Thermogravimetry as a possible tool for determining modification degree of thermally treated Norway spruce wood

**Romana Cerc Korošec · Barbara Lavrič ·
Gregor Rep · Franc Pohleven · Peter Bukovec**

Abstract Thermal treatment is one of environmental friendly wood modification processes, developed in order to improve wood's natural durability and dimensional stability. Beside wood species, mainly isothermal temperature of heat-treatment and process duration affect these properties, which also correlate with the mass losses caused by the treatment. However, there is a lack of suitable external quality control methods. In this work thermogravimetry as a potential method for determining the degree of thermal modification is presented. Several calibration curves, representing the mass losses in a certain temperature range (the values obtained from the TG curves) compared to weight losses caused by previous heat-treatment (known values), were established for spruce wood samples modified at different isothermal temperatures (from 170 to 220 °C). Linear plot and good correlation factors ($R^2 = 0.95$ and 0.96) were obtained for the TG mass losses from 130 to 280 °C and from 130 to 300 °C, both under nitrogen atmosphere. The predominant cause of mass loss in this temperature region was depolymerisation and thermal decomposition of hemicelluloses residues. Lower correlation factors were obtained under the air atmosphere and in the wider temperature range, respectively.

Keywords Thermal treatment · Wood modification · Wood · Spruce · Thermogravimetry · Calibration curve · Monitoring

R. Cerc Korošec (✉) · B. Lavrič · P. Bukovec
Faculty of Chemistry and Chemical Technology, University of Ljubljana, Aškerčeva 5, SI-1000 Ljubljana, Slovenia
e-mail: romana.cerc-korosec@fkkt.uni-lj.si

G. Rep · F. Pohleven
Biotechnical Faculty, Department of Wood Science and Technology, Rožna dolina, Cesta VIII/34, SI-1000 Ljubljana, Slovenia

Introduction

Several environmental friendly wood modification processes have been developed and optimized in order to improve its natural durability, dimensional stability, and to diminish its hygroscopicity. One of them is thermal treatment, where wood is heated at elevated temperatures (from 160 to 260 °C) under different atmospheres (steam, nitrogen, vacuum) in the absence of oxygen. During heat-treatment a multitude of chemical reactions take place in the cell wall, leading to improved properties. The wood cell wall consists mainly of hemicellulose, cellulose and lignin; pectin, starch, extractives and inorganic salts are included in much smaller quantities [1]. Due to the complex wood structure many methods have been used to determine the sequence of chemical reactions which take place during heat-treatment: infrared spectroscopy [2–4], magnetic resonance spectroscopy [5, 6], X-ray diffraction [7] and chemical analysis (determination of lignin content, elemental analysis and GC-MS) [8–10]. Since heat-treated wood has already been produced on industrial scale and its properties strongly depend on process parameters, a development of a reliable and rapid method for post-evaluation of the process quality is presently needed. With the help of multivariate chemometric method, Kotilainen and co-workers have successfully solved this problem by measuring FTIR spectra [2] or reflectance UV/Vis spectra [11] of the representative samples with known mass losses and compared them to the unknown ones. The lack of a simple and established standardised external method for controlling a degree of thermal treatment has focused us on the question whether there is a correlation between this parameter and additional mass loss of a sample during TG measurement within a certain temperature range.

Thermogravimetry (TG) and differential scanning calorimetry (DSC) as complementary methods of thermal

analysis were in the past used for a variety of studies made on wood samples, but to our knowledge never for determining a degree of heat-treatment. In the article written by Tinh and co-workers thermal analysis of lignocellulosic materials is reviewed in 187 references [12]. Kinetic modeling and studies on thermal decomposition of cellulosic and lignocellulosic materials were performed on the basis of dynamic and isothermal TG measurements [13–15] while thermal degradation of wood treated with fire retardants was studied with both, TG and DSC techniques [16–20]. DSC was also used for characterization of wood for musical instruments [21], to determine softening temperature of moist wood [22] and as a complementary tool in wood biodegradation studies [23]. The influence of heat treatment temperature and duration on the swelling of thermally modified wood was also investigated. DSC was applied to determine fiber saturation point [24]. DSC curves of wood and its components obtained in static air atmosphere were explained by Tsujiyama and Miyamori [25]. Cellulose and lignin content was quantitatively determined thermogravimetrically from the mass loss of the wood sample in a certain temperature range [26, 27]. However, it is difficult if not impossible to make such a determination accurately due to simultaneous decomposition reactions taking place in both constituents during heating [6, 10].

The purpose of this study was to find a good calibration curve, which represents mass loss in a certain temperature range, obtained from TG curves, compared to mass loss obtained during previous heat-treatment (known values). A set of spruce wood samples heat-treated in a temperature range from 170 to 220 °C was investigated. Thermal decomposition, which was not completed during heat-treatment, had continued in wood samples during TG measurements. At the end the most promising results are discussed together with future research perspective.

Experimental

Wood blocks (dimensions $t \times r \times l$: 20 mm × 20 mm × 10 mm) of the same Norway spruce (*Picea abies* (L.) Karst) pole were put into the vacuum-pressure chamber and isothermally treated for three hours at 170, 180, 190, 200, 210 and 220 °C, respectively. A detailed heat-treatment procedure description has been published elsewhere [28]. Five woodblocks were prepared for each process (temperature), except for 200 °C where only four samples were investigated. The samples were first oven-dried at 103 ± 2 °C for 12 h and weighted before and after the heat treatment. The mass losses of dry specimens varied from 0.52% (after isothermal treatment at 170 °C) to 8.58% (after isothermal treatment at 220 °C). Mass loss for each separate sample is given in Table 1. After thermal

treatment the blocks were milled and sieved to obtain particles smaller than 1 mm. Untreated samples (control) were also examined.

Dynamic thermogravimetric measurements were performed on a Mettler Toledo TG/SDTA 851^e instrument under a dynamic nitrogen, air or oxygen flow with a flow rate of 100 mL min^{-1}. Temperature range was from 25 to 600 °C in the case of nitrogen atmosphere and from 25 to 500 °C in an air or oxygen atmosphere. Heating rate was always 5 K min^{-1}. Approximately 10 mg of milled wood sample was placed in a platinum crucible with a diameter of 8 mm. A baseline was subtracted in all measurements.

Temperature calibration of the TG/SDTA instrument was performed at two temperatures using indium and aluminum calibration standards. Both metals were provided by Mettler Toledo. Mass was automatically internally calibrated with two well-defined calibration weights.

Results and discussion

Norway spruce contains 40–46% of cellulose and 27–28% of lignin [29]. The rest represents predominantly hemicellulose, which is mainly composed of glucomannans and xylan. This fraction, due to the lack of crystallinity, shows a lower thermal stability in comparison with cellulose, which is a linear homopolysaccharide. Lignin exhibits high structural diversity and degrades gradually over a wider temperature range than carbohydrates. Deterioration of hemicelluloses already begins at or below 180 °C [6] and of lignin from 250 to 450 °C [30, 31]. The minimum temperature for the decomposition of cellulose crystals in an inert atmosphere is considered to be between 300 and 360 °C [7].

Figure 1 represents dynamic TG curves of thermally untreated sample in nitrogen, air and oxygen atmosphere. The first step from room temperature up to 130 °C is a dehydration process and takes place, as expected, very similar in all three types of atmospheres used. The mass losses during this process were from 6 to 7%. After that, thermal decomposition of a wood sample depends very much on the oxygen partial pressure in the gas phase. In a dynamic oxygen flow thermal decomposition occurs in one sharp step slightly below 300 °C, while under an air and nitrogen atmosphere this is at least a two-step process. Under an air atmosphere mass loss is around 60% in a temperature range between 200 and 325 °C and an additional 33% from 325 to 440 °C. The former is mainly ascribed to thermal degradation of hemicellulose and cellulose fibers. Lignin deterioration begins at a slow rate already at 200 °C, but mainly takes place during the second step [10]. After thermal decomposition a residual mass between 0.2 and 0.3% was obtained in oxidative gases, corresponding to the presence of inorganic salts [1]. In

Table 1 Weight losses of wood samples during three-hours isothermal treatment and their mass losses during additional TG measurements

Sample preparation		TG measurements under nitrogen atmosphere			TG measurements in an air atmosphere	
Thermal tratment	Δm during thermal treatment/%	Δm [26–130 °C]/% (Fig. 3)	Δm [130–280 °C]/% (Fig. 5a)	Δm [130–300 °C]/% (Fig. 5b)	Δm [26–130 °C]/% (Fig. 7)	Δm [130–250 °C]/% (Fig. 8)
Untreated	0	6.68	7.38	14.25	6.28	3.40
Untreated	0	7.25	7.33	14.03	6.18	3.25
Untreated	0	6.55	7.77	14.58	6.08	3.45
Untreated	0	6.59	7.18	14.03	6.17	3.16
Untreated	0	6.66	7.43	14.39	6.17	3.28
170 °C	0.52	5.71	6.94	13.80	5.68	2.95
170 °C	0.75	5.55	6.64	13.40	5.63	2.75
170 °C	0.85	5.96	6.76	13.53	5.75	2.77
170 °C	0.89	6.30	7.01	14.20	5.53	2.84
170 °C	0.66	6.13	6.64	13.18	5.23	2.79
180 °C	1.35	5.61	6.58	13.28	5.33	2.78
180 °C	1.33	6.53	6.67	13.28	5.23	2.60
180 °C	1.71	5.48	6.79	13.50	5.10	2.93
180 °C	1.71	5.46	6.75	13.45	4.99	2.80
180 °C	1.25	5.64	6.67	13.42	4.94	2.79
190 °C	3.29	5.14	5.51	11.98	4.65	2.14
190 °C	2.83	4.96	5.84	12.42	4.61	2.34
190 °C	2.71	5.00	5.56	12.16	4.58	2.06
190 °C	2.08	5.24	5.83	12.13	5.15	2.41
190 °C	2.12	5.40	6.16	12.97	5.47	2.36
200 °C	3.66	4.64	4.93	10.95	4.17	1.97
200 °C	3.98	4.66	4.92	11.20	4.35	1.97
200 °C	3.79	5.06	4.95	11.21	4.42	1.90
200 °C	4.27	4.88	5.21	11.51	4.50	2.24
210 °C	5.29	4.68	4.60	10.79	4.35	1.87
210 °C	5.65	4.53	4.45	10.50	4.27	1.84
210 °C	5.46	4.54	4.53	10.64	4.30	1.81
210 °C	5.78	4.39	4.55	10.56	4.25	1.81
210 °C	4.74	4.65	4.76	10.98	4.28	1.95
220 °C	8.20	4.11	3.85	9.37	3.90	1.59
220 °C	8.58	3.97	3.71	8.99	3.95	1.69
220 °C	8.22	4.15	3.61	8.93	4.08	1.58
220 °C	7.05	4.80	3.54	8.89	4.12	1.46
220 °C	8.20	4.26	3.47	8.49	4.17	1.80

nitrogen, the mass loss of 70% was observed from 200 to 375 °C. In this range all structural constituents thermally decompose, particularly hemicellulose already at lower temperatures. Pyrolysis of cellulose took place at temperatures higher than 300 °C. After 375 °C thermal decomposition became slow. The residual mass was 15.1% and is in good agreement with the observation of Bartkowiak and Zakrzewski [10] that mass losses during the pyrolysis of lignin up to 600 °C do not exceed 60%. The degree of thermal decomposition of cellulose is more than 80% up to this temperature.

TG curves of wood samples, thermally treated to a different degree, are presented in Fig. 2a. The magnification of the region from 25 to 150 °C is given in Fig. 2b. For the clarity from the seven curves (thermally untreated sample, treated at 170, 180, 190, 200, 210 and 220 °C) only four are represented. At first sight small differences are observed between them. Thermally treated wood retains some hydrophilicity and this is the reason why samples, kept under atmospheric conditions (relative humidity from 40 to 60%), rehydrated. The first mass loss in the range from 25 to 130 °C is therefore ascribed to dehydration. The amount of
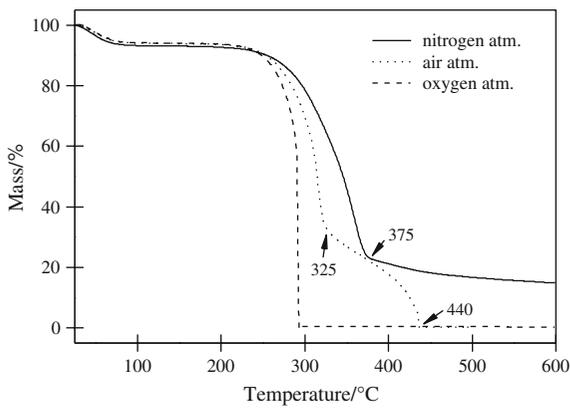
Fig. 1 Dynamic TG curves of thermally untreated spruce wood sample in three different atmospheres
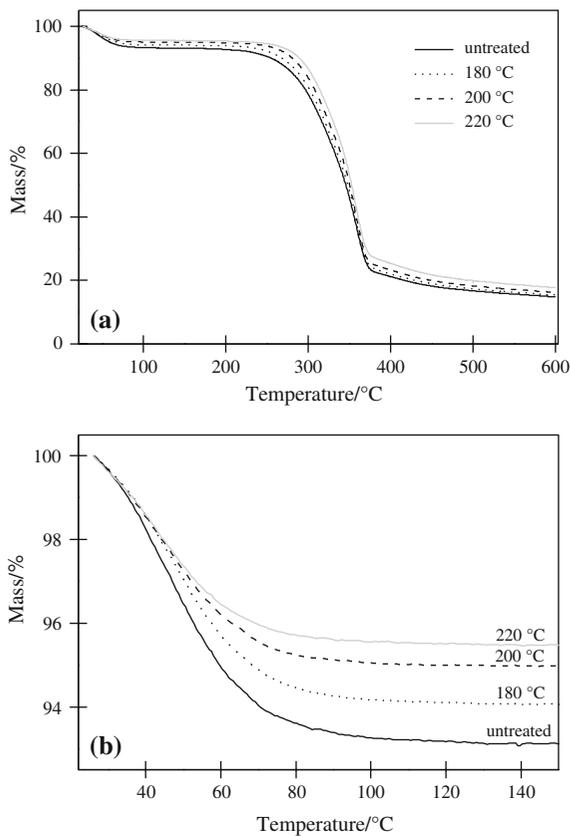

Fig. 2 TG curves of thermally untreated and previously isothermally treated spruce wood samples (they were exposed for three hours to 180, 200 and 220 °C under vacuum conditions). TG measurements were performed in nitrogen atmosphere (**a**) and the magnification of the mass loss curves in the temperature region from 25 to 150 °C (**b**)
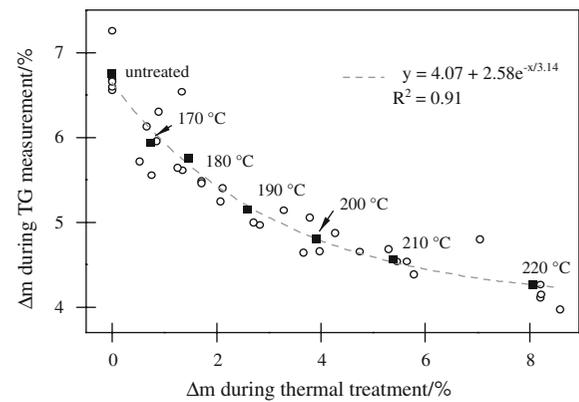

Fig. 3 Mass loss in a temperature range from 26 to 130 °C (obtained during TG measurements in nitrogen atmosphere) versus mass loss during thermal treatment (see Table 1). Circles represent each individual sample while filled squares calculated average values for each isothermal temperature

The heat-treatment of wood in the temperature range between 200 and 260 °C causes strong hemicellulose degradation with an important release of acetic acid [32]. Water and carbon oxides are also evolved [9]. A low pH and high temperatures are conditions which give rise to acidic hydrolysis of polysaccharides and lignin. The depolymerisation reactions mostly affect amorphous polysaccharides. The amount of generated free radicals increases sharply when the treatment temperature is over 200 °C. This leads to both depolymerisation and condensation reactions. Lignin cleavage and its autocondensation lead to formation of extensive hydrophobic polymeric network resembling lignin [6, 33]. The formation of lignin-carbohydrate complex was also observed [5, 25].

Dependence of the amount of rehydrated water on the mass loss during thermal-treatment is given in Fig. 3 and is exponential. The thermal treatment principally affects the most hydrophilic polymer of wood—hemicellulose, which undergoes dehydration reaction with the destruction of numerous hydroxyl groups. As a result, the treated wood has a low affinity to water and therefore a good dimensional stability [3]. Some authors attributed this stabilization to cross-linking of wood polymers during treatment [5]. Esterification of hydroxyl groups also result in a decreased hygroscopicity although its role is supposed to be minor compared to the influence of cross-linking [4]. Significant increase of wood hydrophobicity for wood samples treated between 130 and 160 °C was also explained by a modification of conformational arrangement of wood biopolymers due to the loss of residual water [34]. No noticeable mass loss was observed in this temperature range, indicating that no hemicellulose degradation occurred in this range. However, deterioration of hemicellulose already begins below 180 °C [6] and most probably the contributions of all above mentioned effects were observed in this experiment.
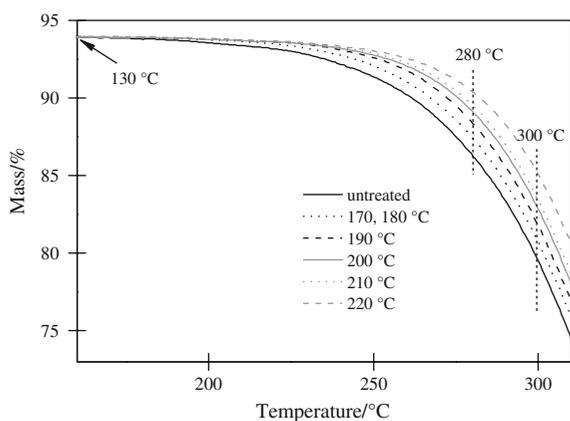
rehydrated water depends on the degree of previous thermal treatment (see Fig. 2b); wood samples thermally treated to a higher degree became more hydrophobic. Detailed explanation of this phenomenon is given under the description of Fig. 3. At higher temperatures (>200 °C) thermal decompositions, which had not been completed during previous heat-treatment in a vacuum chamber, continued.

Fig. 4 TG curves of the wood samples in a temperature region from 160 to 310 °C. The same curves as represented in Fig. 2a were in this Figure put at the same starting point at 130 °C
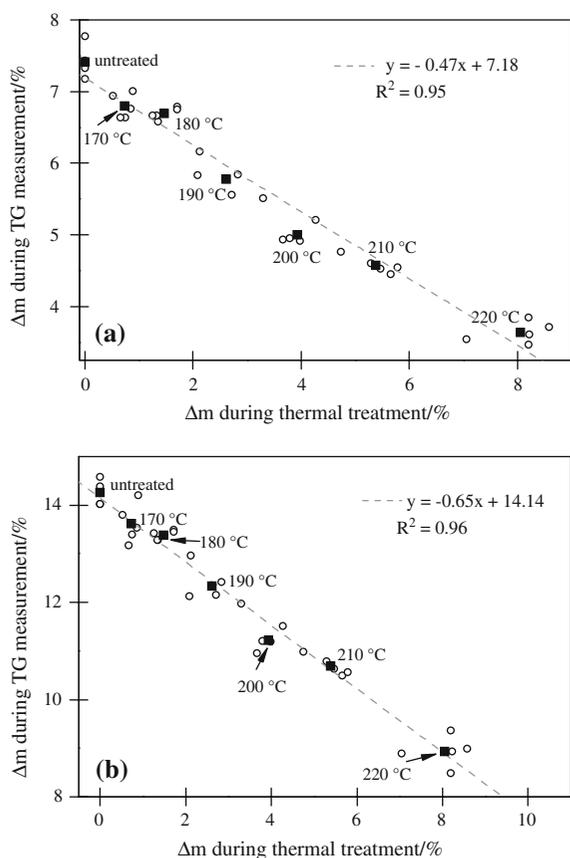

Fig. 5 Mass loss in a temperature range from 130 to 280 °C versus mass loss during heat- treatment (**a**) and a calibration curve in a range from 130 to 300 °C (**b**)

Neglecting the various amount of water in the samples, TG curves of different heat-treated samples were compared by putting the mass of all samples at the same starting point at 130 °C (Fig. 4). It can be clearly seen that the mass loss of less thermally treated samples is higher in the

temperature range from 200 to 310 °C as compared to more thermally treated samples. At temperatures higher than 250 °C the differences became more pronounced. From 280 to 300 °C there is a maximal difference in the mass loss between thermally untreated and the most thermally treated sample. For both mentioned temperature regions (from 130 to 280 and from 130 to 300 °C) calibration curves were constructed (Fig. 5a, b). Again circles represent each individual sample while filled squares calculated average values for the separate isothermal temperature. Obtained correlation coefficients were 0.95 and 0.96, respectively. At higher temperatures TG curves came closer together and some of them even overlapped. Consequently, for the wider temperature range (from 130 to 320 °C for instance or to 370 °C where a minimum of DTG curve is positioned) considerably lower values of R^2 were calculated.

As already seen in Fig. 1, TG curves under air atmosphere are different form those obtained in nitrogen atmosphere. Four various heat-treated samples are shown in Fig. 6a, b. In dynamic air-flow measurement hemicellulose and lignin started to thermally decompose at temperatures higher than 200 °C. Decomposition rate is maximal at around 300 °C. At
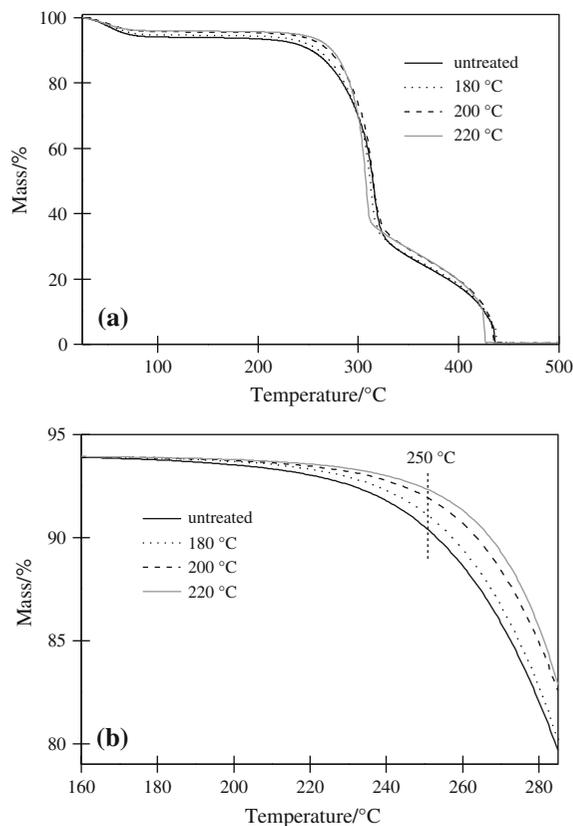

Fig. 6 TG curves of spruce wood samples under dynamic air atmosphere (**a**) and a magnification of the mass loss curves in the temperature range from 160 to 285 °C (**b**) where the curves were put at the same starting point at 130 °C

this temperature crystalline cellulose underwent depolymerisation and combustion. The majority of lignin content most probably decomposed during the last step.

A comparison of the amount of rehydrated water under an air and under nitrogen atmosphere is given in Fig. 7 (only average values are presented). The results should be the same but from figure a discrepancy of around 0.5% is observed. The reason for this deviation is that in a room where the samples were kept, relative humidity was lower during experiments performed in air atmosphere. It is believed that more promising results in this range would be obtained by controlling the RH and temperature of the room enabling for all samples to achieve the same equilibrium water saturation.

Correlation coefficients of calibration curves observed under an air atmosphere were much lower. The best obtained is presented in Fig. 8 and refers to a temperature range from 130 to 250 °C. Mass loss in this range is lower than between 130 and 280 °C in nitrogen atmosphere; the difference between untreated sample and of that exposed to 220 °C is approximately 2% whereas in nitrogen atmosphere it was 4%
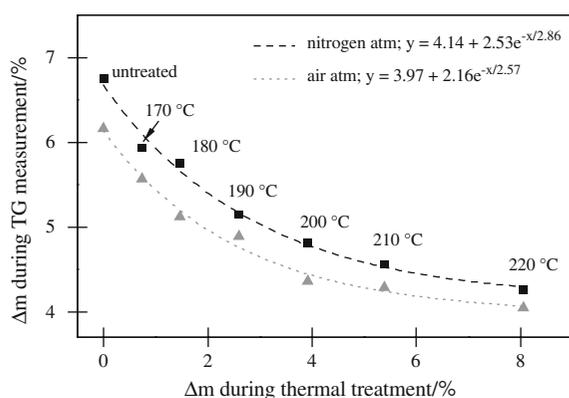
in the range from 130 to 280 °C and 6% in the range from 130 to 300 °C, respectively. Larger mass loss difference in the whole range means that a better distinction between similar spruce wood samples can be made.

Conclusions

Thermogravimetry could be a useful tool for determining a modification degree of heat-treated samples of the individual species. The obtained results showed that there was a different content of hemicelluloses and/or hemicelluloses residues in spruce wood samples, which were isothermally modified for three hours under vacuum at 170, 180, 190, 200, 210 and 220 °C, respectively. The amount of rehydrated water (i) and thermal stability of modified spruce wood samples (ii) can be followed by thermogravimetry.

(i) Samples stored under ambient conditions (room temperature, 40–60% relative humidity) rehydrated. Higher degree of heat-treatment led to lower hemicelluloses content and consequently to lower affinity to water. The amount of rehydrated water therefore correlated with a degree of heat-treatment; the dependence is exponential. Since dehydration is not dependent on the type of the atmosphere used, similar results ware expected in both atmospheres (nitrogen and air). The observed discrepancy suggests that it would be worth to study more carefully the moisture content of milled, heat-treated samples, pre-equilibrated at constant ambient humidity.

(ii) Thermal decomposition, which was not completed during heat-treatment, had continued in wood samples during TG measurements. In temperature regions where calibration curves were constructed, depolymerisation and thermal decomposition of hemicellulose was predominant reason for the mass loss. Due to lower hemicelluloses content, lower mass loss during TG measurements in the range from 130 to 300 °C (nitrogen atmosphere) or from 130 to 250 °C (air atmosphere) exhibited samples, thermally treated at higher temperatures. Calibration curves, representing mass loss during TG measurements versus mass loss during previous heat-treatment, show good correlation. The best correlation factor (0.96) was obtained for a temperature range from 130 to 300 °C under nitrogen atmosphere.

Fig. 7 A comparison of a mass loss in a temperature range from 25 to 130 °C versus mass loss during thermal treatment, obtained under nitrogen and air atmosphere
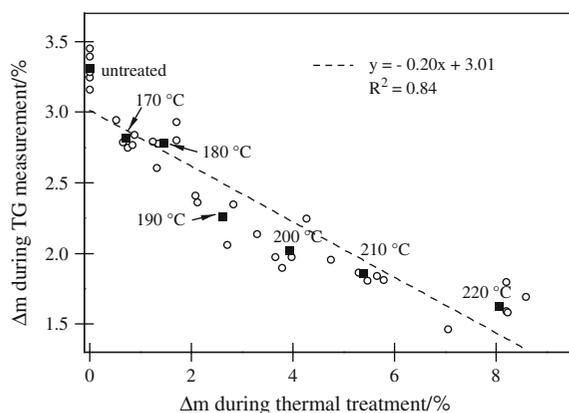

Fig. 8 A calibration curve in a range from 130 to 250 °C obtained under an air atmosphere

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