ESTERIFICATION OF WILLOW WOOD WITH CYCLIC
ACID ANHYDRIDES

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ABSTRACT

This study made an attempt to determine whether the initial wood activation with sodium hydroxide exerts a beneficial influence on the degree of its modification. For this purpose, willow wood esterification with two acid anhydrides: maleic and succinic was carried out. Both untreated and mercerized woods were modified during the performed experiments and the authors determined weight percent gain (WPG) and carried out product thermogravimetric analysis (TG). Values of WPG indices of the mercerized wood were considerably higher than WPG values obtained for the modification of wood which was not subjected to the initial treatment. The obtained results confirmed that mercerization enhanced substitution of wood active functional groups. It should be emphasised that mercerized wood subjected to esterification showed better thermostability in comparison with the modified wood which was not treated with sodium hydroxide.

KEYWORDS: Willow wood, acid anhydrides, mercerization, thermogravimetric analysis.

INTRODUCTION

In recent years, a rapid development of wood chemical modification methods has been observed. The modification involves the reaction of active functional hydrophilic groups occurring in wood principal constituents, i.e. cellulose, lignin and hemicelluloses with the applied modifiers (Hon 1996). The most frequent modifiers used in the wood modification process include: carboxylic acids, silanes, isocyanates, alkyl halides, lactones and nitriles (Rowell 1983; Kumar 1994; Hill 2006).

From among the many methods of chemical wood modification, one of the most effective processes is its esterification with dicarboxylic acid anhydrides. Reactions of wood with acid anhydrides may already take place at room temperature in solvents such as xylene, dimethylformamide (DMF), dimethylsulfoxide (DMSO), 1,2-dichloroethane, tetrahydrofuran

and pyridine (Matsuda et al. 1984a, Marcovich et al. 1996, Hill and Papadopoulos 2002). This process can also be carried out without solvent in the presence of catalysts: sodium carbonate, ammonium sulfate, sodium acetate, zinc chloride, boron trifluoride and hydrofluoric acid (Matsuda et al. 1984b) or without catalyst and solvent (Li et al. 2000). The reaction of wood with acetic (Rowell et al. 1986), propionic (Hill and Jones 1999; Papadopoulos and Gkaraveli 2003), butyric (Hill and Jones 1999), crotonic (Cetin and Ozmen 2001) and hexanoic anhydride (Hill and Jones 1999) were investigated. Longer chain anhydrides show much lower reactivity with wood, which decreases as the molecular weight of the anhydride increases. These reactions proceed with the separation of the organic acid by-products. However, reaction of wood with cyclic anhydrides do not yield a by-product, leaving the modified wood polymers with a covalently bonded caboxylic group. Wood was modified with following cyclic anhydrides such as maleic, succinic, glutaric and aromatic - phthalic anhydride (Hill 2006). Matsuda (1987) carried out the esterification reaction of wood with succinic anhydride. When the reaction temperature exceeds 100°C was observed by formation of crosslinking wood diesters.The possibility of the reaction of acid anhydrides with cyclic structures in the form of monoesters and diesters also reported Hill and Mallon (1998).

It is evident from literature reports (Wu et al. 2000) that in order to increase the degree of wood modification, it is necessary to perform initial activation of its surface. Surface activation of lignocellulosic material can be carried out employing many different physical methods, e.g. stretching, calendering and electrical discharges. One of the more frequently applied methods, in the case of natural fibres, is mercerization. The influence of wood mercerization on the course of its modification has not been elucidated sufficiently yet. Hon and Ou (1989) stated that mercerization by removing natural impurities results in increased diffusion of modifiers into wood which, in turn, facilitates chemical modification of lignocellulosic material.

Already in 1844, John Mercer found that 12-20 % aqueous NaOH solutions, acting on cotton fibres, caused their swelling. Treatment with alkali results in wood swelling; simple sugars, tannins, dyes, hemicelluloses, resin acids and depolymerised cellulose are dissolved. Using higher temperature, concentration of sodium hydroxide and pressure lignin also undergoes degradation and changes into soluble form. The activity of hydroxide increases with wood comminution (Prosiński 1984).

Mercerization is a multi-phase process and its course is influenced by the concentration and temperature of the sodium hydroxide solution as well as by the duration of the process (Borysiak and Doczekalska 2005, 2008 b, c). Cellulose I undergoes a number of transformations before it changes ultimately into cellulose II. The process is accompanied by polymorphic conversion. During the first stage of the process, under the influence of NaOH, alkali-cellulose is formed. Penetration of NaOH molecules inside the spatial network of cellulose I leads to "disintegration" of macromolecules and characteristic changes of parameters determining the network structure. In the next step, alkali-cellulose is treated with water leading to the washing out of NaOH molecules which results in the development of hydrated cellulose. The final stage of the transformation comprises the removal of H_2O molecules (drying stage) and formation of cellulose II. The parameters of the elementary cellulose I cells are as follows: a =16.34 Å, b=15.72 Å, c=10.32 Å, γ=97.0°, and of cellulose II: a=8.01 Å, b=9.04 Å, c=10.36 Å, γ=117.1° (Young and Rowell 1986). In an earlier studies by the authors of this paper (Doczekalska and Zborowska 2010 a), the impact of the sodium hydroxide concentration and duration of treatment on the content of the structural constituents of willow wood (*Salix viminalis* L.) was measured. It was demonstrated that the content of these constituents was, practically speaking, independent of the treatment duration with NaOH. The highest percentage increase in cellulose proportions of about

10 % was determined for wood samples treated with 10 % NaOH solution. For the remaining concentrations, this increase was smaller in comparison with the control sample and the cellulose content fluctuated from 42.3 to 52.5 %. The observed higher cellulose percentage content in the samples treated with 10 % NaOH solution could probably be attributed to the occurrence of only one form of crystalline cellulose – cellulose I. When higher NaOH concentrations were employed, i.e. 15 to 20 %, the second variant of cellulose – cellulose II – was also present confirming the occurrence of the mercerisation process (Doczekalska and Borysiak 2007, 2008a, b, c). Alkalisation of willow wood with sodium hydroxide solutions of 10 to 20 % concentrations resulted in the removal of significant quantities of wood non-structural substances. The content of substances soluble in the ethanol-benzene mixture from willow wood treated with NaOH decreased by about 80 %, in cold water – by about 90 %, in hot water – by about 45 % and in 1 % NaOH solution – by about 50 % (Doczekalska and Zborowska 2010 b).

This study made an attempt to determined whether the initial wood activation with sodium hydroxide exerts a beneficial influence on the degree of its modification. For this purpose, willow wood esterification with two acid anhydrides: maleic and succinic was carried out. Both untreated and mercerized woods were modified during the performed experiments and the authors determined weight percent gain (WPG) and carried out product thermogravimetric analysis (TG).

MATERIAL AND METHODS

Wood: In the performed experiments was used willow sawdust (*Salix viminalis* L.) of size 0.5 to 1.0 mm.

Investigation of Wood Chemical Components: Chemical composition of willow sawdust before and after mercerization was investigated according to the analytical methods used in wood chemistry as follows:
- humidity by oven-drying at 105°C (TAPPI T 264 om-88),
- cellulose - Seifert method,
- lignin – Tappi method,
- pentosans – with phloroglucinal (Prosiński 1984),
- extractives by reaction with 2:1 (v/v) mixture of benzene and ethanol (TAPPI T 204 om-88),
- extractives by reaction with 1 % NaOH (TAPPI T 212 om-88),
- extractives in cold and hot water (TAPPI T 207 om-88).

Mercerization: Part of sawdust samples were subjected to the process of mercerization prior to their reaction with anhydrides. Wood dried in a vacuum oven for 24 h at 70°C was treated at room temperature with the aqueous solution of sodium hydroxide at 17.5 % (in weight) concentration for 90 min. The material activated in this way was rinsed with distilled water to neutralize excess sodium hydroxide and then it was dried for 48 h at ambient temperature (Doczekalska and Borysiak 2008 a).

Esterification: The modification process of wood (untreated or mercerized) was conducted in a three-necked flask of 500 ml volume equipped in a heat coat, reflux condenser, stirrer and a thermometer. Approximately 25 g of comminuted wood material was introduced into the flask containing 230 ml solution of maleic or succinic anhydride (MERCK) in xylene (1 mol.dm^{-3}). The esterification process was conducted for 2, 4 and 8 hours. Once the esterification was finished, the product was filtered, washed several times with distilled water and then extracted

using the ethanol - toluene mixture in the Soxhlet apparatus for 8 h in order to remove the unreacted anhydride. The modified wood after extraction was dried at room temperature for 48 h (Doczekalska et al. 2007 a, b).

Weight percent gain index (WPG): The extent of reaction was calculated as weight percent gain (WPG) determined by the differences in oven dry weight of the samples before modification (W_1) and after modification (W_2) according to equation (1):

$$WPG = \frac{W_2 - W_1}{W_1} \cdot 100 \quad (\%)$$ (1)

Thermogravimetric analysis: The analysis of the esterified wood was carried out on a Labsys^{TM} thermobalance of the Setaram Company in the following conditions: Final temperature - 600°C, rate of temperature increase - 5 deg.min^{-1}, atmosphere – helium flowing at the rate of about 2 dm^3.h^{-1}.

RESULTS AND DISCUSSION

Modification of the *Salix viminalis* wood was performed with two anhydrides: Saturated – succinic anhydride and unsaturated – maleic anhydride. During this process, no by-products are produced (Fig. 1).
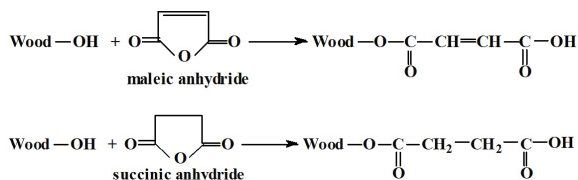

Fig. 1: Wood chemical modification by reaction with cyclic anhydrides.

Untreated and mercerized woods were esterified. Parameters of willow wood mercerization process were described in earlier publications (Doczekalska and Borysiak 2007, 2008a). It was found that under the influence of 10 % NaOH solution at the temperature of 20°C for 90 minutes no willow wood mercerization took place. On the other hand, the application of 15, 17.5 and 20 % NaOH solutions resulted in the appearance on roentgenograms of diffraction maxima confirming the development of cellulose II. Its content in the examined samples ranged from 46 to 66 %. The mercerization parameters applied in this study, i.e. the treatment with 17.5 % NaOH solution for 90 min., caused that 65 % of cellulose I underwent polymorphic transformation into cellulose II (Doczekalska and Borysiak 2007).

Chemical composition of wood

In order to obtain characterization of the initial wood material before and after mercerization concentrations of structural and non-structural constituents were determined in accordance with methods employed in wood chemistry. The obtained results are presented in Tab. 1.

Tab. 1: Chemical composition of willow wood.

	CELLULOSE (%)	LIGNIN (%)	PENTOSANS (%)	SUBSTANCES SOLUBLE IN:			
				ETHANOL-BENZENE MIXTURE (%)	COLD WATER (%)	HOT WATER (%)	1 % NaOH (%)
WILLOW	43.9	24.3	18.4	7.2	5.2	5.4	26.3
WILLOW (mercerized)	46.9	28.2	16.8	1.5	-	2.9	15.9

The percentage cellulose content (Tab. 1) in the initial willow wood amounted to 43.9 % and was by 3 % lower in comparison with the proportion of cellulose in willow wood after mercerization. The observed change in the amount of cellulose could have been caused by the removal from wood, during the mercerization process, of extractive compounds. On the other hand, the lignin percentage content in the willow initial wood reached 24.3 % and was by about 4 % lower in comparison with its content in the mercerized willow wood. The quantity of pentosans found in the mercerized willow wood was lower in comparison with the initial wood samples – it dropped from 18.4 to 16.8 %. These results indicate that the applied NaOH solution dissolved part of hemicelluloses.

Analyzing the obtained research results, it can be said that the treatment of willow wood with NaOH solution removed, primarily, low molecular substances soluble in the ethanol/benzene mixture, in 1 % NaOH solution as well as in cold and hot water.

Furthermore, it was also found that willow wood subjected to mercerization was characterized by a lower content of substances dissolved in 1 % NaOH solution. It is evident from literature on the subject that water dissolves most mineral salts, sugars, pectins, tannins, dyes and other substances. Hot water dissolves higher quantities of substances than cold water. Simple sugars and disaccharides which develop during the process of hydrolysis of hemicelluloses are dissolved (Prosiński 1984). Most of these substances were removed from wood as a result of the mercerization process.

Weight percent gain index of modified wood

Values of the weight percent gain index of modified wood are presented in Tab. 2. The obtained research results were used to carry out analyses of the impact of the following parameters on the WPG index values: Modification time, type of employed anhydride and wood initial (mercerization) process.

Tab. 2: Values of weight percent gain index of esterified wood.

Anhydride	Time of esterification (h)	WPG (%)	
		Willow	Willow mercerized
maleic	2	0.8	1.9
	4	5.9	10.4
	8	14.6	20.2
succinic	2	9.3	14.5
	4	21.0	28.8
	8	35.2	45.1

The analysis of the obtained results (Tab. 2) revealed that values of the WPG index increased together with the lengthening of the reaction time, irrespective of the employed acid anhydride. However, it should be emphasised here that, according to literature data (Dominikovics et al. 2007), values of wood WPG during esterification with the maleic and succinic anhydrides increase up to a certain boundary value above which the duration of the reaction process no longer plays a significant role and the majority of active hydroxyl groups in wood undergoes substitution as exemplified by the benzylation process of wood meal which was used as a filler of composites with polypropylene (PP). It was observed that the majority of hydroxyl groups found in wood were substituted already during the first two hours of the modification process. Further prolongation of the reaction did not have a significant effect on product properties.

It was noticed, in the course of the esterification process that the succinic anhydride reacted with wood easier than the maleic anhydride (Tab. 2). Values of the WPG index for the esterification with the succinic anhydride were higher than for the esterification carried out using the maleic anhydride as exemplified by the modification of the initial willow during 8 hours. The WPG value for the modification conducted using the succinic anhydride reached 35.2 %, while for the modification carried out with maleic anhydride – 14.6 %.

The observed higher values of the WPG index obtained for the modification carried out with the assistance of succinic anhydride could have resulted from a complex character of the esterification mechanism. Doczekalska et al. (2007a) put forward a hypothesis that in the course of this process, one of the following two things might happen: 1/ attachment to wood of molecules of succinic anhydride in the form of diesters, 2/ lengthening of the chain consisting, initially, in the attachment of monoester molecules to wood active hydroxyl groups and, later, successive monoesters to the carboxyl groups formed as a result of these reactions.

Values of WPG indices of the mercerized wood were considerably higher than WPG values obtained for the modification of wood which was not subjected to the initial treatment (Tab. 2). Values of WPG indices recorded for esterified modified wood ranged from 1.9 to 45.1 %, whereas for the wood modified without mercerization – from 0.8 to 35.2 %. The obtained results confirmed that mercerization enhanced substitution of wood active functional groups. High cellulose II content favoured wood reactions with modifiers. It is quite possible that during mercerization the following substances are removed from wood: Pectins, fatty acids, natural oils (fat substances) which can block the availability of hydroxyl groups during the modification process. The more active hydroxyl groups available during the modification process, the higher WPG values are obtained (Mwaikambo and Ansell 1999). This means that it appears advisable to apply mercerization before the esterification process with anhydrides in order to activate wood for the modification process and, consequently, to obtain higher degree of modification.

Thermogravimetric analysis

The obtained modified lignocellulosic material was subjected to thermogravimetric (TG) investigations. In addition, the authors also examined thermal properties of the initial and mercerized wood samples. Wood principal constituents (cellulose, hemicelluloses and lignin) undergo degradation at different temperatures (Hill 2006). The rate of cellulose degradation at temperatures below 250°C is small. The performed experiments showed that amorphic regions in cellulose undergo degradation at lower temperatures than crystalline regions. Crystalline cellulose undergoes degradation at the temperature range from 300 to 340°C (Kim et al. 2001). It is assumed that hemicelluloses are thermally less stable than cellulose (Fengel and Wegener 1989). On the other hand, lignin is considered to be one of the thermally most stable biomass constituents, although it does undergo slight degradation already at relatively low temperatures

as a result of development of different phenol degradation products (Sanderman and Augustin 1964).

The performed thermogravimetric analysis of willow samples (Figs. 2-5) demonstrated that the area of active thermolysis was contained within 190-365°C interval and the temperature at which the mass loss reached its maximum rate amounted to 334°C. The mass loss within this temperature range reached 59.7 %, while the total mass loss at to 600°C–77.5 % (Tabs. 3 and 4).

The course of the DTG curve of wood subjected to the mercerization process (Figs. 3 and 5) differed from the untreated willow wood thermogram. The temperature of the beginning of the active thermolysis was by about 20°C higher in comparison with the control sample and amounted to 209°C. Similar results were obtained for the mercerized poplar wood. The initial thermolysis temperature of poplar samples was higher than that of the initial wood and reached 205°C (Doczekalska et al. 2008). Due to the removal of low-molecular and the most thermophilic wood constituents, mercerization should increase the temperature of the beginning of the decomposition.
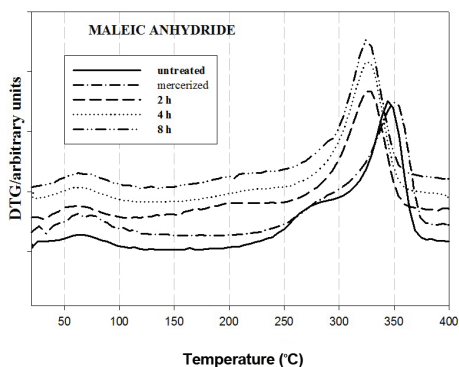

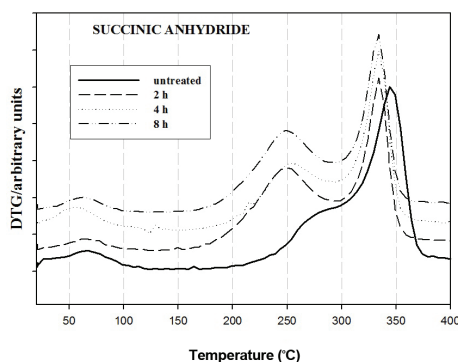Fig. 2: DTG curves of modified wood with maleic anhydride.

Fig. 3: DTG curves of mercerized and modified wood with maleic anhydride.

Wood esterification with acid anhydrides affects thermal wood stability (Tabs. 3 and 4, Figs. 2-5). In this study, temperature corresponding to the beginning of the decomposition, i.e. T_i or T_{i1} was adopted as a measure of thermostability.

The performed thermal analysis of samples revealed a significant lowering of the initial temperature of thermal decomposition of wood modified with maleic anhydride in comparison with the control sample (Tab. 3). Modification of the mercerized willow reduced the temperature of the begining of thermal decomposition by about 45°C. On the other hand, this temperature for the esterified material which was not subjected to NaOH activation was by about 70°C lower. It was also found that with the lengthening of the modification time, i.e. the degree of wood modification, the wood thermostability also increased. The dynamics of the thermal degradation of esterified samples was found to decline at the temperature of about 370-380°C, i.e. several degrees higher than for the untreated wood. Mercerization influenced temperatures of the maximum rate of mass loss of esterified wood (T_{max}) which declined by about 10°C in comparison with the control sample and by about 25°C in comparison with mercerized willow. The T_{max} temperature for esterified willow samples without NaOH activation during 2 and 4 hours was similar to the temperature determined for the control sample and it dropped to 327°C only in the case of the sample modified for 8 hours. Moreover, also the mass loss (W_{Tmax}) recorded at these

temperatures was smaller. Total mass losses (W_T) of esterification products reached: 78-82 % for esterified samples not treated with NaOH and 74-81 % for the mercerized and modified samples.

Tab. 3: Thermogravimetric characteristics of willow wood modified with maleic anhydride.

Sample	T_i (°C)	W_{Ti} (%)	T_{max} (°C)	W_{Tmax} (%)	T_f (°C)	W_{Tf} (%)	W_T (%)
Willow (control)	190	7.5	334	55.2	365	67.2	77.5
Willow mercerized	209	3.2	349	46.8	379	62.9	70.1
WILLOW							
2 h	114	6.4	334	56.0	369	70.3	82.5
4 h	117	4.7	332	48.8	370	65.0	76.4
8 h	120	6.7	327	48.5	370	66.7	78.6
WILLOW MERCERIZED							
2 h	131	5.6	327	46.3	379	63.7	74.3
4 h	142	8.4	325	47.3	380	67.1	79.2
8 h	147	7.6	325	48.2	367	67.2	80.6

T_i – temperature corresponding to the beginning of the decomposition,

T_{max} – temperature corresponding to the maximum rate of mass loss,

T_f – temperature corresponding to the ending of the decomposition,

W_{Ti}, W_{Tmax}, W_{Tf} – mass loss at T_i, T_{max}, T_f,

W_T – total mass loss (temperature 600°C).

After esterification with maleic anhydride only one weigh loss was observed between 200-450°C. This phenomenon has also been reported (Rowell et al. 1984, Bodirlau et al. 2008).

DTG curves obtained for the willow wood esterified with succinic anhydride are presented in Figs. 4 and 5. The course of this process differs from the thermolysis process of products esterified with maleic anhydride. In the case of DTG curves of willow wood esterified with succinic anhydride, two degradation stages can be distinguished. In the case of samples esterified without NaOH activation, these stages are clearly separated and it was possible to determine their temperature ranges, i.e. T_{i1}, T_{f1}, T_{i2} and T_{f2} (Tab. 4). On the other hand, in the case of the esterification products of mercerized wood, these regions overlapped and, therefore, the authors determined only temperatures to the beginning of the decomposition of the first region (T_{i1}) and the ending of the second region (T_{f2}).

The first region of the degradation of products which were not subjected to NaOH treatment and esterified (Fig. 4), which appeared on DTG curves as a distinct peak, was most probably associated with the thermal decomposition of the ester bond and breaking away of molecules of the modifying agent. This effect is associated with a very high WPG index (Tab. 2) and weak bonding of the succinic anhydride with wood. In the case of DTG curves of mercerized and esterified products (Fig. 5), this effect disappears gradually together with the lengthening of the modification time (a small peak is observed) which might indicate increased bonding stability of the modifying agent with the wood substance.

Thermal destruction of willow wood esterified with the succinic anhydride began at temperatures lower (T_{i1}) than those of untreated wood (Tab. 4) but, with the lengthening of the modification time, this temperature increased slightly. A similar dependence was observed for samples modified with maleic anhydride. However, it should be stressed that, in comparison with

the control sample, the determined T_{i1} temperature for the products esterified without the stage of activation with sodium hydroxide was by about 30°C lower and for mercerized products – by about 15°C lower. The thermal decomposition of the mercerized and modified material decreased its intensity when temperature (T_{f2}) of 380°C was exceeded. The T_{f2} temperature for the material modified without activation amounted to about 368°C.
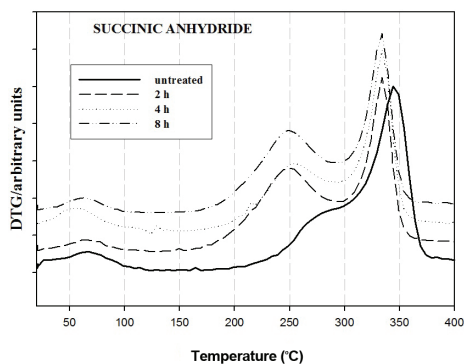

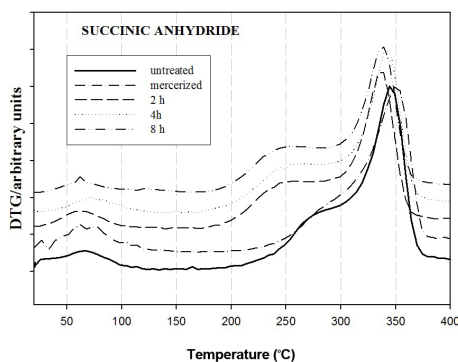*Fig. 4: DTG curves of modified wood with succinic anhydride.*

Fig. 5: DTG curves of mercerized and modified wood with succinic anhydride.

Mass losses recorded at the temperature of 600°C (Tab. 4) determined for the modified products without mercerization were higher than W_T obtained for the control sample and ranged from 80-84 %. Mass losses recorded for mercerized and esterified samples for the period of 2 and 4 hours were similar. W_T was lower and amounted to 74.5 % only in the case of the product mercerized and esterified for the period of 8 hours.

Tab. 4: Thermogravimetric characteristics of willow wood modified with succinic anhydride.

	Willow	Willow	Willow			Willow mercerized		
	(control)	mercerized	2 h	4 h	8 h	2 h	4 h	8 h
T_{i1} (°C)	190	209	155	157	158	179	172	174
W_{Ti1} (%)	7.5	3.2	4.5	9.3	6.5	9.7	6.7	7.4
T_{max1} (°C)	334	349	249	254	250	-	-	-
W_{Tmax1} (%)	55.2	46.8	22.0	23.6	24.4	-	-	-
T_{f1} (°C)	365	379	289	290	289	-	-	-
W_{Tf1} (%)	67.2	62.9	36.8	35.5	39.1	-	-	-
T_{i2} (C)	-	-	299	294	297	-	-	-
W_{Ti2} (%)	-	-	39.7	36.7	41.3	-	-	-
T_{max2} (°C)	-	-	334	334	334	336	337	338
W_{Tmax} (%)	-	-	57.6	56.8	60.9	55.1	53.0	51.8
T_{f2} (°C)	-	-	369	368	365	382	384	386
W_{Tf2} (%)	-	-	69.2	69.2	72.6	70.5	68.5	65.3
W_T (%)	77.5	70.1	79.9	80.7	84.4	82.4	79.1	74.5

T_{i1}, T_{i2} – temperature corresponding to the beginning of the decomposition of the first region or of the second region,
T_{max1}, T_{max2} – temperature corresponding to the maximum rate of mass loss of the first region or of the second region,
T_{f1}, T_{f2} – temperature corresponding to the ending of the decomposition of the first region or of the second region,
W_{Ti1}, W_{Ti2}, W_{Tmax1} or W_{Tmax2}, W_{Tf1}, W_{Tf2} – mass loss at T_{i1}, T_{max1}, T_{f1} or at T_{i2}, T_{max2}, T_{f2},
W_T – total mass loss (temperature 600°C).

CONCLUSIONS

The treatment of lignocellulosic materials with alkali results not only in the removal of low-molecular, non-structural substances from wood but, in addition, it leads to the development of a reactive polymorphic structure of cellulose II. Willow wood mercerization increased the WPG index and, therefore, the degree of modification of lignocellulosic material. Irrespective of the applied anhydride, the obtained values of the WPG index were higher for the esterification products of mercerized wood than for the products derived from wood which was not subjected to NaOH treatment. Therefore, it can be said that the applied mercerization process exerted a favourable impact on increased reactivity of active functional groups of wood with anhydrides.

Moreover, the performed thermogravimetric analysis (TG) also revealed that willow wood treated with anhydrides was characterised by poorer thermostability in comparison with natural wood. However, it should be emphasised that mercerized wood subjected to esterification showed better thermostability in comparison with the modified wood which was not treated with sodium hydroxide.

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