STUDIA UBB CHEMIA, LVIII, 1, 2013 (p. 141 – 149)
(RECOMMENDED CITATION)

# WOOD FIBERS CHARACTERIZATION BY TGA ANALYSIS

AMALIA MIHAELA IURIAN[a], IOANA PERHAIŢA[b],
RALUCA ŞEPTELEAN[c], ALINA SAPONAR[b,c*]

**ABSTRACT.** The thermal analysis for some wood fibers (from sawdust) and for the corresponding composites plate is reported. The thermal stability domains, the partial and the total weight loss and the $T_{max}$ of the weight loss maxima were determined on the basis of TG and DTG plots registered in nitrogen flow. It was demonstrated that, in the case of chemically treated sawdust fibers, the maximum of decomposition temperature decreased with the increasing of the concentration of alkaline solution and in the case of the composite plates, with the increasing of the alkaline solution concentration, the thermal stability of the composite plate increases.

***Keywords***: *wood, thermal analysis, lignin, cellulose*

## INTRODUCTION

In the last period, a particular attention is given to the new materials with improved properties including composite materials reinforced with wood fibers. The latest research in the field highlights the use of sawdust in obtaining such materials [1].

Thermogravimetric analysis (TGA) has become the most frequently used characterization method for many materials. The TGA is particularly more adapted for the mass variation study. The protocols used depend on the quality and the physical characteristic of the discussed materials. The measurements in TGA can be performed during a rising in temperature, in static rate (isotherm) or under a temperature program, in controlled atmosphere.

---

[a] *Technical University of Cluj-Napoca, Faculty of Materials and Environmental Engineering, B-dul Muncii Nr. 103-105, RO-400641 Cluj-Napoca, Romania*
[b] *“Raluca Ripan” Institute for Research in Chemistry, Babes-Bolyai University 400294, Cluj-Napoca, Romania*
[c] *Babes-Bolyai University, Faculty of Chemistry and Chemical Engineering, 40084, Cluj-Napoca, Romania*
* *Corresponding author: saponar_alina@yahoo.com*

The thermogravimetric analysis of the raw materials (wood fibers) and the composite plates with wood waste and resin is performed to determine their chemical characteristics and it’s based on tracking weight changes of the materials depending on temperature. By the use of TGA method we can study the structure of wood fibers, the oxidative stability, and the moisture- or volatile content [1-7]. Thermal degradation of the wood fibers in chemical constituents was also studied, knowing that, this degradation begins at 250ºC with cellulose degradation and ends at 450ºC with degradation of lignin [8-12]. According the literature data [13] natural lignin contains some functional groups like methoxyl, phenolic hydroxyl, primary and secondary aliphatic hydroxyl, aldehyde and ketone which can be modified during the thermal treatment. A qualitative determination of the composition of thermoplastic wood composites was performed using TGA technique [14].

Our interest in the study of these new types of composite materials [15-18] is due to the interesting properties and multiple applications that lignin based composite materials can have.

We present a detailed analysis of the thermal behavior of wood fiber and the corresponding composite materials, subjected to various surface chemical treatments.

## RESULTS AND DISCUSSION

The thermogravimetric analysis offers important details to determine the properties of the new composite materials based on wood fibers. Until now, for the best of our knowledge, only the mechanical and the morphological properties of these types of treated and untreated sawdust materials have been studied [16]. Considering the possible applications of composite materials based on sawdust, a study on thermal behavior, is necessary. The thermal degradation of wood is a crucial aspect for the manufacturing process, because it determines the maximum processing temperature that can be used. On the other hand, the thermal analysis can offer useful information about the stability or the temperature range in which the compounds can be used, without changing their composition and properties.

Due to its lower thermal stability, wood is usually used as filler only in polymers that are processed at temperatures below 200 °C. Because of the high temperatures, the degradation of wood can lead to undesirable properties, such as odor, discoloration and loss of mechanical strength.

The mixed deciduous and coniferous sawdust samples used were treaded (using the literature procedure [16]) as shown in Table 1. The temperature domains of the decomposition stages, including the starting point (onset), the partial and total weight loss (on TG plots) and the $T_{max}$ [ºC] of the weight loss maxima (on DTG plots) are also described.

For the untreated and treated sawdust (with NaOH and KOH), the weight loss varies between 69.2 and 81.1% and for the composite plates (untreated and treated sawdust impregnated with resin) between 81.2 and 85.3% (Figure 1).

The total mass loss is higher for untreated wood fibers, in comparison with the treated wood. This may be due to the impurities that are on the surface of the wood fibers. For the wood fibers treated with NaOH solution, the mass loss is smaller, due to the advance cleaning of the fiber surface. The smallest weight loss (69.2%) was obtained in the treatment with KOH in solution (10%), which shows a thorough cleaning of fibers by this method.

By treatment with alkaline solution, the cell-wall components such as ester-linked molecules of the hemicellulose can be cleaved. The resulting dissolved hemicellulose and lignin (formed by the hydrolysis of acetic acid esters) together with the swelling of cellulose, decrease the crystallinity of cellulose. Due to the cleavage of the lignin - hemicellulose or lignin – cellulose bonds, the biodegradability of the cell-wall increases [19], this tends to increase the hydrophilic behavior and hence the solubility of the material, leading to a decrease in thermal stability of the sample.

**Table 1.** Data of thermogravimetric analysis (TG and DTG) for the sample **1-8**

| **Sample no.** | **Treatment** | **Temperature domain [ºC]** | **$T_{onset}$* [°C]** | **$T_{max}$ [°C]** | **Partial mass loss ($\Delta m_p$) [%]** | **Total mass loss ($\Delta m_T$) [%]** |
|---|---|---|---|---|---|---|
| **1** | Untreated | 25 - 150 | - | 71 | 4.2 | 80.7 |
| | | 150 - 330 | 254 | - | 26.2 | |
| | | 330 - 800 | 336 | 357 | 50.3 | |
| **2** | Treated with 2% NAOH | 25 - 150 | - | 66 | 4.8 | 75.2 |
| | | 150 - 270 | 200 | - | 9.3 | |
| | | 270 - 800 | 267 | 314 | 61.1 | |
| **3** | Treated with 5% NaOH | 25 - 150 | - | 70 | 4.2 | 72.5 |
| | | 150 - 250 | 180 | - | 8.9 | |
| | | 250 - 800 | 249 | 298 | 59.4 | |
| **4** | Treated with 5% KOH | 25- 150 | - | 64 | 4.0 | 81.1 |
| | | 150 - 800 | 281 | 354 | 77.1 | |
| **5** | Treated with 10% KOH | 25 - 150 | - | 66 | 5.0 | 69.2 |
| | | 150 - 250 | 180 | - | 9.6 | |
| | | 250 - 800 | 249 | 293 | 54.6 | |
| **6** | Composite plate: impregnated untreated sawdust | 25 -150 | - | 65 | 3.4 | 81.2 |
| | | 150 - 800 | 271 | 354 | 77.8 | |
| **7** | Composite plate: impregnated sawdust treated with 5% KOH | 25 - 330 | 248 | 315 | 24.2 | 85.3 |
| | | 330 - 800 | 339 | 389 | 61.1 | |

| **Sample no.** | **Treatment** | **Temperature domain [°C]** | **$T_{onset}$* [°C]** | **$T_{max}$ [°C]** | **Partial mass loss ($\Delta m_p$) [%]** | **Total mass loss ($\Delta m_T$) [%]** |
|---|---|---|---|---|---|---|
| **8** | Composite plate: impregnated sawdust treated with 10% KOH | 25 - 330 | 213 | 303 | 23.4 | 82.8 |
| | | 330 -800 | 350 | 394 | 59.4 | |

$T_{onset}$* = starting temperature of mass loss steps.

The thermogravimetric analysis shows that the first stage of degradation of the analyzed material occurs in the 25 ÷ 150 °C temperature range and corresponds to the loss of water (Table 1). This partial mass loss does not exceed 5%, even if the alkaline surface treatment was applied.

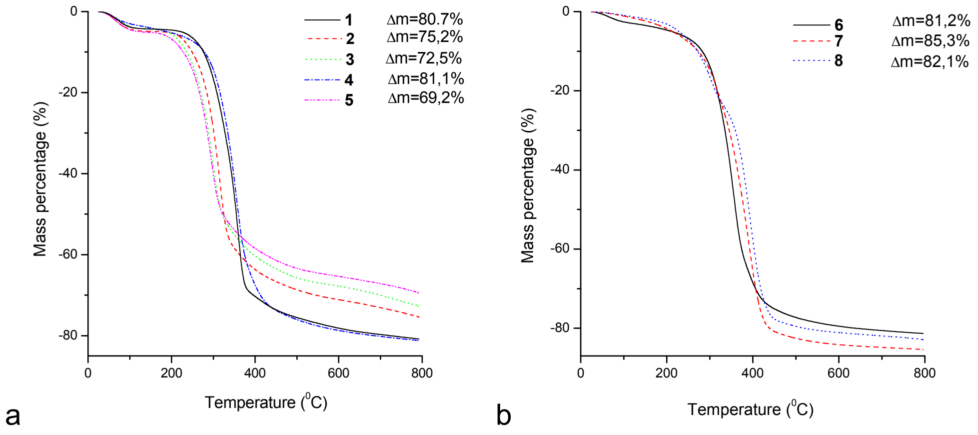

**Figure 1.** TG curves of the treated and untreated sawdust (a) and of the treated and untreated composite plates (b)

For all the samples, it was found that by drying these fibers at room temperature, the water absorbed during alkaline treatments was not completely removed. In order to determine how the water molecules were bonded to the wood surface, a controlled drying at 105 ºC was performed, using a temperature controlled oven. The amount of water removed at this temperature does not differ substantially between treated and untreated fibers. This fact can be explained by the presence of hydrogen bonds formed between the hydroxyl groups from the water molecules and the OH fragments forming the cellulose fiber.

The second stage of fiber degradation occurs in the 150 ÷ 300 °C temperature range and is associated with the degradation of hemicellulose from the wood fibers, which according to the literature has a deterioration interval between 150 ÷ 280 °C [9]. ]. This is because cellulose has a monodimensional structure and thus a relative small number of bonding sites, while hemicellulose has a bidimensional structure which could afford the formation of a higher number of interactions between their components.

Major mass loss is observed, for untreated sawdust fibers (sample **1**), at 357 °C, where the decomposition of lignin occurs, as already established in the literature [9]. In the case of the chemically treated sawdust fibers, the temperature of maximum decomposition decreased with the increasing of the concentration of the alkaline solution. Thus when applying a treatment with a solution of 10% KOH, the major weight loss is achieved at a maximum temperature of 293 °C, sample **5** being the sample with the lowest thermal stability (Figure 2a).

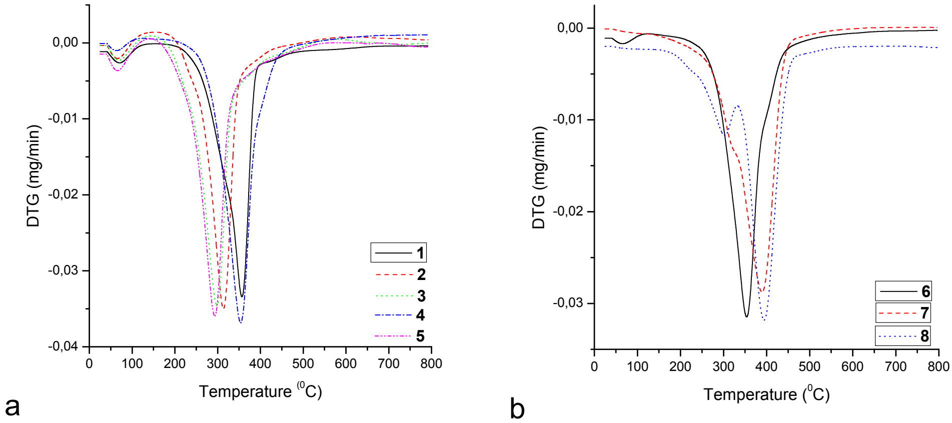

**Figure 2**. DTG curves of the treated and untreated sawdust (a) and of the treated and untreated composite plates (b)

In the case of the composite plates, with the increasing of the concentration of alkaline solution used in the treatment of sawdust, the thermal stability of the composite plate increases. This behavior can be explained by the amount of resin incorporated and thus giving a higher thermal stability (Figure 2b).

In order to complement this study, a FT-IR analysis was performed on samples **1**, **5**, **6** and **8** (Figure 3).

In the case of sample **1** and **5**, all the specific bands were evidenced according with literature data [20a]. The vibrations of –OH group (alcoholic or phenolic) involved in the hydrogen bonds appear in the case of sample **1,** at 3405 cm$^{-1}$ and **5** at 3385 cm$^{-1}$, respectively. The stretching vibration of the C=O bonds (in ketone groups) in $\beta$ location, relative to the aromatic ring, is observed at 1735 cm$^{-1}$ in sample **1** and is not present in the treated sample **5**. The same behavior was previously described for fibers in which a reduction with lithium aluminum hydrate was performed [20b]. Stretching vibration of C=O bonds in $\alpha$ or $\gamma$ location, relative to the aromatic rings, were observed at 1638 cm$^{-1}$ in sample **1** and at 1595 cm$^{-1}$ in sample **5** (Figure 3). The appearance of the –OH vibration bands in the treated sample occurs with a lowering in intensity of the vibration bands corresponding to the carboxyl groups (at 1596-1600 cm$^{-1}$), suggesting the partial reduction to hydroxyl groups after treatment with alkaline solution.

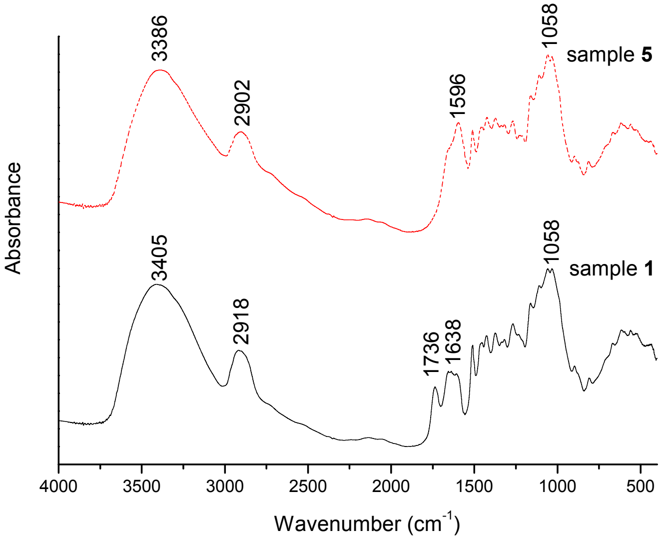

**Figure 3**. FT-IR spectra of sample **1** (untreated sawdust) compared to sample **5** (treated sawdust with 10% KOH)

The recorded FT-IR spectra for samples **6** and **8** (untreated and treated plates) don't show significant changes for the lignin bands when compared to the parent wood sawdust (samples **1** and **5** respectively) all the vibration bands appearing in the specific ranges.

## CONCLUSIONS

The thermal behavior of sawdust (treated and untreated), in comparison with the composite plates (treated and untreated) was evaluated, on the basis of thermogravimetric plots.

The total mass loss is higher for untreated wood fibers, relatively with the treated wood. For the wood fibers treated with NaOH solution, the mass loss is smaller, due to the advance cleaning of the fiber surface. The smallest weight loss (69.2%) was obtained in the treatment with 10% KOH solution, showing a thorough cleaning of fibers by this method.

The first stage of degradation occurs in the 25 ÷ 150 °C temperature range and corresponds to the loss of water. The second stage of the fiber degradation occurs in the 150 ÷ 300 °C temperature range and is associated with the degradation of hemicellulose from the wood fiber.

The maximum of decomposition temperature decreased with the increasing of the concentration of alkaline solution, the sample **5**, being the sample with the lowest thermal stability. This could be justified by the fact that a higher concentration of the alkaline solution, creates a more intense cleaning of the wood fibers by destroying the inter-connections between the wood fibers, which thus leads to a decrease of the thermal stability of the sample.

In the case of the composite plates, a higher concentration of the alkaline solution increases the thermal stability of the plate, due to a increased amount of resin incorporated and thus sample **8** has the highest thermal stability.

## EXPERIMENTAL SECTION

### Samples preparation

The samples 1 ÷ 8 were prepared and treated according with the protocols presented in literature [16].

### Investigation methods

*Thermal analysis*

Thermogravimetric analysis (TGA) was performed using a Mettler Toledo TGA/SDTA851$^{e}$ Thermal Analysis System. The measurements were carried out in the temperature range of 25 ÷ 800 °C, in alumina crucible, in nitrogen with a flow rate of 50 mL min$^{-1}$. A heating rate of 10 °C min$^{-1}$ was used and the samples weighted between 19 ÷ 27 mg.

*Infrared spectroscopy*

Infrared absorption spectra were recorded on a Thermo Scientific Nicolet 6700 FT-IR spectrometer, using KBr pellets.

Sample 1: (KBr, $\nu_{max.}$, $cm^{-1}$) $\nu_{OH} = 3405$; $\nu_{-C-H} = 2918$; $\nu_{C=O} = 1736$ (β location, in COOH group); $\nu_{C=O} = 1638$ (α and γ location); $\nu_{C-O} = 1058$;

Sample 5: (KBr, $\nu_{max.}$, $cm^{-1}$) $\nu_{OH} = 3386$; $\nu_{-C-H} = 2901$; $\nu_{C=O} = 1596$ (α and γ location); $\nu_{C-O} = 1058$;

Sample 6: (KBr, $\nu_{max.}$, $cm^{-1}$) $\nu_{OH} = 3423$; $\nu_{-C-H} = 2925$; $\nu_{C=O} = 1737$ (β location);$\nu_{C=O} = 1608$ (α and γ location); $\nu_{C-O} = 1033$;

Sample 8: (KBr, $\nu_{max.}$, $cm^{-1}$) $\nu_{OH} = 3423$; $\nu_{-C-H} = 2924$; $\nu_{C=O} = 1602$ (α and γ location); $\nu_{C-O} = 1033$.

## ACKNOWLEDGEMENTS

This work was financially supported by CNCSIS-UEFISCSU, project number PCCE 129/2008 and project number PCCE 140/2008.

## REFERENCES

1. H. Jeske, A. Schirp, F. Cornelius, *Thermochim. Acta*, **2012**, *543*, 165.
2. S. Singh, C. Wu, P.T. Williams, *J. Anal. Appl. Pyrol.*, **2012**, *94*, 99.
3. F. Sliwa, N.El. Bounia, G. Marin, F. Charrier, F. Malet, *Polym. Degrad. Stabil.*, **2012**, *97*, 496.
4. H.-S. Yang, M.P. Wolcott, H.-S. Kim, H.-J. Kim, *J. Therm. Anal. Calorim.*, **2005**, *82*, 157.
5. J. Bourgois, M.C. Bartholin, R. Guyonnet, *Wood Sci. Technol.*, **1989**, *23*, 303.
6. C. Popescu, *Thermochim. Acta*, **1996**, *285*, 309.
7. J.J. Weiland, R. Guyonnet, R.Gibert, *J. Therm. Anal.*, **1998**, *51*, 265.
8. W. K.Tang, W. K. Neill, *J. Polym. Sci: Part C*, **1964**, *6*, 65.
9. J. Kudo, E. Yoshida*, J. Japan. Wood Res.*, **1957**, *3(4)*, 125.
10. J. Guo, “Pyrolysis of wood powder and gasification of wood-derived char”, Technische Universiteit Eindhoven, **2004**, 170.
11. S. Hafsi, M. Benbouzid, *Res. J. Appl. Sci.*, **2007**, *2*, 810.
12. S. Renneckar, A.G. Zink-Sharp, T.C. Ward, W.G. Glasser, *J. Appl. Polym. Sci.*, **2004**, *93(3)*, 1484.
13. V.M. Nikitin,” Lignins”, Goslesbumizdat Leningrad, **1961**.
14. F.M.B. Coutin, M.P. Wolcott, H.-S. Kim, H.-J. Kim, *J. Therm. Anal. Calorim.*, **2005**, *82*, 157.

15. A. Borlea (Tiuc), T. Rusu, S. Ionescu, O. Nemes, *Rom. J. Mat.*, **2012**, *42(4)*, 405.
16. O. Nemes, A.M. Chiper, A.R. Rus, V.F. Soporan*, O. Tataru, P. Bere, Studia UBB Chemia*, **2010**, *55*, 101.
17. A.M. Gombos, O. Nemes, V.F. Soporan, A. Vescan, *Studia UBB Chemia*, **2008**, *3*, 81.
18. O. Nemes, F. Lachaud, R. Piquet, *Studia UBB Chemia*, **2008**, *53(3)*, 25.
19. E. Sjöström, "Wood chemistry Fundamentals and applications". Press: Academic Press inc., London, Ltd, **1981**.
20. a) H.L. Herget, *J. Organomet. Chem.,* **1960**, 25, 405; b) H.L. Herget, E.F. Kurth, *J. Am. Chem. Soc.,* **1953**, *75*, 1622.