THERMAL ANALYSIS OF CORRUGATED PACKAGING PAPER AND ITS COMPONENTS

Barnabás TÓTH[1], László KOLTAI[1], László TRIF[2], Péter BÖRÖCZ[3],

1 Óbuda University Rejtő Sándor Faculty of Light Industry and Environmental Engineering, Budapest
2 Research Centre for Natural Sciences, Institute of Matertials and Environmental Chemistry, Budapest
3 Széchenyi István University, Győr

Abstract: *In the present work, thermal behavior of corrugated packaging paper and its components were investigated. The various pyrolytic processes appeared as overlapped endotherms on the heat flow curves and as non-separated mass loss steps on the mass loss (TG) and derivative thermogravimetric curves (DTG), as weell, which correspond to the thermal decomposition of the components of the investigated sample, such as cellulose, hemicellulose and lignin. The variable amount of these components appeared as peak height differences on the corresponding endothermic peaks, as well as variable peak heights and widths on the DTG curves. The mass loss curves were also somehow characteristic to the investigated sample, and it was found, that the the straw samples had the lowest thermal stability, while the cotton samples were more stable, their thermal degradation started at least 80 °C higher, compared to the straw samples. It was determined, that in the function of hemicellulose content of the sample, on the corresponding DTG curves smaller shoulders appeared on the lower temperature side (225 and 300 °C) of the main pyrolitic steps (between 225 and 400 °C), which could be used as an analytical markers of the hemicellulose content. The observed smaller endotherms between 400 and 450 °C could be the result of some reorganization in the carbonized remainder and it needs further investigations to clarify the ongoing processes in this temperature interval.*

Keywords: TG-DSC, corrugated cardboard, pyrolysis, carbonization

INTRODUCTION

The thermal behaviour of the main constituents of the packaging paper were investigated with simultaneous thermogravimetric coupled with differential scanning calorimetric (TG-DSC) on various samples, such as NaOH treated cotton as primary source of alpha cellulose with its over 90 % content, three types of bleached sulphates, non-bleached sulphate, straw and an assorted basepaper type (namely the testliner). Testliner basepaper was also involved as a reference material for comparative purposes as a base of a future introduced analytical identification method. Using thermogravimetric analysis (TG) and differential scanning calorimetry (DSC), the characteristics of the energetic processes (endothermic or exothermic), marginal temperature peaks and the weight losses were measured during the tests. [1]

EXPERIMENTAL

Samples

In the present work, three types of bleached sulphates (bleached -sulphate poplar, - sulphate pine, - sulphate beech, - sulphate), a bleached straw, a non-bleached sulphate pine and NaOH treated cotton were investigated by thermal analysis. NaOH treated cotton was chosen to represent its high cellulose content (over 90% α-cellulose as a primary resource). The testliner sample used both fluting and cover layer for normal cardboard paper production, consisted of mainly cellulose from secondary recycled source and great amount of incrust and filler materials, which can be classified as a complex chemical system among other samples. The bleached

sulphates, bleached straw, the non-bleached sulphate and the NaOH treated cotton were provided by the Material Laboratory of Óbuda University, Hungary. Testliner samples were provided by Dunapack Kft., Hungary. All samples were provided in board form with the size of 210x297 mm. This preparation method has been proven suitable for preventing differences in moisture content, by the variable moisture absorption affinity of the various samples.

Thermal analysis

The thermal experiments were performed on a Setaram LabsysEvo TG-DSC system in flowing (80 mL/min) high purity (99.999%) argon. Suitable amount of samples were cut in approximately 1x5 mm pieces (Figure 1) and were placed in 100 microliter aluminium crucibles. The measurements were carried out in the 25 – 500 °C temperature range, with a heating rate of 10 °C/min. The dimensions of the samples were chosen to have the highest usable sample mass, with the highest possible surface to be in contact with the inert gas. The measurement results were blank corrected and evaluated with the thermal analyzer's software (Calisto v2.04).

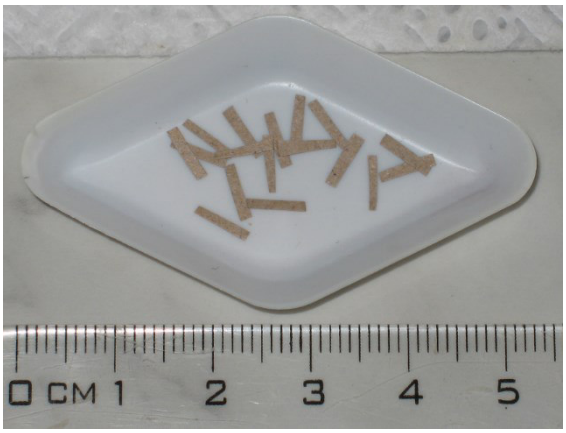


Figure 1. Dimensions of the samples used for thermal measurements

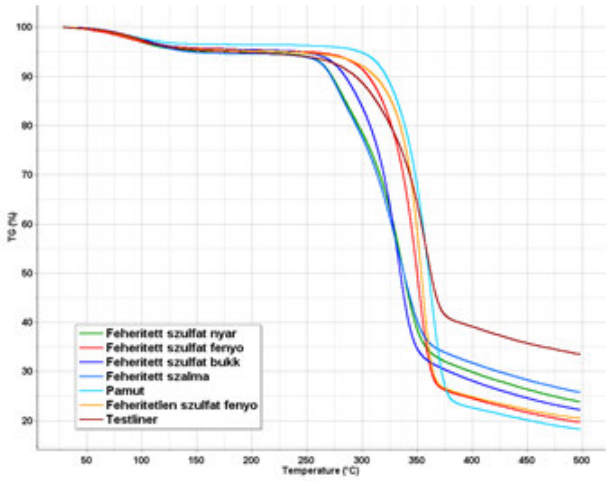
During the measurements, the pyrolytic processes were monitored by a plate type DSC rod, which provided information on the specific temperature (°C) peaks and energetic processes (endothermic, exothermic), which can refer to the characterisation of chemical changes taking place for each component.[10] The samples were analyzed from 30 °C to 500 °C under inert atmosphere (argon), at a heating rate of 10 K/min. This inert carrier gas was used to remove the gaseous and condensable products, thus minimizing any secondary vapor-phase interactions [9]. The energy changes (more specifically the heat flow curves) were recorded during the heating periods based on equation (1) [2-5]

$$dH\ dt = Cp\ dT\ dt + f(T, t) \qquad (1)$$

where dH/dt is DSC heat flow signal
Cp is a sample heat capacity (heat specific x weight);
dT/dt is the heating rate;
f (T,t) is heat flow that function of time at an absolute temperature (kinetic)

RESULTS AND DISCUSSION

On figures 2, 3 and 4 the mass loss (TG), derivative thermogravimetric (DTG) and heat flow (DSC) curves are plotted against temperature. Monitoring the chemical processes by TG and DSC taking place during the heating from 30 °C to 500 °C, four phases were identified (Δ1, Δ2, Δ3, Δ4) by the aid of the DTG curves. The temperature intervals of these phases are followings: Δ1 – between 25 and 150 °C; Δ2 – approximately between 150 and 225 °C; Δ3 – approximately between 225 and 400 °C and Δ4 – from 400 °C up to the end of the measurements (~ 500 °C). During the first phase, the physically bound water (moisture) evaporated. It was found, that in average 3-6% of mass loss occurred in this region. This is in agreement with the values described in the literature for conditioned and non conditioned samples [14].



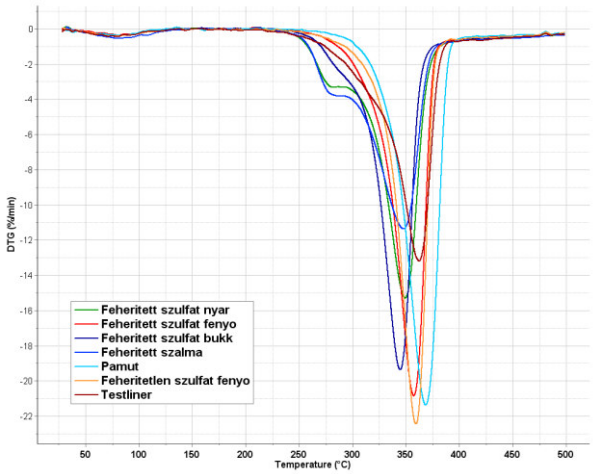


Figure 2. (left) Mass loss (TG) curves of the blenched sulphates [poplar (green curve), beech (dark blue curve) and pinewood (red curve)] non-blenched sulphates (pinewood – orange curve) blenched straw (lighter blue), NaOH cotton (light blue) and testliner basepaper (brown curve);
Figure 3. (right) DTG traces of blenched sulphates [poplar (green curve), beech (dark blue curve) and pinewood (red curve)] non-blenched sulphates (pinewood – orange curve) blenched straw (lighter blue), NaOH cotton (light blue) and testliner basepaper (brown curve)

In Δ2 phase from 150 °C to 225 °C no degradation processes took place in the samples, since there is practically no mass loss in this temperature interval, nor visible energetic processes are taking place in this temperature region. According to the literature, the depolymerization of the hemicellulose takes place usually between 180 and 250 °C, which could be seen as an endotherm on the heat flow signals. This process is not visible in our case, since the present measurements were optimized for best TG and DTG signal resolution and not for obtaining optimal heat flow (DSC) signals, the latter was recorded because of the combined nature (simultaneous TG-DSC) of the technique. Such measurements will be performed and presented later.

In Δ3 phase, the pyrolytic processes specific to the degradation of the paper's components are taking place, which appear as more or less overlapped peaks of the DTG curve (figure 3) and as endothermic peaks on the heat flow curves (figure 4). Hemicellulose is made up of low molecular weight polysaccharide units, including D-mannose, D-xylose, D-glucose, D-galactose, L-arabinose etc., which are linked together with β-1,4 glycosidic bonds and sometimes with β-1,3 glycosidic bonds. Because of their amorphous nature, short chains and the low molecular weight of sugar molecules, are degrading at lower temperature. Usually the pyrolytic degradation of hemicellulose starts around 250 °C and is completed around 320 °C.[8,9,10] However, cellulose is a linear polymer that is composed of D-glucose units linked in conjunction with β-1,4 glycosidic bonds. These glucose units are linked together by hydrogen bonds and van der Waals forces to form long chain macromolecules. Therefore, cellulose has higher thermal stability than hemicellulose, and its pyrolysis takes place in the temperature range of approximately 320–400 °C. These processes appeared clearly in the 225 and

400 °C temperature region of the DTG curves, where a small shoulder is mainly visible on the lower temperature side of the large peaks, which based on the above described processes is characteristic to the pyrolytic decomposition of the already depolymerised hemicellulose. The large peaks between 310 and 400 °C are characteristic to the degradation of the cellulose [14, 15]. We have also observed, that the low temperature shoulders on the DTG curves are somehow characteristic markers of the hemicellulose content, as higher is its content, the more separated and visible these shoulders are. It can also be noted, that the determinant part of the mass loss takes place in this phase (Δ3). We have also noticed, that the peak minima on the DTG curves also shifts towards higher temperatures in the function of the cellulose content, as higher is the cellulose, the higher is the peak minima. Despite the fact, that these two degradations are two different processes, they do not appear as separate or overlapped peaks on the heat flow curve, which is not surprising, since –as described earlier- our measurements were optimized for optimal mass loss and not for the detection of the heat flow. [11,12,13]

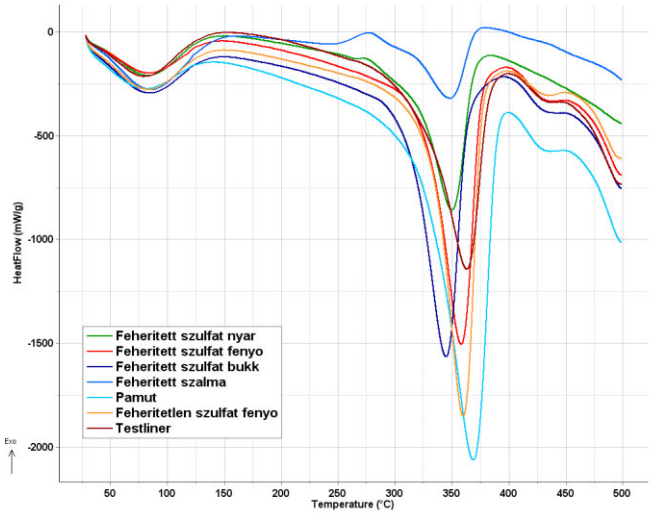


Figure 4. DSC measurement of blenched sulphates [poplar (green curve), beech (dark blue curve) and pinewood (red curve)] non-blenched sulphates (pinewood – orange curve) blenched straw (lighter blue), NaOH cotton (light blue) and testliner basepaper (brown curve)

In the last Δ4 phase, a far much smaller mass loss occurs in the case of all investigated samples, which is accompanied by a small and broad endotherm, which, based on the findings described in the literature, could be the result of the pyrolytic decomposition of lignin. Lignin is mainly an amorphous tridimensional polymer composed of three basic units, namely p-coumaryl (4-hydroxycinnamyl), coniferyl (3-methoxy 4-hydroxycinnamyl) and sinapyl (3,5-dimethoxy 4-hydroxycinnamyl) alcohols, which are also known as p-hydroxyphenyl (H), guaiacyl (G) and syringyl (S) units, respectively. The main difference in the three basic units is the number of methoxyl groups attached to an aromatic ring. The H, G and S units have none, one and two methoxyl groups, respectively. The proportion of H/G/S units in lignin largely depends on the biomass species. Softwood lignin has a high content of guaiacyl units, hardwood lignin presents a mixture of guaiacyl and syringyl units [16]. Since this small exotherm is also visible in the case of NaOH treated cotton, which does not contains lignin, it could arise from some internal rearrangement of the already pyrolized remainder. Further investigations will be performed in order to clarify the ongoing processes in this temperature interval.[6,7,8]

On figure 5, the quantitatively evaluated TG curve of the NaOH treated cotton is plotted against temperature, showing the characteristic mass losses fpr the previously determined Δ1 - Δ4 phases. Relevant mass loss values for each sample is given in table 1.

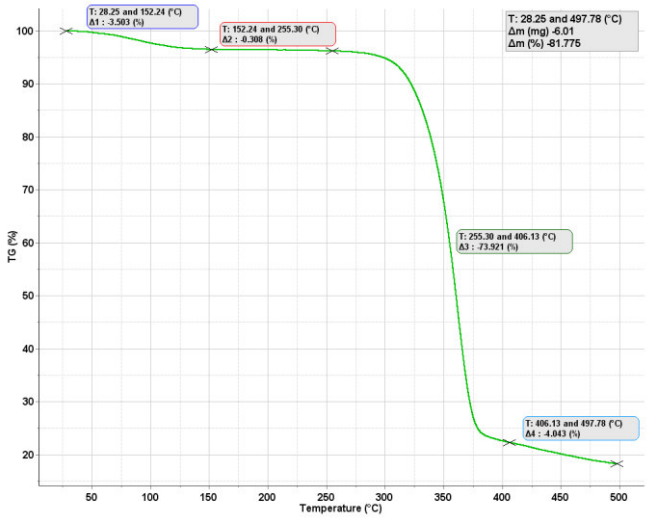


Figure 5. NaOH treated cotton's quantitatively evaluated TG curve (example)

Table 1: Mass loss values of blenched sulphates (poplar, bleech and pinewood) non-blenched sulphates (pinewood) blenched straw, NaOH cotton and testliner basepaper

Samples	Δ1 TG (%)	Δ2 TG (%)	Δ3 TG (%)	Δ4 TG (%)
Non- blenched sulphate pine	4.522	0.502	69.544	4.989
Blenched straw	5.223	0.327	61.837	6.848
Blenched sulphate beech	4.390	0.378	65.636	7.394
Blenched sulphate pine	4.149	0.738	70.215	5.228
Blenched sulphate poplar	4.906	0.435	64.328	6.495
NaOH treated cotton	3.503	0.308	73.921	4.043
Testliner	4.734	0.644	54.996	6.131

CONCLUSIONS

In this present research, thermal behaviour of corrugated packaging paper and itscomponents were investigated. It was found, that all samples contain a few percents of moisture, the depolymerization of the hemicellulose can not be observed under the used experimental conditions. At higher temperatures, the thermal decomposition of hemicellulose and cellulose takes place, which can be clearly separated and visible on the DTG curves. Additionally, the intensity of the shoulders (on the DTG curves) on the lower temperature side of the main decomposition process is characteristic to the lignin content of the sample. Above 400 °C up to the end of the measurements the degradations of the lignin are taking place, or some internal rearrangements in the pyrolized mass could also take place in this phase.

REFERENCES

[1] Ball, R., McIntosh, A. C., & Brindley, J. (2004). Feedback processes in cellulose thermal decomposition: implications for fire-retarding strategies and treatments. Combust. Theor. Model. 8 (2): 281-291. doi:10.1088/1364-7830/8/2/005

[2] Böröcz, P., Pidl, R., Tóth, B. (2016). Thermo-Analytical Technique to Analize the Quality of Paper for Packaging. J. App. Packag. Res., 8(1): Article 6. 31-37. https://scholarworks.rit.edu/japr/vol8/iss1/6

[3] Ibrahim, S. F., El-Amoudy, E. S., Shady, K. E. (2011). Thermal analysis and characterization of some cellulosic fabrics dyed by a new natural dye and mordanted with different mordants. Int. J. o Chem., 3(2): 40-54. doi:10.5539/ijc.v3n2p40

[4] Mackenzie, R. C., Mitchell, B. D. (1962). Differential thermal analysis. A review. Analyst, 87 (1035): 420-434.

[5] Pöhler, T., Jetsu, P., Fougerón, A., Barraud, V. (2017) Use of papermaking pulps in foam-formed thermal insulation materials. Nord. Pulp Pap. Res. J. 32 (3):367–374. doi:10.3183/npprj-2017-32-03-p367-374.

[6] Raunio, J., Asikainen, T., Wilo, M., Kallio, E., Csóka, L. (2020). Affecting the bonding between PLA fibrils and kraft pulp for improving paper dry-strength. Nord. Pulp Pap. Res. J. 35 (2): 185-194. doi:10.1515/npprj-2019-0033

[7] Raveendran, K., Ganesh, A., Khilar, K. C. (1995). Influence of mineral matter on biomass pyrolysis characteristics. Fuel. 74 (12): 1812-1822. doi:10.1016/0016-2361(95)80013-8

[8] Soares, S., Camino, G., Levchik, S. (1995). Comparative study of the thermal decomposition of pure cellulose and pulp paper. Polym. Degrad. Stab. 49 (2): 275-283. oi: 10.1016/0141-3910(95)87009-1

[9] Stewart, J. M. (1966). The characterization of a peat profile by thermal methods. Agrochimica, 11, 92-104.

[10] Tsujiyama, S. I., Miyamori, A. (2000). Assignment of DSC thermograms of wood and its components. Thermochim. Acta, 351 (1-2): 177-181. doi:10.1016/ S0040-6031(00)00429-9

[11] Yang, H., Yan, R., Chen, H., Zheng, C., Lee, D. H.,Liang, D. T. (2006). In-depth investigation of biomass pyrolysis based on three major components: hemicellulose, cellulose and lignin. Energy Fuels, 20 (1): 388-393. doi:10.1021/ef0580117

[12] Nadežda Števulova, Viola Hospodárova, Adriana Eštoková STUDY OF THERMAL ANALYSIS OF SELECTED CELLULOSE FIBRES; Geoscience Engineering, Volume LXII (2016), No. 3 p. 18-21, ISSN 1802-5420

[13] V. Ramiah THERMOGRAVIMETRIC AND DIFFERENTIAL THERMAL ANALYSIS OF CELLULOSE, HEMICELLULOSE, AND LIGNIN, Journal of Applied Polymer Science vol. 14, pp. 1323-1337 (1970)

[14] Raj Kumar, Vishal Sharma, Neha Verma, Pawan Kumar Diwan, Vinay Kumar & Vijay Kumar, Analysis of writing/printing paper via Thermogravimetric Analysis: application in forensic science, Australian Journal of Forensic Sciences, DOI: 10.1080/00450618.2017.1310921.

[15] Nadežda ŠTEVULOVA, Viola HOSPODÁROVA, Adriana EŠTOKOVÁ,STUDY OF THERMAL ANALYSIS OF SELECTED CELLULOSE FIBRES, GeoScience Engineering Volume LXII (2016), No. 3, p. 18-21, ISSN 1802-5420, HTTP://GSE.VSB.CZ

[16] Shurong Wang, Gonxin Dai, Haiping Yang, Zhongyang Luo, Lignocellulosic biomass pyrolysis mechanism: A state-of-the-art review, Progress in Energy and Combustion Science, 62 (2017) 33-86, DOI: 10.1016/j.pecs.2017.05.004.

Corresponding author:

Barnabás TÓTH
ÓE-ATDI
Bécsi út 96/B
Budapest 1034, Hungary
+36304850802
barnabas_zoltan.toth@icloud.com