

THERMAL DECOMPOSITION OF CELLULOSE INSULATION

PETER RANTUCH and TOMÁŠ CHREBET

*Faculty of Material Science and Technology in Trnava, Slovak University of Technology in Bratislava,
Bratislava, Slovakia*

✉ *Corresponding author: Peter Rantuch, peter.rantuch@stuba.sk*

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The article focuses on the behaviour of cellulose insulation during thermal load. The tested samples were stressed by heating rate of 5 °C.min⁻¹, as well as isothermally at temperatures of 210 °C, 250 °C, 295 °C, 300 °C, 400 °C and 500 °C. The mass loss of the samples was observed. It is obvious from the measured values that the decomposition of cellulose insulation begins at the temperature of 250-260 °C. The values of the peaks of mass loss rate, as well as the temperatures of reaching 95% and 30% of the mass of the samples, confirm that the decomposition rate of cellulose insulation is affected by its own density in the first phase. A similar dependence was also determined for the mass loss of carbonaceous residue. Based on the measured data, linear equations, which describe the dependence of temperatures of reaching the above mentioned states on the density of the samples, were determined.

Keywords: thermogravimetry, thermal insulation, cellulose, density

INTRODUCTION

The importance of materials obtained by recycling has been continually increasing in recent years. This trend is also clearly visible in the case of materials based on cellulose, e.g. paper. Increasing consumption leads to an increase in the number of studies devoted to this problem.¹⁻⁸ Observation of the thermal degradation of cellulose confirmed that, unlike lignin, cellulose achieved a significant peak during the DTG analysis.⁹ The maximum decomposition rate of cellulose during tests on linden wood was 370 °C.¹⁰

Aggarwal, Dollimore and Heon indicate that major mass loss begins at the temperature of about 250 °C, and may be attributed to the oxidation of partially decomposed cellulose.¹¹ During the test on paper, only the dehydration of cellulose has been observed by this temperature.¹² In the case of old paper, its cellulose decomposes at lower temperatures.¹³

The main step in the mass loss of cellulose was determined by several studies. Soares, Gamino and Levchik indicate the range from 270 °C to 340 °C with a maximum rate between 317 °C and 329 °C,¹⁴ Poletto *et al.* at temperatures around 350 °C,¹⁵ and Wang *et al.* at temperatures from 277 °C to 397 °C with the peak around 373 °C.¹⁶

In Geo and Wu's work, the reaction becomes exothermal at the temperature of 300 °C with a peak at 366 °C, due to the oxidation of volatile products. Another exothermal curve, peaking at 468 °C, represents the oxidation of the charred residues.¹⁷ Silvia *et al.* report the temperature range from 260 °C to 360 °C with 88% mass loss for the first stage of cellulose decomposition and the range between 360 °C and 525 °C for the second stage.¹⁸ The results of isothermal load of White birch wood samples show that, at temperatures of up to 450 °C, no further significant decomposition of the carbonaceous residue takes place.¹⁹ Gaan *et al.* indicate three thermal stages of cellulose decomposition: 1st stage around 100 °C, corresponding to the release of physically adsorbed water; 2nd stage around 360 °C, which is rapid, corresponding to the dehydration and decarboxylation reactions, which produce combustible gasses like aldehydes, ketones, ethers etc.; and the slow 3rd stage around 400 °C, which corresponds to the decomposition of the char formed in the second stage.²⁰ Three thermal stages of mass loss during the heating of cellulose (water evaporation, oxidation of cellulose, oxidation of carbonaceous residue) are also described by Bernabé *et al.* (Table 1).²¹

During the research on spruce and eucalyptus wood samples, an initial mass loss was observed between temperatures of 20 °C and 120 °C, which

is attributed to the vaporization of the water from the fibres.

Table 1
Results of thermal gravimetric analysis²¹

ΔT (°C)	T_{MAX} (°C)	ΔT (°C)	Δm (%)
143.6-381.7	327.52	30-100	3.43
		100-359	66.35
381.7-566.5	447.94	359-600	24.97
		higher	5.25

The thermal stability decreases above 280 °C for spruce wood and above 260 °C for eucalyptus wood. The first stage was associated with the thermal depolymerisation of hemicelluloses, pectin and the cleavage of glycosidic linkages of cellulose, whilst the second one corresponds to the degradation of cellulose present in the wood fibres.²² Similar results were also achieved by Sunol *et al.*, who pointed out the first mass loss due to evaporation of water at temperatures around 100 °C and the second mass loss, at about 250-270 °C.²³

The addition of inorganic salts has a significant influence on the decomposition of cellulose. While some salts act as catalysts at lower temperatures ($ZnCl_2$), others only slightly affect degradation, but they move the maximum mass loss to higher temperatures ($NiCl_2$, H_2PtCl_6).²⁴ For the samples of cellulose impregnated with an aqueous solution of $KHCO_3$, a significant reduction of temperature was observed, in which the maximum mass loss rate against pure cellulose was observed on the thermogram.²⁵

For a fire retardant wood and its residue, the temperatures of the main peaks in the DTG were between 260 °C and 275 °C; 100 °C lower than that of untreated wood and its residue, whose corresponding value was 360-370 °C.²⁶ In the thermal degradation of cotton cellulose, the temperatures and activation energies of pyrolysis were lower in the case of samples that contained fire retardant. The yield of carbon residue and limiting oxygen index (LOI) were higher in the case of cellulose containing fire retardant.²⁷

Thermogravimetric analysis indicates that the presence of mineral matter significantly influences the pyrolysis behaviour of cellulosic materials. In general, the mass loss of paper mill waste materials started at lower temperatures than that of pure cellulose. In the case of wastes from

recycled paper, the mass loss continues at temperatures higher than 500 °C, due to kaolinite dehydration and carbonates decomposition.²⁸

EXPERIMENTAL

The cellulose insulation is produced from paper waste. Besides the main component, which is cellulose, producers add substances with the objective to improve the fire characteristics of the insulation, as well as its resistance to biodegradation. For this purpose, the following substances are added to the base material: boric acid, ammonium sulphate, and mono-ammonium phosphate.²⁹

The aim of the experimental part of this paper was to characterize the impact of increasing temperature on cellulose insulation *via* thermogravimetric analysis.

To test the influence of cellulose insulation density on its thermal decomposition, 38 samples with the density from 0.034 g.cm⁻³ to 0.16 g.cm⁻³ were used. These samples were heated by the rate of 5 °C/min. Another 6 samples were tested under isothermal conditions at temperatures of 210 °C, 250 °C, 295 °C, 300 °C, 400 °C and 500 °C, whereby they were exposed to the given temperature for a 100-minute time period. The samples, which were heated with a constant rate, were dried during 24 hours at the temperature of 102 °C. Isothermally stressed samples were not dried.

The diagram of the testing device is illustrated in Figure 1. In order to achieve uniform heating of the sample, a hot-air furnace (2) was used, which is described in more detail in ISO 871:2010.³⁰ The mentioned furnace was adjusted for the purpose of thermal gravimetric analysis. The sample was placed into a metal crucible (3) having an inner volume of 15 cm³, which was mechanically interconnected with digital scales (5). Every 10 seconds, the sample weight was recorded using a computer (6).

RESULTS AND DISCUSSION

Thermal gravimetric analysis

A typical course of the thermogravimetric analysis of the cellulose insulation samples is shown in Figure 2, which presents the TGA of a

sample with the density of 0.096 g.cm^{-3} . The first phase demonstrates a small increase in weight. This increase occurs in the temperature range from ambient temperature to $100 \text{ }^\circ\text{C}$ and is probably caused by absorption of air moisture into the sample. Subsequently, the absorbed moisture is repeatedly evaporated, and from the temperature of $120 \text{ }^\circ\text{C}$, the curve has a characteristic shape for TGA. It is possible to determine the initiation temperature of the

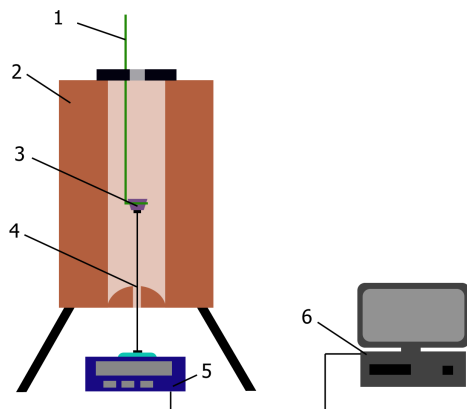


Figure 1: Schematic illustration of the measuring device; 1 – holder for sample insertion, 2 – hot-air furnace, 3 – crucible with tested sample, 4 – mechanical interconnection between sample and scales, 5 – digital scales, 6 – computer

Keerthana and Mahendran state in their work that the fire resistance of cellulose insulation appeared to have some dependence on its density.⁷ Therefore, the influence of density of cellulose insulation on its thermal decomposition was also tested. Figures 3, 4, 5, 6 show the results of this test. The division of the measured values into three categories is evident from the dependence of temperature DTG peak on density. The first category includes density range from 0.034 g.cm^{-3} to 0.075 g.cm^{-3} . This category is characterized by a linear dependence of temperature on the DTG peak, which is regressive. Equation (1) describes the mentioned dependency, where T_p is the temperature of reaching the peak in $^\circ\text{C}$, and ρ is the density of cellulose insulation in g.cm^{-3} .

$$T_p = 342.8 - 492.8 \rho \quad (1)$$

The second category represents a region of densities from 0.075 g.cm^{-3} to 0.095 g.cm^{-3} , where the values of the DTG peaks are constant. The samples reached the maximum degradation rate

decomposition of the cellulose insulation, which is approximately $255 \text{ }^\circ\text{C}$, from the curve. A rapid increase in the decomposition rate with the maximum at the temperature of $301.5 \text{ }^\circ\text{C}$ follows. Further, the decomposition slows down and proceeds until the temperature of $378 \text{ }^\circ\text{C}$. During subsequent heating, the third mass loss occurs at temperatures around $450 \text{ }^\circ\text{C}$, due to the reaction of carbonaceous residue with air oxygen.

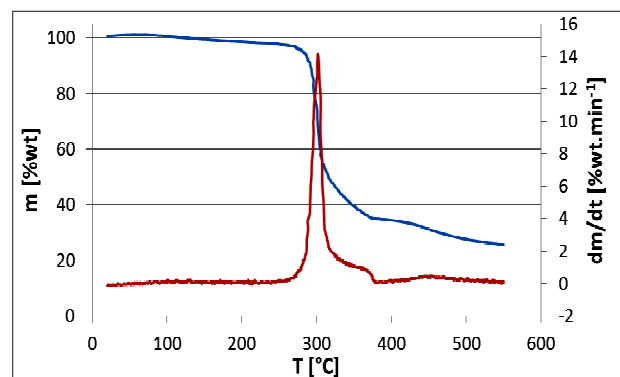


Figure 2: TG/DTG samples with a density of 0.096 g.cm^{-3}

almost identically at the temperature of $305.5 \text{ }^\circ\text{C}$. The last category includes interval of densities from 0.095 g.cm^{-3} to 0.16 g.cm^{-3} . One can see much more pronounced dispersion of the values in this region. For better clarity, there are vertical lines in Figure 3, which mark the limiting values of the density of the cellulose insulation used in construction industry.

The graph, showing the dependence of temperature, when 5% mass loss of the sample is reached, on its density (Figure 4), has a clearly decreasing tendency. However, its course does not seem to be divided into regions as in the case of the graph in Figure 3. The temperature, corresponding to the sample with a density of 0.077 g.cm^{-3} , varies significantly from the other measured values. If we omit this value, we can place a line with equation (2) through a set of measured values; where $T_{95\%}$ is the temperature of 5% mass loss in $^\circ\text{C}$, and ρ is the density of cellulose insulation in g.cm^{-3} :

$$T_{95\%} = 304.6 - 181.3 \rho \quad (2)$$

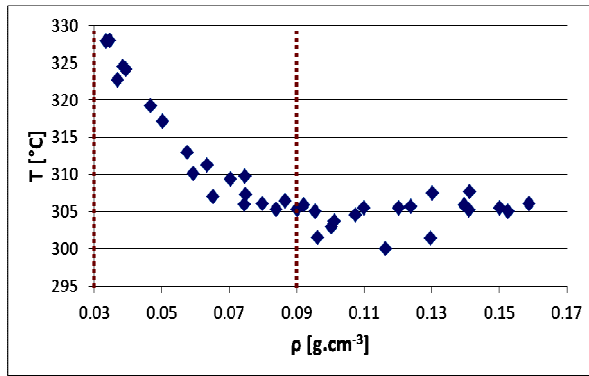


Figure 3: Dependence of mass loss rate peak on density of the sample

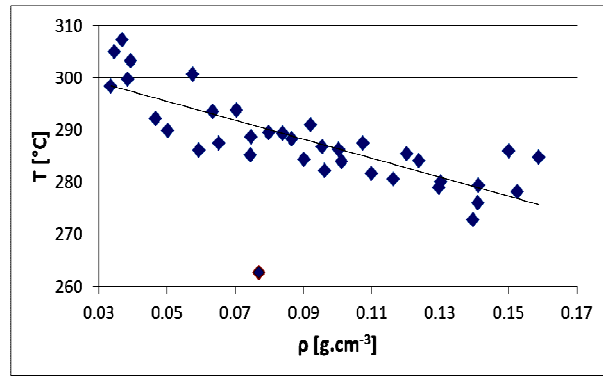


Figure 4: Dependence of temperature on density at 5% mass loss

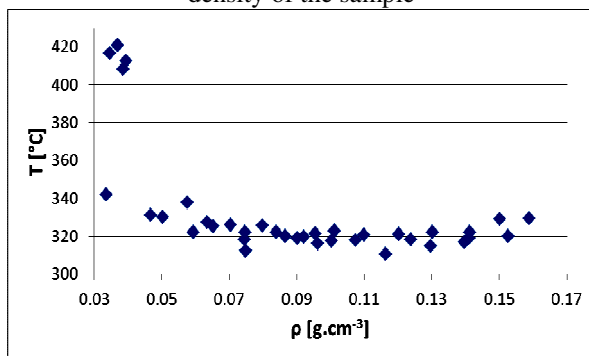


Figure 5: Dependence of temperature on density at 50% mass loss

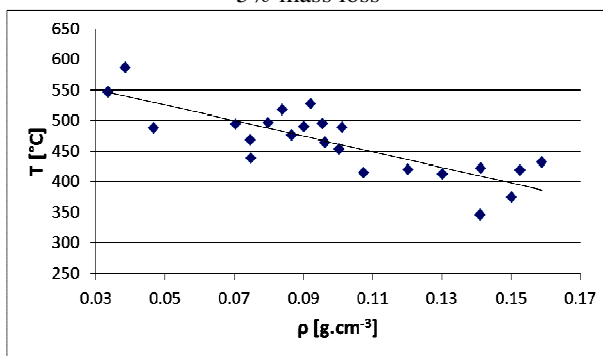


Figure 6: Dependence of temperature on density at 70% mass loss

In the case of the temperature of the half-time decomposition of the cellulose insulation, it is not quite clear whether this function has a decreasing or increasing course (Figure 5). Therefore, we can conclude that the density does not play such a significant role in the last phase of cellulose decomposition as in the previous cases. Contrariwise, at the 70% mass loss, the effect of density on the thermal decomposition occurs again. Similar to the 5% mass loss, in this case, the temperature of reaching the mentioned limit decreases with increasing density of the sample. This dependency is expressed by equation (3):

$$T_{30\%} = 589.5 - 1277.8 \rho \quad (3)$$

Analogously to the previous equations, $T_{30\%}$ is the temperature at 70% mass loss in °C and ρ is the density of the cellulose insulation in g.cm^{-3} . According to the temperature range (345-587 °C), one can assume that it represents the thermal decomposition of carbonaceous residue. The amount of measured data in this temperature range is lower, because several measurements were interrupted before reaching the 70% mass loss.

From the box diagram of temperatures T_p , $T_{95\%}$, $T_{50\%}$ and $T_{30\%}$ (Figure 7), it is evident that the smallest dispersion of values was measured in the case of T_p , followed by temperatures $T_{95\%}$ and $T_{50\%}$ with almost identical variances and, finally, $T_{30\%}$ with significantly greater variance than in the case of the other temperatures. Similar dispersions of the first three mentioned thermal regions are probably caused by the fact that they are situated in the area of cellulose decomposition. By contrast, as it was already mentioned, $T_{30\%}$ is situated in the area of decomposition of carbonaceous residue. In case of $T_{50\%}$, there are four distinct values in the graph, which significantly differ from the other measured values.

Isothermal heating

The density of the samples at isothermal heating ranged from 0.075 g.cm^{-3} to 0.082 g.cm^{-3} , which corresponds to a stabilised region during uniform heating, as well as to the densities of the tested insulation in real use. Changes in the mass loss in time for particular temperatures are shown in Figure 8. A small decrease in mass in a very

short time from the beginning of the measurement is clearly visible from this graph. This decrease is probably caused by the dehydration of the samples. After the drying of the sample during isothermal heating, which is characterised by the temperature of 210 °C, the course of sample mass loss stabilises and becomes almost uniform.

However, at temperatures of 250 °C, there is a modest but constant decrease in mass until the end of the measurement. We can assume that this is the temperature at which the cellulose decomposes, but this decomposition takes place only slowly.

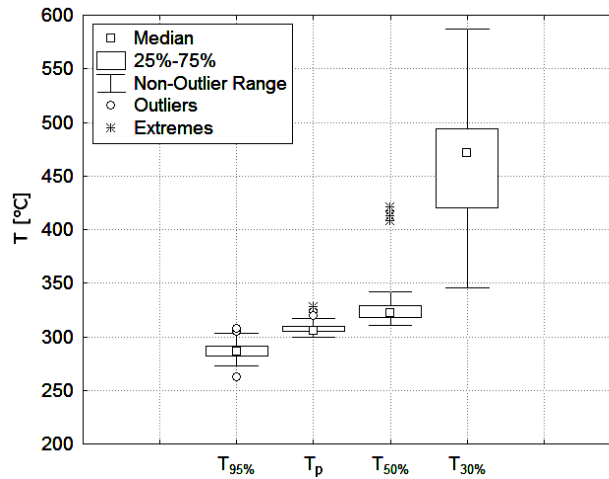


Figure 7: Graph box of temperatures $T_{95\%}$, T_p , $T_{50\%}$ and $T_{30\%}$

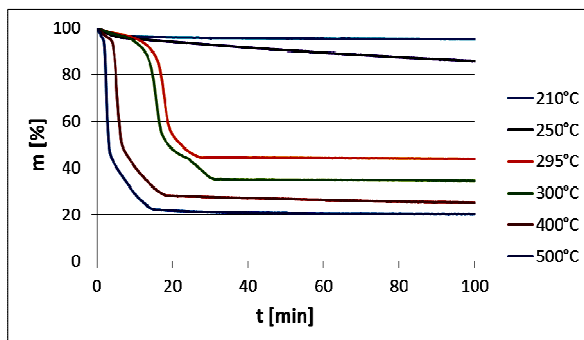


Figure 8: Time dependence of sample weight during isothermal heating

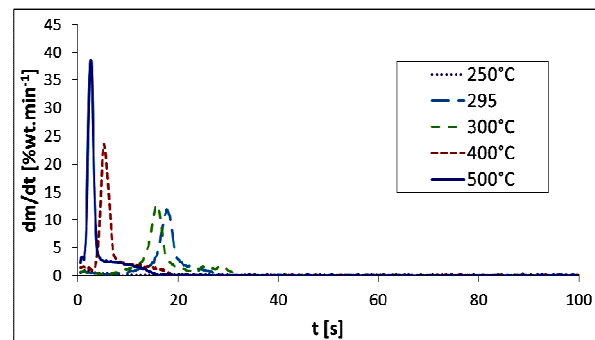


Figure 9: Time dependence of sample mass loss rate during isothermal heating

It is interesting to compare the curves corresponding to 295 °C and 300 °C. In both cases, the decomposition of cellulose is clearly visible and it occurs in 1065 s, or more precisely in 965 s. However, at the temperature of 295 °C, the curve has a typical shape for substances whose decomposition takes place in a single step, whereas the curve corresponding to the temperature of 300 °C indicates the thermal decomposition in two steps. This fact can be apparently assigned to additives that are added to cellulose in order to improve its properties.

The course of the remaining two temperature curves (400 °C and 500 °C) is similar to the one

of the temperature of 300 °C, with the difference that the mass loss rate varies. This fact is best noticeable from the courses of the mass loss rates, which are illustrated in Figure 9. Along with increasing temperature, the rate of sample decomposition also increases, while the time to reach the maximum rate of decomposition decreases. An exception from this rule is a curve that corresponds to the temperature of 250 °C, which reaches the maximum in a short time from the beginning of the measurement. It is caused by a very slow decomposition of cellulose, which is greatly exceeded by the rate of mass loss associated with the evaporation of moisture. In

order to increase the clarity of the graph, the course of isothermal heating at 210 °C, where the

decomposition of cellulose was not recorded, is not displayed.

Table 2
Time of reaching the determined mass losses during isothermal heating of cellulose insulation

T (°C)	t_{max} (s)	$t_{95\%}$ (s)	$t_{50\%}$ (s)	Residue (wt%)
210	50	-	-	95.2
250	90	780	-	85.8
295	1065	660	1330	43.8
300	965	580	1150	34.4
400	340	250	430	25.0
500	170	120	210	20.2

The main numerical results of isothermal loading of the samples are summarized in Table 2. The first column contains the temperatures, labelled as T , to which the samples were exposed. The following columns represent the time of reaching the maximum mass loss t_{max} , the time of mass reduction of the sample by 5%, labelled as $t_{95\%}$, the time of reaching half the mass of the sample $t_{50\%}$, the time when the mass of the sample was 30% of the original mass $t_{30\%}$ and, finally, the residue that remains after 100-minute heating. It is clear from the presented values that the heating temperature affects all described values, including the amount of residue. This amount, similar to the time of particular losses, decreases with increasing temperature. This phenomenon occurs probably due to the increasing velocity of decomposition reactions and of their efficiency, which are influenced by the increasing temperature.

CONCLUSION

During the thermal stress of the cellulose insulation in the temperature range from 50 °C to 550 °C, three regions of its mass loss occur. The first phase, characterised by temperatures below 120 °C, is caused by drying. The second phase, the main one, occurs in the temperature range from 250 °C to 380 °C. During this phase, the basic component of cellulose insulation – cellulose – decomposes. The third phase (about 450 °C) can be described as the reaction of carbonaceous residue with oxygen in the air. This phase is not clearly bounded.

Density has a considerable influence on the thermal decomposition of the cellulose insulation. It becomes more obvious at the beginning of decomposition. This fact is evident in the case of the peak of the mass loss rate, as well as in the case of the temperature when the 5% mass loss

occurs. In both cases, the decrease in the insulation density leads to an increase in the temperature required to achieve the mentioned state. However, in the case of the mass loss rate peak at higher densities than 0.075 g.cm^{-3} , the course changes to constant and is therefore independent of the density. The increasing density of the sample also leads to a reduction in the temperature of reaching 30% of its mass.

Isothermal heating proved a slight decomposition of the sample already at the temperature of 250 °C, as well as the influence of the additives at temperatures from 295 °C to 300 °C. The maximum rate of decomposition increases with temperature, while the time of reaching this maximum rate decreases. The temperature of isothermal heating also affects the amount of carbonaceous residue. This amount declines with increasing temperature. At the temperature of 210 °C, the decomposition of the tested insulation was not observed. Therefore, this temperature can be considered as safe for the short term.

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