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THERMOGRAVIMETRIC ANALYSIS OF COMMERCIAL THERMALLY MODIFIED WOOD

In the article the results are shown of a thermogravimetric analysis of four thermally modified wood species. Thermally modified wood before and after the extraction process was used for the tests. The extraction process had no significant effect on changes in the thermal characteristics either in the raw wood or in the modified wood, irrespective of the tested wood species.

Keywords: wood modification, thermal modification, thermogravimetric analysis, mass loss, temperature

Introduction

Thermal modification of wood was first applied in the 1920s [Jämsä, Viitaniemi 1998], although since then wood modification methods have developed considerably, particularly with the use of high temperatures [Boonstra et al. 1998; Jämsä, Viitaniemi 1998; Garrote et al. 1999; Rapp et al. 2000; Syrjanen et al. 2000], which in some cases has led to their commercial application. The primary objective of thermal modification is to partly reduce the hydrophilic properties of wood. This is facilitated by a change in the chemical structure of the wood, resulting in the formation of environmentally friendly “thermowood”, containing no additional chemicals and produced by the application of steam and temperature. As a result of chemical reactions, the wood colour changes and the higher the applied temperature and the longer the process, the more intensive the colour becomes. The main wood components, i.e. lignin and cellulose, are responsible for the change in colour and an increased resistance to UV radiation [Grzeškiewicz 2003; Dekka et al. 2008].

After modification, wood has a characteristic aroma, which is probably caused by the release of furfural, terpenes and acetic acid [Militz 2002; www.finnforest.com]. Another characteristic of modified wood is connected with the moisture content, which decreases by approx. 50% in comparison to that of non-modified

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wood. Thanks to a reduction in its moisture content, the wood strength and resistance to biodegradation increases. The chemical composition of wood changes as a result of the modification process. Cellulose and lignin are degraded at higher temperatures than hemicellulose. Other components are also readily degradable. During heating, changes occur both in the cellulose and hemicellulose. High temperatures reduce the strength of the cellulose chain bonds, then they reduce the degree of polymerisation and crystallisation of the cellulose. Heated air contributes to the formation of carbonyl groups and carboxylic acid esters through the oxidation of the hydroxyl ion groups of cellulose. Prolonged heating leads to an increase in the number of carbonyl groups at the expense of carboxylic acids [ThermoWood Handbook 2003; Hill 2006; Metsa-Kortelainen et al. 2006]. As a result of heating, acetic acid acts as a catalyst in the hydrolysis of hemicelluloses. Hemicelluloses are degraded at a temperature of 200–260°C, while cellulose is degraded at 240–350°C. Insulation properties are improved and dimensional stability also changes. The change in hygroscopicity and the improvement in dimensional stability are explained by the fact that cellulose microfibrils are surrounded by a permanent and non-elastic network comprising cross linkages formed in the lignin structure. Cellulose microfibrils exhibit a limited swelling capacity, thus reducing their susceptibility to increased water penetration [Tjeerdma et al. 1998]. Apart from the reduced moisture content, certain nutrients required for fungal development are eliminated [Vernois 2000; Mazela et al. 2003; Mazela et al. 2010]. Changes in the composition in the course of modification depend on [Hill 2006; Huber 2006]:

- the maximum temperature and duration of the process,
- the gradient of the temperature,
- the atmosphere of the process,
- the pressure,
- the moisture content and species of wood,
- the process and its parameters,
- the dimensions of the modified elements,
- the application of the catalysts.

As a result of the thermal modification of the wood, its mechanical strength decreases. This disadvantage is connected with an increase in cleavability and a deterioration in bending strength by 10–20%, as well as a decrease in compressive strength. Wood becomes brittle. For this reason, this type of wood should not be used in load-carrying structures and should not be in direct contact with the subsoil. Another drawback is the slower absorption of water-based adhesives and lacquers. This process is typically 3 to 6 times longer and its duration increases with modification temperatures [Jabłoński 2005]. Literature concerning studies on the properties of thermally modified wood contains a limited body of data on the behavior of this material under the influence of high thermal radiation [Grzeškowiak, Bartkowiak 2010a, 2010b].

Materials and methods

Analyses were conducted on modified wood coming from a commercial wood modification plant. The analyses were conducted on thermally modified oak, ash, poplar and locust wood, both before and after extraction carried out under laboratory conditions. Before the modification process, the elements were pre dried in the drying kiln, for a time period relating to the wood species, to obtain 8% moisture content. The temperature, humidity and airflow speed were automatically adjustable and related to the initial moisture and dimension of the wood elements. Reference material was taken after pre-drying and before the modification process. The wood samples were collected at random from batches modified in the atmosphere of steam under different conditions:

- oak – temperature 185°C, time 3 hours
- ash – temperature 195°C, time 3 hours, and 205°C, 3 hours
- locust – temperature 165°C, time 3 hours
- poplar – temperature 165°C, time 3 hours.

The wood was collected in the form of deck and parquet boards as well as timber. The samples of raw wood, the parquets prepared for modification and the control samples were collected for comparison. Additionally, steamed locust wood was sampled (temperature 105°C). The samples for thermogravimetric analyses came from individual randomly selected elements. The elements from the reference and modified materials were conditioned for 14 days at a temperature of $23\pm 2^\circ\text{C}$ and humidity of $65\pm 5\%$. The wood was shredded and then ground. The ground material was sieved through a set of sieves with a mesh size of 0.5–1 mm. The thermogravimetric analyses were conducted on the ground fraction with a grain size < 0.5 mm. Extraction was run in a Soxhlet apparatus using an alcohol/benzene mixture (1:1, v/v) in order to reduce the effect of the extractives on the thermal characteristics of the wood, as well as in order to conduct a chemical analysis and determine the contents of individual wood components. After extraction, the wood was dried at 105°C for 24 h until constant mass.

Thermogravimetry (TG) consists of recording changes in the sample mass during heating as a function of time or temperature (polythermal measurements) or changes in the mass under isothermal conditions as a function of time.

TG analysis makes it possible to plot curves for the changes in the mass of the tested samples as a function of temperature or measurement time. The results of TG analyses facilitate the presentation of the thermal characteristics of the tested material, including e.g.:

- determination of the initial breakdown temperature,
- identification of the range of temperatures in which degradation occurs dynamically (the area of active thermolysis),

- identification of the temperatures in which thermolysis reaches the maximum value (maximum decomposition rate, temperature of extreme decomposition rate),
- determination of the mass losses at individual stages of thermal destruction.

The thermogravimetric analysis was conducted using a Labsys™ thermobalance by Setaram. Measurements were taken up to a temperature of 600°C with a temperature rise rate of 5°C/min in a helium atmosphere. The tests were performed in three replications for each analytical variant (the results presented are the averaged results from the replications).

Results

The thermal decomposition of lignocellulose materials is a two-stage process. The first degradation stage affects the carbohydrate fraction of the material (hemicelluloses, cellulose), while aromatic compounds (lignin) – due to their greater thermal resistance – break down at higher temperatures. This fact is reflected in the DTG and TG curves recorded during the thermolysis of the natural and modified wood.

When analysing the thermograms, the initial temperature of the thermal decomposition of the modified oak samples (D185 and D185/E) increased in comparison to the initial samples (D and D/E) (table 1, figs. 1 and 2).

Table 1. Thermal characteristics of original and modified oak wood (before and after extraction)

Material	Area of active thermolysis [°C]	Thermal decomposition stages [°C]	Max. temp. of decomposition rate [°C]	Max. decomposition rate [%/min]	Weight [%]	
					in the area of active thermolysis	to 600°C
Oak control (D)	200–366	- -	285 332	2.0 5.5	58.0	73.2
Oak thermo 185°C/3h (D185)	206–366	- -	282 332	1.8 6.2	58.2	72.1
Oak control after extraction (D/E)	196–366	- -	279 335	2.1 5.7	58.7	74.3
Oak thermo 185°C/3h after extraction (D185/E)	206–365	- -	286 334	1.8 6.0	58.6	70.4

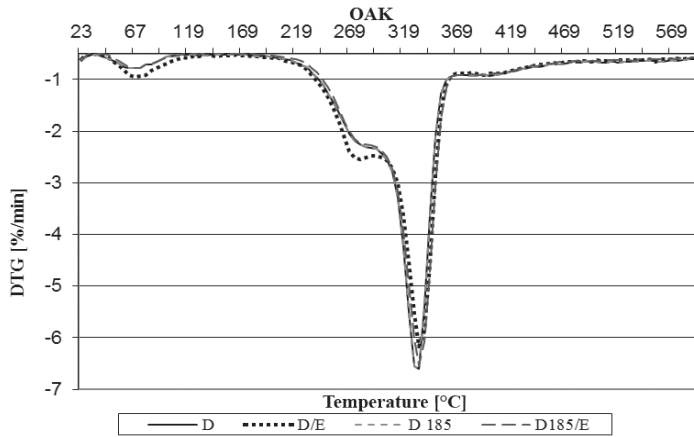


Fig. 1. DTG curves of oak wood

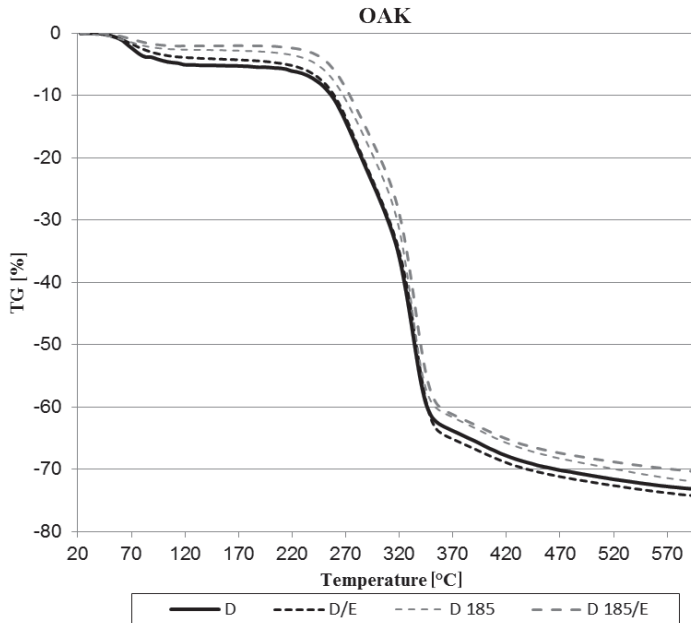


Fig. 2. TG curves of oak wood

The thermolysis of the tested oak wood ran in two overlapping stages (connected with the thermal decomposition of the structural wood components). The temperatures at which the samples of the control (D) and modified oak wood (D185) reached extreme decomposition rates were comparable. The maximum destruction rates in the first stage in the modified and extracted oak wood (D185/E) were reached at a temperature several degrees higher (286°C) than in the case of the extracted non-modified wood (D/E) (279°C). The temperatures of thermo-

lysis extremes for the second stage of the discussed experimental material were comparable. The final temperatures of active thermolysis areas for the tested oak wood (D, D185, D/E, and D185/E) were similar. Thermal destruction in the areas of active thermolysis caused a mass loss amounting to approx. 58% in all the tested oak wood samples. In turn, the total mass loss determined at a temperature of 600°C in the modified wood (D185 and D185/E) was lower in comparison to the original wood (D and D/E).

Table 2. Thermal characteristics of original and modified ash wood (before and after extraction)

Material	Area of active thermolysis [°C]	Thermal decomposition stages [°C]	Max. temp. of decomposition rate [°C]	Max. decomposition rate [%/min]	Weight [%]	
					in the area of active thermolysis	to 600°C
Ash control (J)	195–372	- -	288 343	2.1 5.6	64.8	76.4
Ash thermo 195°C/3h (J195)	200–377	- -	288 342	1.9 5.5	61.1	72.5
Ash thermo 205°C/3h (J205)	191–375	-	340	5.9	60.6	69.8
Ash control after extraction (J/E)	189–384	- -	295 338	2.2 4.4	64.0	71.6
Ash thermo 195°C/3h after extraction (J195/E)	198–373	- -	288 342	2.0 5.9	61.7	73.7
Ash thermo 205°C/3h after extraction (J205/E)	192–375	-	341	6.4	62.3	73.3

The thermal decomposition of the ash wood (J) was initiated at a temperature of 195°C. The onset of thermolysis for the ash thermowood (J195) was recorded at 200°C, while for the J205 sample it was at 191°C (table 2). The thermal decomposition of the non-modified wood and wood exposed to a temperature of 195°C occurred in two overlapping stages. The extremes of decomposition rates and temperatures at which they were reached were comparable for the raw and thermally modified ash wood. In the case of the Thermo205 sample, one decomposition extreme at 340°C was established on the DTG curve (figs. 3 and 4).

The dynamics of the thermolysis of the raw ash wood (J) were reduced at 372°C, while for the thermally modified wood, this temperature was 377°C for sample J195 and 375°C for sample J205, respectively. The higher the wood modification temperature, the lower the mass loss of the modified ash wood (J195 and J205), caused by thermal degradation in the area of active thermolysis and at a temperature of 600°C.

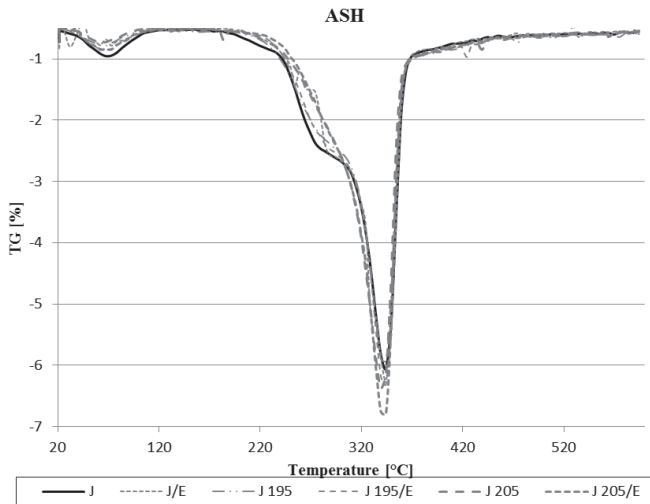


Fig. 3. DTG curves of ash wood

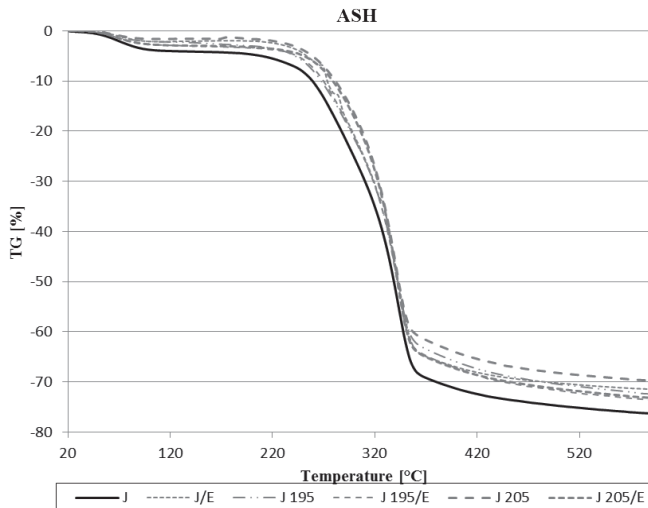


Fig. 4. TG curves of ash wood

The recorded thermograms indicated an increase in the initial thermolysis temperature of the thermally modified and extracted wood (J195/E and J205/E) in

comparison with the extracted control wood. Moreover, the ash wood Thermo205 was characterised by a lower temperature of the onset of thermolysis than the Thermo195 ash wood. Pyrolysis of the extracted raw wood (J/E) and the wood exposed to a temperature of 195°C (J195/E) occurred in two stages in contrast to the thermal destruction of the Thermo205 ash wood (J205/E). For the original extracted ash wood (J/E) and the Thermo195 sample (J195/E), similar values were observed for the maximum decomposition rates in the first stage. However, the temperature at which the extreme was reached was higher for the extracted non-modified wood (J/E). The second stage of thermolysis for the extracted Thermo195 ash wood (J195/E) was characterised by a higher temperature of the maximum decomposition rate and a higher maximum decomposition rate in comparison to the extracted control wood (J/E). In the case of the thermolysis of the extracted Thermo205 ash wood (J205/E), only one decomposition extreme at 341°C was observed. The intensity of the pyrolysis of the thermally modified ash wood after extraction (J195/E and J205/E) decreased at a temperature approx. 10°C lower than that of the extracted raw wood. The temperatures finishing the active pyrolysis of the extracted modified wood were comparable. The mass loss of the extracted modified wood (J195/E and J205/E) at 600°C was approx. 2% greater than in the case of the control material (J/E).

Table 3. Thermal characteristics of thermally modified locust wood (before and after extraction)

Material	Area of active thermolysis [°C]	Thermal decomposition stages [°C]	Max. temp. of decomposition rate [°C]	Max. decomposition rate [%/min]	Weight [%]	
					in the area of active thermolysis	to 600°C
1	2	3	4	5	6	7
Locust control (R)	206–372	- -	289 343	1.6 6.5	56.3	69.5
Locust thermo 165°C/3h (R165T)	203–372	203–229	222	0.3	1.0	70.8
		231–309	248	0.8	18.1	
		-	273	0.5		
		-	289	1.6		
		-	303	1.8		
		310–372	344	6.2	38.2	
Locust steamed 105°C (R105P)	193–375	- -	292 346	1.6 6.3	59.4	72.2

Table 3. Continued

1	2	3	4	5	6	7
Locust control after extraction (R/E)	208–374	- -	282 347	1.9 6.8	63.4	75.7
Locust thermo 165°C/3h after extraction (R165T/E)	192–370	192–219 222–309 - - - -	210 242 274 290 303 345	0.2 0.5 1.5 1.7 1.9 6.5	0.5 18.0	69.6
Locust steamed 105°C after extraction (R105P/E)	192–376	- -	291 347	1.7 6.6	61.6	73.6

The conducted thermal analysis indicated a reduction in the initial decomposition temperature for the thermally modified locust wood (R) both before and after extraction (R165T, R105P, R165T/E, and R105P/E) in comparison to the respective control wood (R and R/E) (table 3, figs. 5 and 6). The steamed locust wood (R105P) had a lower temperature at the onset of pyrolysis than the thermowood sample (R165T). In turn, the samples of modified and extracted locust wood had the same initial thermolysis temperature (192°C).

The original wood (R and R/E) and steamed wood (R105P and R105P/E) had thermal spectra typical of lignocellulose materials, i.e. in the area of active thermolysis, two overlapping decomposition stages could be identified. The temperature of the maximum decomposition rate for the steamed locust (R105P and R105P/E) in the first stage was higher than that of the respective control wood (R and R/E). In the second stage, the maximum temperatures of the decomposition rate for the raw and steamed wood samples were comparable. The values of the maximum decomposition rates in the second stage were similar for the steamed and control samples. The locust thermowood (R165T and R165T/E) was characterised by a rich thermal spectrum. In the area of active thermolysis, several separate stages of decomposition and overlapping stages could be distinguished. The final temperatures of the enhanced thermal destruction for the tested samples of modified wood (R165T, R105P, R165T/E, and R105P/E) and raw wood (R and R/E) ranged from 370°C to 376°C. The mass loss at the assumed final temperature of the steamed locust wood (R105P) was higher in comparison with the control

wood (R), while that of the extracted steamed locust wood (R105P/E) was lower than for the respective control wood (R/E). A similar dependence was observed for the locust thermowood (R165T, R, R165T/E, and R/E). The steamed locust wood underwent thermolysis to a greater degree in comparison to the samples of locust thermowood, as manifested by higher total mass losses recorded for the steamed wood.

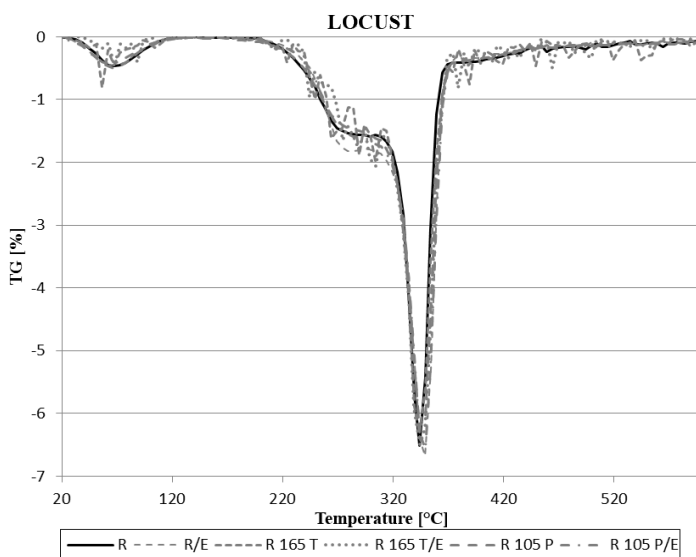


Fig. 5. DTG curves of locust wood

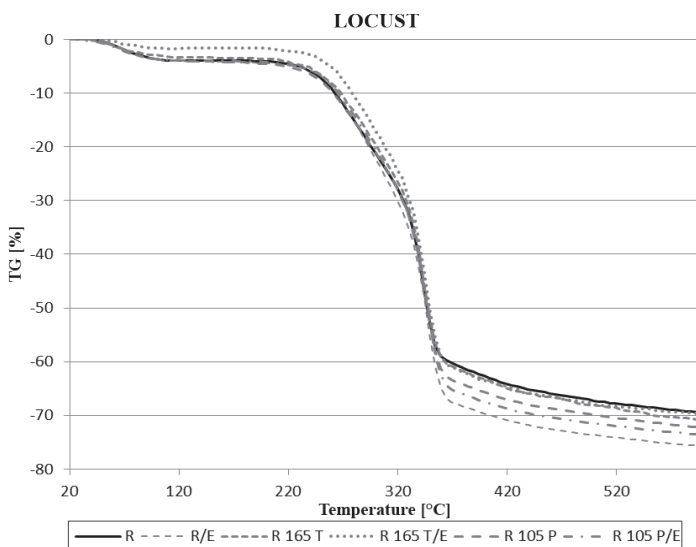
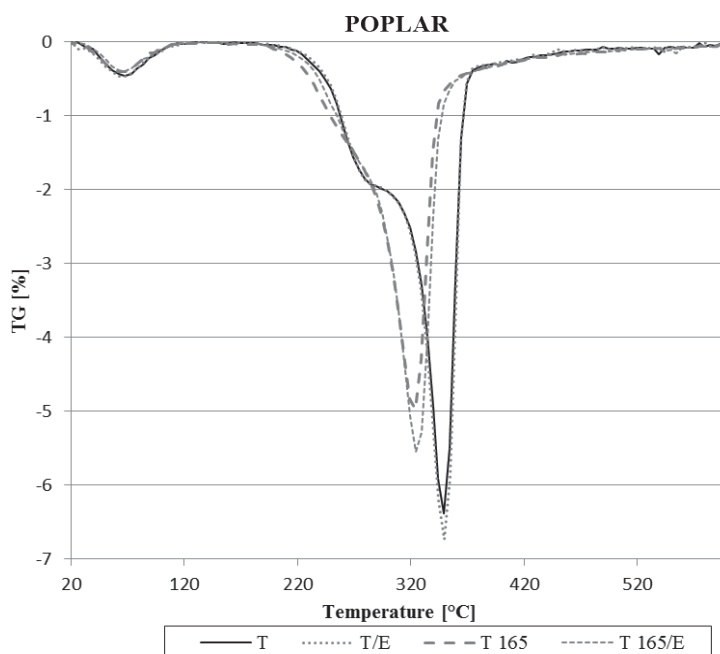


Fig. 6. TG curves of locust wood

Table 4. Thermal characteristics of thermally modified poplar wood (before and after extraction)

Material	Area of active thermolysis [°C]	Thermal decomposition stages [°C]	Max. temp. of decomposition rate [°C]	Max. decomposition rate [%/min]	Weight [%]	
					in the area of active thermolysis	to 600°C
Poplar control (T)	202–382	- -	290 348	2.0 6.4	66.9	77.00
Poplar thermo 165°C/3h (T165)	191–380	- -	262 322	1.4 4.9	56.4	67.5
Poplar control after extraction (T/E)	203–379	- -	291 349	2.0 6.8	68.1	78.6
Poplar thermo 165°C/3h after extraction (T165/E)	194–378	- -	265 325	1.4 5.6	58.9	69.5

**Fig. 7. DTG curves of poplar wood**

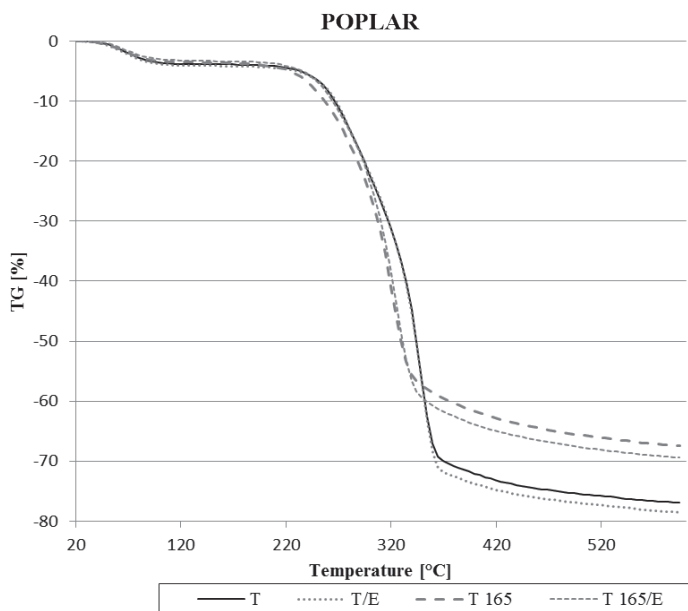


Fig. 8. TG curves of poplar wood

The data obtained from the thermogravimetric analysis indicated a reduction in the initial thermolysis temperature for the samples of extracted and non-extracted modified poplar wood (T165 and T165/E), in comparison to the respective control samples (T and T/E) (table 4, figs. 7 and 8).

The thermal destruction of all the tested samples occurred in two overlapping decomposition stages. The temperatures of the maximum decomposition rates for the modified poplar wood (T165 and T165/E) were lower than those determined for the raw wood (T and T/E). The temperatures at which the dynamics of thermolysis decreased were similar for all the tested poplar wood variants. The mass losses caused by the thermolysis of the poplar thermowood (T165 and T165/E) were lower than those for the respective control wood (T and T/E), both in the area of active thermolysis and those determined at the final measurement temperature, i.e. 600°C.

Conclusions

From the conducted analyses it can be concluded that the extraction process had no significant effect on changes in the thermal characteristics either in the raw wood or modified wood, irrespective of the tested wood species.

The courses of the DTG and TG curves for the control and modified wood, non-extracted and extracted, were similar, which resulted in similar thermal characteristics of the tested wood. An exception in this respect was found for poplar

wood modified at a temperature of 165°C for both variants: non-extracted (T165) and extracted (T165/E), for which a marked reduction was observed for the initial temperature of thermolysis in comparison to the respective control samples.

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