13] alter the decomposition reactions of wood components in different ways depending on the type and chemistry of the retardant [7, 12, 13]. The changes in the thermal reactions of wood and wood products caused by fire

retardants can be studied by various physicochemical methods [1, 7, 12, 13]. Thermogravimetric analysis (TGA) gives very good indication of the overall results of such chemical changes [6, 7, 12, 13, 18].

Thermogravimetric analysis involves weighing a sample while it is exposed to heat. The chief use of this technique has been to study the thermal decomposition of polymeric materials and to accumulate kinetic informations about such decomposition [7]. The degradation of the structural components of wood is accomponied by the production of gaseous and liquid products and char. The progress in the production of gases and the non-volatiled products can be recorded by thermogravimetric analysis [13]. Weight loss is recorded as a function of time and temperature. In isothermal TG, the change in weight of the sample is recorded as a function of time as the temperature remains constant. In dynamic or nonisothermal thermogravimetry, the change in weight is a function of both temperature and time as the temperature is raised at a given heating rate [7].

YunChu, H., et. al [18], used thermographic curves of Chinese fir wood untreated and fire retardant treated, which were analysed by the TG-DAT simultaneous method and by the thermokinetic method to obtain thermokinetic parameters of different phases during wood pyrolysis. It was found that the activation energy reduced in the drying phase, and the activation energy in both the charring phase and the calcining phase was different for different fire retardants used.

Fojutowski, A., et. al [1], treated samples of Scots pine and beech wood with various fire retardants containing inorganic salts. The TG results showed that some compounds catalyse thermal decomposition of wood.

Lieu, J., et. al [8], used hermogravimetric analysis in combination with oxygen index measurements, toxicity measurements and nitrous oxide determination, in order to determine the effectiveness of various fire retardants to different wood species.

Kosik, M, et. al [5], used thermogravimetric methods on wood specimens of Norway spruce and Populus 'Marilandica' impregnated with aqueous solutions of fluoborate salts of NH_4, Mg, Zn and Ni. The most effective retardant was the complex NH_4 salt which also showed the highest temperature of active thermal decomposition (300-400 °C).

Simkovic, I., et. al [16], used TG and DSC analysis in lignocellulose materials that were activated with concentrated acids and subsequently modified with sulphur containing inorganic salts. The analysis indicated that the sulphur containing compounds were gasified at temperatures close to 200 °C and were not incorporated in the residue.

Miyafuji, H., et. al [9], in TG curves of the various ternary $Si0_2$-P_20_5-B_20_3 composites, showed that these composites are all shifted to the lower temperature for flaming with residues after flaming, compared with untreated wood.

Miyafuji, H. and Saka, S. [10], used TG analysis on wood treated with several $Ti0_2$ components and found higher residues after flaming at 370°C than the untreated ones.

Panayotov, P. [12], compared the thermogravimetric analytical data of fir wood and wood treated with three commercial fire retardants containing nitrogen, phosphorus or cloride. He found that the modified wood lost less of its mass than the natural fir wood, and consequently it was more resistant to thermal destruction. He also observed in the thermogram of the

modified wood that the rate of formation of the volatiled products reaches its maximum at a lower temperature compared with natural fir wood.

Osvald, A. and Reh, R. [11], and Reh, R. et. al [14], used TG analysis in particleboards treated with $NH_4H_2P0_4$. Weight loss of the particleboards decreased with increasing level of the retardant application and this was evident in the whole temperature interval. The reason was probably the begining of the endothermical degradation of the retatdant used connected with the releasing H_20 and NH_3.

Ishihara, S. and Kawai, S., [2], used TG analysis in order to examine the fire endurance of carbon-material overlaid particleboards.

Vovelle, C, et al, [17], compared the thermal stability of painted and unpainted particleboards by means of thermogravimetric analysis. Thermal degradation of particleboards started around 250 °C and the mass loss rate reaches maximun for a temperature close to 300 °C. This maximum corresponds to the degradation of cellulose. For all painted particleboards the beginning of mass loss is observed at a higher temperature, demonstrating that paints are more stable than wood. In the painted particleboards also, only a fraction of the initial mass of paint was gasified and the proportion of solid residue remaining at the end of the reaction could be as high as 70 %.

The aim of the work discussed in this presentation was to study the overall effect of various fire retardant chemicals on the thermal decomposition of particleboards using thermogravimetric analysis.

Materials and methods

One-layer laboratory particleboards were made using various fire retardants, as shown in Table 1.

Table 1 Variables of the materials used

Particleboard code	Fire retardant used
A	-
B	-
C (control)	-
D	Waterglass
E	"
F	Ammonium Sulfate
G	Ammonium hydrogen Phoshate
H	Ammonium Sulfate + Ammonium hydrogen Phoshate + Borax + + Boric acid

The boards were manufactured using urea-formaldehyde resin (7 % dry basis) and had a density of about 0,700 gr/cm^3. Also some UF-bonded commercial particleboards (of the same

density) were used to study their behaviour to heat (Table 1, codes A and B). In the case of the laboratory boards (Table 1, codes D, E, F, G and H), the fire retardants were sprayed onto the wood particles before the application of the glue. In this case, four different types of fire retardants were used:

- Waterglass, in percentage level of dry chemical per dry weight of wood particles 10% (code D) and 20 % (code E),
- Ammonium Sulfate, in percentage level of dry chemical per dry weight of wood particles 15 %(code F),
- Ammonium hydrogen Phosphate, in percentage level of dry chemical per dry weight of wood particles 15 % (code G), and
- Mixture of chemical containing Ammonium Sulfate, Ammonium hydrogen Phosphate with borax and boric acid (1:6:1:2, per weight correspondigly), in percentage level of dry chemicals per dry weight of wood particles 15 % (code H).

For the thermal analysis of the above materials, the system Mettler TA4000 with cells TG-50 was used in the temperature range from 30 up to 500 °C. Air, in a flowing rate of 200 ml/min, was used to remove the volatile gases from the samples. The temperature was raised in a rate of 20 °C/min. 10 mg of each meterial was tested. Weight gain (TG curves) and rate of mass loss (DTG curves) of the material were determined. The material for the analyses was granulated in a sample mill in order to obtain maximum diameter of 1 mm and screened in a laboratory test sieve (BS 410/1986) with apertures of 850 μιη (mesh S/steel).

Results and discussion

The tliennoanalytical data of all the materials tested are shown in Table 2 and in Figures 1-3.

From Table 1 and Figures 1-3 we can see that the thermal decomposition of all the tested materials follows three thermogravimetric regions. In the first region (30 °C - 124 °C) there is a small peak due mainly to loss of absorbed water. In the second region (125 °C - 405 °C) formation of volatile combustible compounds and high loss of weight take place. In the third thermogravimetric region (378 °C - 492 °C) formation of char and loss of gases take place. We can also see that the fire retardant treatments increased the resistance of particleboards to thermal degradation, altering their pyrolysis route and increasing the amount of char produced. In all cases fire retardants reduced substantially the rate of weight loss (formation of volatile combustible compounds) and lowered the temperature at which the peak in the rate of volatiles formation occurs. The effect is different for each type of retardant.

Figure 1 shows the TG and DTG of the untreated boards (commercial A and B and laboratory C). The first loss of weight of the untreated boards took place in the region between 30-123 °C with the peak at about 51 °C, the second between 125-396 °C with the peak at about 333 °C, and the third above 390 °C, with the peak at about 470 °C.

The weight loss of the boards was 5.349, 4.712 and 4.932 % respectively for A, B and C boards (see Table 2). The small difference seen in the three untreated boards is probably due to different wood species and manufacturing conditions used to manufacture the boards, indicating the importance of the type of material to fire behavior.

Table 2 Thermoanalytical data of the materials tested.

Name code *(mg)*	**Initial sample mass** ℃	**Temperature range** ℃	**Temperature peak** %	**Mass loss e mass** *(%)*	**Residue sampl**
A	10.020	32-114 125-396 397-492	55.7 335.7 466.3	5.97 61.33 25.24	5.349
B	10.009	30-123 191-389 390-492	51 331 447	5.35 64.02 25.14	4.712
C (control)	10.017	30-124 125-391 392-492	53.3 331 464	5.67 63.14 24.08	4.932
D	10.089	30-158 159-377 378-492	51 321 431.3	6.11 54.61 28.35	8.881
E	10.045	30-144 145-384 385-492 30-132	53.3 312.3 433.7 51	5.47 53.57 27.18 5.54	10.732
F	10.081	133-405 406-492	289 489	62.10 17.75	12.251
G	10.049	30-144 145-396 397-^492	53.3 296 487.3	5.35 51.44 14.39	26.749
H	10.043	32-142 143-382 383-492	51 307.7 489.7	5.96 50.25 17.96	23.618

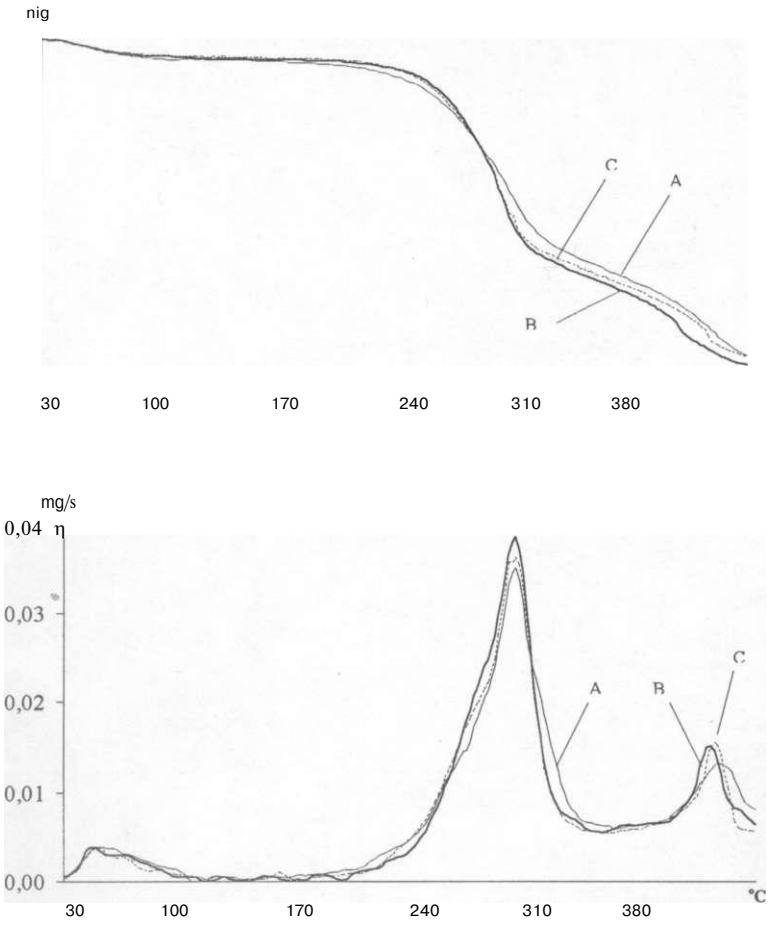

Figure 1 TG and DTG curves of the commercial (codes A and B) and the laboratory boards (code C)

Figure 2 shows the TG and DTC curves of the laboratory particleboards treated with waterglass (boards D and E) and the untreated (board C). In the case of particleboard D, the first region of weight loss is in the temperature range 30-158 °C, with the peak at 51 °C. The second gravimetric region is in the temperature range 159-377 °C, with the peak on the rate of volatile products formation at 321 °C. The third thermogravimetric region is in the temperature range 378^92 °C, with the peak at about 433 °C.

As compared to untreated board (board C) it is obvious that waterglass appeared to increase the overall resistance of particleboard to thermal degradation. It reduced considerably the rate of weight loss and the temperature at which the peak in the main loss occurred (from 333 °C to 320 °C). Waterglass also had an effect on the temperature at which the peak of char formation occured. It reduced it from 464 °C to 431 °C. The amount of residual increased from 5.0 to 8.89 % and the % of loss in the second temperature range was reduced

from 63 to 53 % (see Table 2). Increasing the amount of waterglass in the boards (boards E versus D) increased the above effects considerably, that is the residuals increased to 10.7 %, the peak temperature of the main weight loss reduced to 312 %.

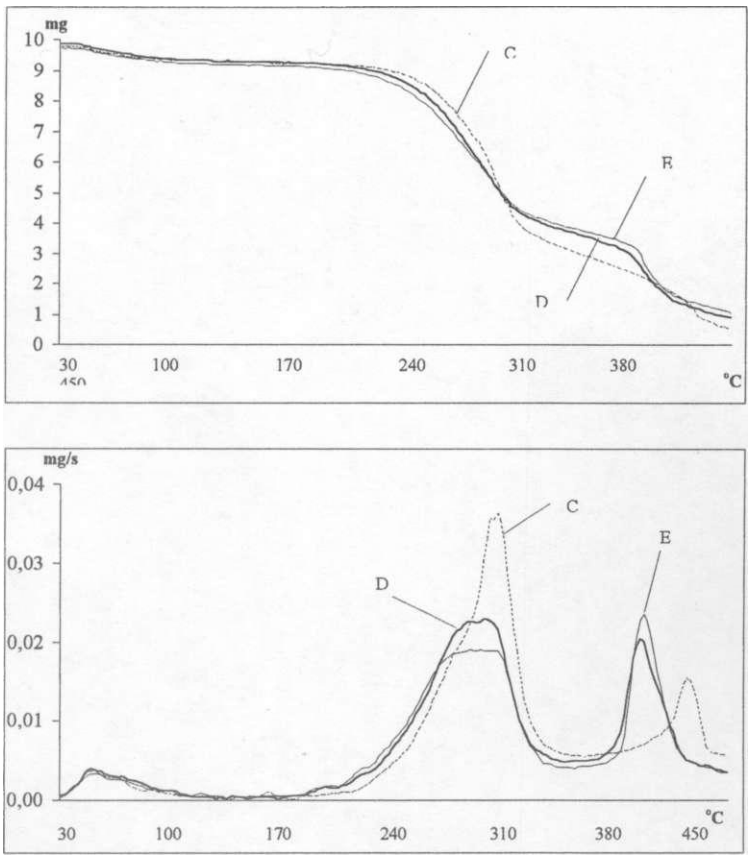

Figure 2 TG and DTG curves of the particleboards treated with waterglass (codes D and E) and the untreated (code C)

Figure 3 shows the TG and DTG curves of particleboards treated with ammonium sulfate (board F), with ammonium hydrogen phosphate (board G) and with the mixture of the above chemicals with borax and boric acid (board H), as well as of the untreated board (board C). In all cases the above fire retardants increased considerably, and much more than waterglass, the resistance of particleboard to heat. The first thermogravimetric region of weight loss was more or less the same for all boards and ranged from 30 to 144 °C. The second region in board F was 133-405 °C with the peak in loss at 289 °C, in board G was 145-396 °C with the peak in loss at 296 °C and in board H was 143 to 382 °C with the peak in weight loss at 308 °C. The above fire retardants had the opposite, as compared to waterglass, effect on the peak temperature of the third temperature region of weight loss (see Figure 2 and Table 2).

It increased the peak temperature of char formation from 464 °C (board C) to 487-489 °C. The amount of residuals (char) was 12.25 % in board F, 26.75 % in board G and 23.62 % in board H (Table 2).

From the various chemicals used, ammonium hydrogen phosphate appeared to have the most positive effect, followed by its admixture of ammonium sulfate, borax and boric acid.

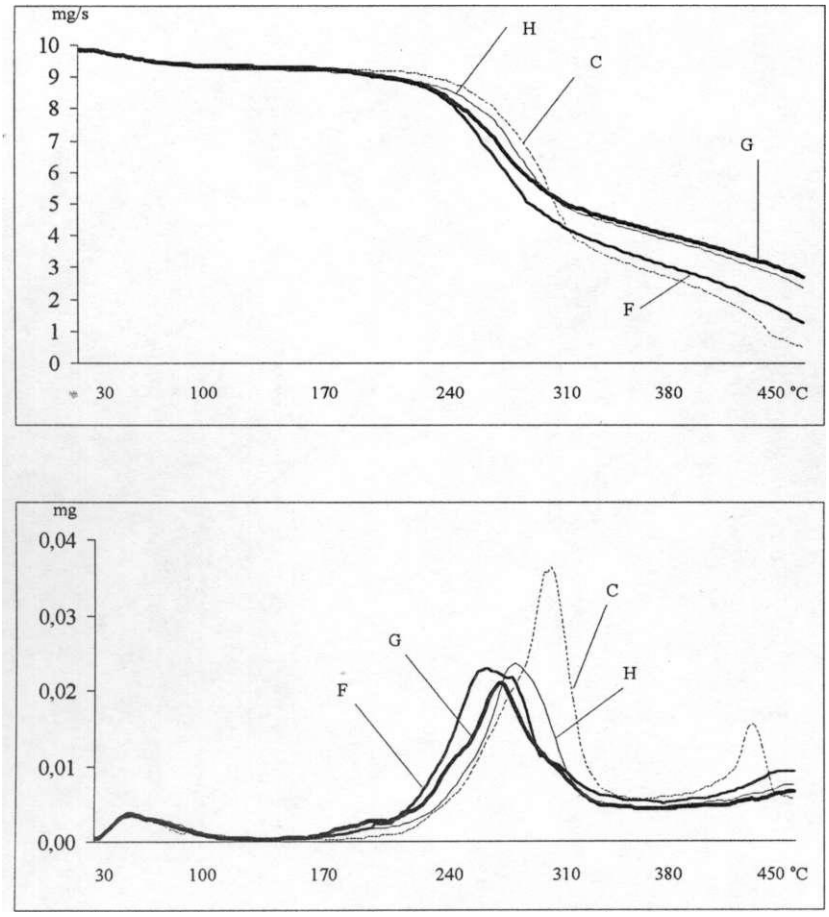

Figure 3 TG and DTG curves of the particleboards treated with Ammonium Sulfate (code F), Ammonium hydrogen Phosphate (code G) and the mixture of chemicals (code H)

Conclusions

The main conclusions we can draw from this study can be summarized as follow:
Thermogravimetric analysis is a useful tool in studying the effect of various fire retardants on the pyrolysis route of wood products.

- Thermal degradation of particleboards treated or untreated with fire retardants particleboards takes place in three stages. In the first stage we have the loss of absorbed water, in the second stage the maximum of formation of volatile products and, in the third stage the formation of char.
- Treatment of particleboards with waterglass, ammonium sulfate, ammonium hydrogen phosphate and a mixture containing ammonium sulfate, ammonium hydrogen phosphate, borax and boric acid, increased the resistance of particleboard to heat. The above chemicals altered the pyrolysis of particleboards, in such a way as to reduce the rate of weight loss (formation of volatile combustible compounds) and to increase the amount (or %) of char produced. Also lowered the temperature at which the peak in the main mass loss occurred.
- The type and amount of fire retardant affect thejoverall pyrolysis of wood particleboard. Ammonium hydrogen phosphate was most effective.

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The work presented in this paper is a part of the senior author's doctoral dissertation.