THERMAL BEHAVIOUR OF THREE WOODS OF MADAGASCAR BY THERMOGRAVIMETRIC ANALYSIS IN INERT ATMOSPHERE

Tantely RANDRIAMANANTENA[1], Fils LAHATRA RAZAFINDRAMISA[1], Georgette RAMANANTSIZEHENA[1], Alain BERNES[2], Colette LACABANE[2]

[1] Laboratoire de Physique de la Matière et du Rayonnement, Université D'Antananarivo, [2] Laboratoire de Physique des Polymères, Institut Carnot CIRIMAT, Université Paul Sabatier Toulouse III

Abstract

In microparticular scale, the thermogravimetric analysis (TGA) is one of the techniques used to determine the thermal properties of wood. Three woods species from the rain forest in eastern part of Madagascar, particularly in Ambavaniasy, were studied: the ebony (*Diospyros sp.)*, the rosewood or the voamboana (*Dalbergia monticola rabevohitra)* and the varongy (*Ocotéa sp.)*. The TGA technique consists to record the lost weight during the increase in temperature from 20°C until 600°C with a 10°Cmn^{-1} heating rate. The samples taken from the sapwood of the trunk are pulverised to the form of sawing powder. The thermograms presented a departure phase of free water (from room temperature to 100°C) before the degradation process of the wood constituents. On the thermogram of ebony, three stages of degradation were observed whereas for voamboana and varongy, there were only two stages. The lignin and hemicellulose play an important role on the degradation of wood at the temperature under 250°C. The degradation of cellulose begins at 250°C and overlaps to that of lignin until 450°C. Each malagasy wood has an intermediary thermal behaviour compared to those of parietal constituents.

Keywords: thermal analysis, wood, lignin, cellulose, malagasy woods

INTRODUCTION

Thermal analysis as Thermogravimetric Analysis (TGA) has become the polymer characterization method the most frequently used. The TGA is particularly more adapted for the mass variation study. The experimental protocols depend on the quality of the material and the ordinary physical characteristic to study [1, 2, 3, 4]. In fact, the measurements in TGA can be performed during a rising in temperature, in static rate (isotherm) or under a temperature programm.

In microparticular scale, the vegetable wall is principally made of the polymer cellulose in the form of microfibrille, hemicellulose, and lignin. The composition of these three constituents of wall in wood tissue varies in one species to one another and presents the different physical structures. Like all the polymer composites, the variation in their rates within wood materials has an impact on the thermomechanical and thermodielectric properties.

The information on the thermic stability of the material is necessary to determine the thermomechanical or thermodielectric properties. Three woods of Madagascar, the ebony (*Diospyros sp.*), the voamboana (*Dalbergia monticola rabevohitra*), and the varongy (*Ocotea sp.*) were analyzed. In this work, we studied the process of the degradation of wood material and tried to know the influence practised by the constituents of wall.

The thermogravimetric analysis was performed to the three malagasy woods, then the comparison of their thermograms with those of cellulose and lignin allows giving information on their thermal behaviours.

I- MATERIALS AND METHODS

I.1) Wood species

The woods studied were the ebony (*Diospyros sp.*), the voamboana (*Dalbergia monticola rabevohitra*) called "Palissandre of Madagascar" and the varongy (*Ocotea sp.*). These hardwoods were collected from the wet forest located at Ambavaniasy in the east of Madagascar. The samples to be analyzed were taken in the sapwood part of the trunk of 10cm of diameter without doing a treatment of drying in advance.

To analyse deeply the thermograms of the woods, we proceed also to the thermogravimetric measures of the commercial cellulose and the lignin supplied in the form of powder (Aldrich). In fact these polymers are parietal constituents of woods.

I.2) Methods of characterization by the thermogravimetric analysis

This analysis consists to record the weight of sample in dynamic conditions between 20°C and 600°C at a constant heating rate 10°C mn^{-1} under an inert atmosphere of N_2. 5mg to 20 mg masses of sample were analysed. The experimental results were achieved using a TGA7 Perkin Elmer. The sample was placed in a little cup made of aluminium hanging from a microbalance. The variation of the mass of the sample allows drawing the TG (variation of the mass in function of the temperature) and TGD (derivative of loss of mass versus the time) thermograms. The combination of these two thermograms gives a clear indication of number of stages of the thermal degradation.

II. Results

II.1) Thermal behaviours of cellulose and lignin

The thermal behaviours of the commercial cellulose and lignin are shown in figure1. From room temperature to 120°C, the derivative curves present one peak which corresponds to evaporation of the water occupying the intercellular vacuum.

On the thermogram of cellulose, one peak of the degradation is observed after the departure of the free water because the cellulose is a homopolymer of glucose. It is a semicrystalline polymer. The degradation of the cellulose begins around 250°C but presents a thin peak on the TGD thermogram indicating the purity of this polymer [5, 6, 7]. It is nearly decomposed totally into volatile product at 400°C (table I).

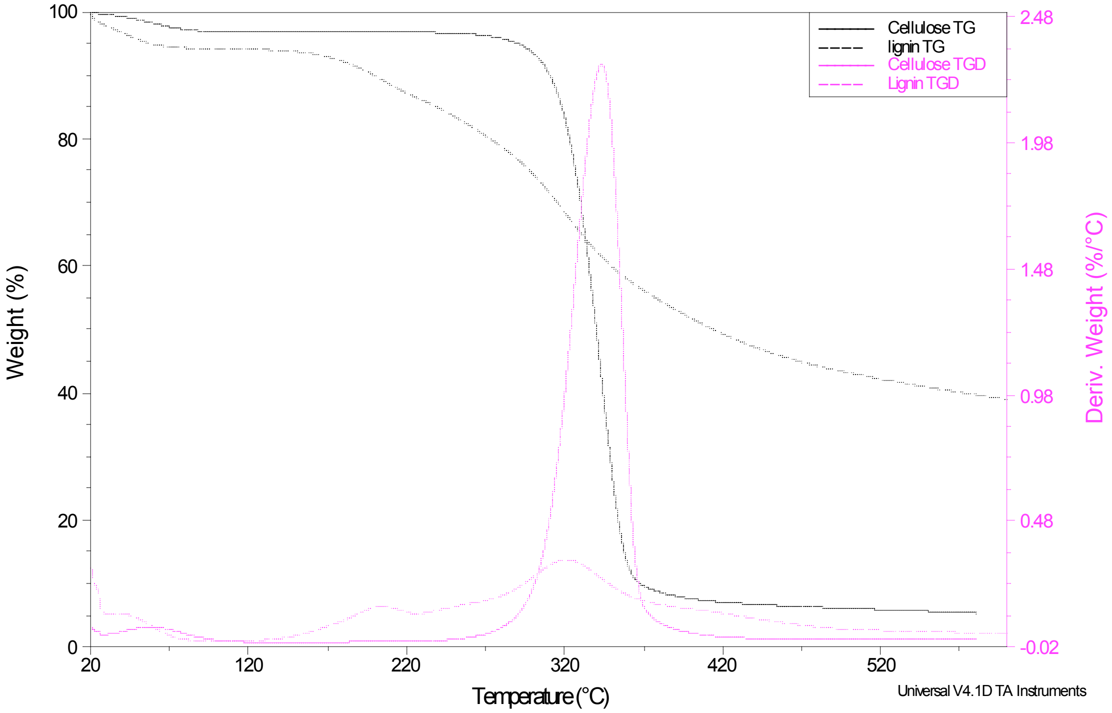

Figure 1: Thermograms (TG and TGD) of cellulose and lignin

The lignin is a polyphenolic polymer formed with three elementary motifs, the coumarylic, sinapylic, and coniferylic alcohols. It has a tridimensional structure. The polymerisation of the lignin is randomly shared at the vegetable secondary wall and its structure varies from one species to one another [8]. Even if the lignin is less stable than the cellulose, its degradation is very slow with the high rate of non volatile products (table II). Several studies confirmed the extensive of the range of the degradation of the lignin in two or three stages [9, 10, 11, 12,]

Table I: Stage of cellulose degradation

Stages of degradation	Temperature range	Maximum peak	Loss of mass
Only one stage	250°C - 400°C	343°C	90.5%

Mass of sample: 19.9 mg; beginning of the degradation: 250 °C; non volatile residue at 500°C: 7%

Table II: Stages of lignin degradation

Stages of degradation	Temperature range	Maximum peak	Loss of mass
1st stage	115°C - 225°C	202°C	7.7%
2nd stage	225°C- 360°C	321°C	28.1%
3rd stage	360°C -500°C	400°C	14.8%

Mass of sample: 5.41 mg; beginning of the degradation: 125 °C; non volatile residue at 500°C : 43%

II.2) Thermal behaviour of three woods of Madagascar

From a room temperature until 100°C, the TG thermograms (figure2) present the loss of mass due to the departure of free water. The phases of degradation of wood materials were observed between 150°C and 475°C.

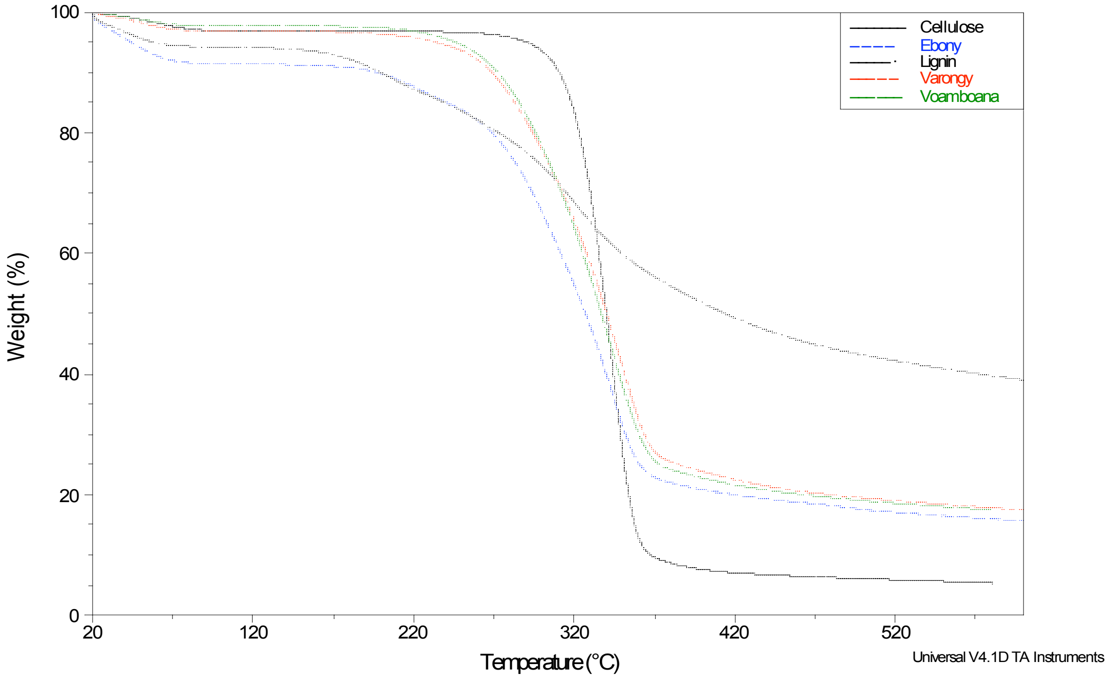

Figure 2: TG thermograms of three malagasy woods, cellulose, and lignin

The sapwood of the ebony has a high quantity of free water than those of varongy and voamboana. The percentage of free water for each species after the measure in ATG (from a room temperature to 100°C) is given by the table III:

Table III: Percentage of free water of ebony, varongy, and voamboana

	Ebène	Varongy	Voamboana
Free water (% of mass)	8.78 ± 0.22	4.10 ± 0.94	3.04 ± 1.03

The TGD thermogram of the ebony (figure 3) shows very well three phases of degradation of constituents whereas two phases were observed for the voamboana and the varongy woods. The different stages of degradation of the three malagasy woods are presented in table IV, table V and table VI.

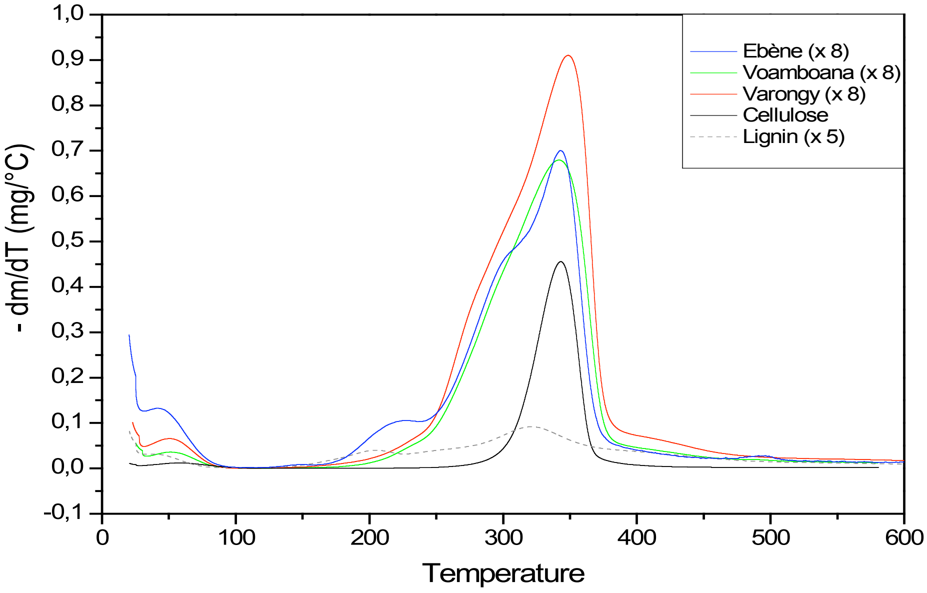

Figure 3: TGD thermograms of the ebony, voamboana, varongy, cellulose, and lignin

Table IV: Stages of degradation of the ebony

Stages of degradation	Temperature range	Maximum peak	Loss of mass
1st stage	125°C - 240°C	224°C	6.1%
2nd stage	240°C - 311°C	302°C	27%
3rd stage	311°C - 425°C	343°C	39%

Mass of sample: 10.2 mg, beginning of the degradation: 125 °C; non volatile residue at 500°C: 18%

Table V: Stages of degradation of the varongy

Stages of degradation	Temperature range	Maximum peak	Loss of mass
1st stage	150°C - 319°C	275°C	27%
2nd stage	319°C -400°C	348°C	45%

Mass of sample: 12.5 mg; beginning of the Degradation: 175 °C; non volatile residue at 500°C: 20%

Table VI: Stages of degradation of the voamboana

Stages of degradation	Temperature range	Maximum peak	Loss of mass
1st stage	175°C - 305°C	224°C	25%
2nd stage	305°C - 400°C	342°C	50%

Mass of sample: 9.3 mg; beginning of degradation: 175 °C; non volatile residue at 500°C: 19%.

III. Discussion

The water in the wood presents in three forms: the free water, the linked water, and the water of constitution. The free water evaporates without energy contribution whilst the linked water and the water of constitution form the chemical bounds with the constituents of the wood wall [13]. Therefore, the temperature range of drying of the material wood lays out from room temperature to about 120°C. It always remains a humidity rate corresponding to water in linkage with the hydrophilic constituents (hemicellulose and cellulose).

The hemicellulose which is also a main constituent of the material wood is principally composed of xylane and xycoglucane. The study previously carried out on poplar [6] gives us the information that the hemicellulose begins to decompose at 160°C. The thermogram of hemicellulose extracted to poplar presents two stages of degradation (from 160°C to 380°C and from 180°C to 560°C). Furthermore, the majority of the hemicellulose decomposes in the first stage [14, 15].

The ebony has a very high mean density compared with the two other species (ebony: 0.990 kg cm^{-3}, voamboana: 0.840 kg cm^{-3}, varongy: 0.600 kg cm^{-3}).The high density of the ebony wood indicates that the cell walls are thick. The size of the pores is then reduced, and the diffusion of the steam diminishes consequently [16]. The first stage of the ebony degradation seems to be due to the superposition of the beginning of the lignin decompositon, the evaporation of the constitution water and the degradation of the most hydrophilic element which is the xylane of the hemicellulose.

The different shapes of the TGD curves can be explained by the distinct percentages of the mass of the wall constituents and the physical structures of the wood for each species.

Conclusion and perspective

In TGA, the observed results give us two essential informations. Firstly, the ebony is the most moisturized wood amongst the three species studied. Secondly this wood species begins to degrade at 125°C which is a lower temperature than those of the varongy (150°C) and the voamboana (175°C). It is noticed that the thermal zone of stability is limited by the temperature of the decomposition beginning of the main constituents of the materials.

By analyzing the TGA thermograms of the parietal constituents, it is shown that the lignin is less thermally stable than the cellulose; but it has a very high rate of residue. The cellulose degradation gives a low residual rate on the other hand. The thermal stabilities of these materials are classified as following:

Lignin < ebony < varongy <voamboana < cellulose

The degradation process of the three woods can be then summarized. After the departure of the free water, the degradation of the main constituents of woods begins at 125°C and presents two or three stages in general. The xylane of the hemicellulose degrades firstly and the products of its decomposition may activate the degradation of one part of the lignin. At the temperatures above 250°C the great part of the material wood is broken down into volatile products. The degradation consists of two stages: the observed peak on the TGD thermograms between 250°C and 320°C is due to the superposition of the lignin and the hemicellulose degradations. For the temperatures higher than 320°C, the deterioration of the cellulose overlaps with the decomposition of the lignin and stabilizes around 425°C [4,17].

In this work, we have determined the thermal stability zones of three malagasy woods. Knowledge of these temperature ranges enables us to carry out the determination of thermomecanical and dielectric properties of ebony, varongy and voamboana. The relationship between structure and properties of these malagasy forest species will be defined.

References

[1] Bourgois J., Bartholin M.C., Guyonnet R., 1989, Thermal treatment of wood : analysis of the obtained product, Wood Sciences and Technology, 23 ,303-310

[2] Popescu C., 1996, Integral method to analyze the kinetics of heterogenous reactions under non-isothermal conditions. A variant on the Ozawa-Flynn-Wall method. Thermochimica Acta 285, 309-323.

[3] J.J. Weiland, R. Guyonnet and R.Gibert, 1998,Analyse de la pyrolyse menagée du bois par un couplage TG-DSC-IRTF, Journal of Thermal Analysis, 51, 265-274

[4] Jieheng Guo, 2004, Pyrolysis of wood powder and gasification of wood-derived char, Technische Universiteit Eindhoven 170 p.

[5] Patrick R., Ian T., André D., Patrick P., 2006, Choix d'un modèle de pyrolyse ménagée du bois à l'échelle de la microparticule en vue de la modélisation macroscopique, Ann. For. Sci. 63, 213–229

[6] Golnaz J. M., 2007, Dynamique macromoléculaire dans la paroi végétale et ses polymères pariétaux, L2P Université Paul Sabatier Toulouse III 186p.

[7] Patricia A., Alon R., Aitor A.,Jose M. K., In˜ aki M., 2009, Mechanical Properties of Natural Fibers/Polyamides Composites , Composite polymer 257-264

[8] Panshin A.J., de Zeeuw C. 1980, Texbook of wood technology 4ème Edition, Mc Graw-Hill Publishing Company, 722p.

[9] Jaroslav BLAŽEK, 2005, Study of the reaction kinetics of the thermal degradation of polymer, Institut National Polytechnique de Toulouse, 262p.

[10] Jakab, E., Faix, O., Till, F., 1997, Thermal decomposition of milled wood lignins studied by thermogravimetry/mass spectrometry, Journal of Analytical and Applied Pyrolysis, 40-41, 171-186.

[11] Sun R.C, Lu Q, Sun X.F, 2000, Physico-chemical and thermal characterization of lignins from Caligonum monogoliacum and Tamarix spp., Polym. Degrade. Stab., 72, 229-238

[12] Franceschi F, Luciano G, Carosi F, cornara L and Montanari C, 2004, Thermal and microscope analysis as a tool in characterization of ancient papyrus, thermochim.acata , 418, 39-45

[13] C. Sales, 1979, le séchage des bois tropicaux, Revue Bois et forêt des Tropiques, 184, 61-71

[14] Vincent R., Alexandre G. and René G., 2005, Thermo-gravimetric analysis as a tool for the optimisation of wood heat treatment parameters, 2nd European conference on Wood Modification, 9p.

[15] S.L.levan, 1989, Thermal Degradation, In: Schniewind, Arno P., ed. Concise Encyclopedia of Wood & Wood-Based Materials, 1, 271-273

[16] P. Perré, B. K. May, 2001, A numerical drying model that accounts for the coupling between transfers and solid mechanics. Case of highly deformable products. Drying Technology. 19 (8), 1929-1643

[17] S. Hafsi and M. Benbouzid, 2007, Slow and Flash Pyrolysis of Eucalyptus blobulus Wood Research of applied Sciences 2, 810- 814