# Chemical and Thermal Properties of Cellulose Acetate Prepared from White Willow (*Salix alba*) and Black Alder (*Alnus glutinosa*) as a Potential Polymeric Base of Biocomposite Materials

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Natural polymeric materials are an interesting alternative to petrochemical products with potential application in almost all areas of human activity. Wishing to expand the field of cellulose acetate application to the biocomposite wood materials, the possibilities of cellulose isolation and its acetylation from two domestic, commercially meagrely used, wood species was investigated in this paper. Cellulose isolated from white willow (*Salix alba*) and black alder (*Alnus glutinosa*) was acetylated using acetic anhydride and perchloric acid catalyst, by treatment at room temperature for 45 minutes. Analysis of the laboratory acetylation process, beside chemical analysis of the gained product by infrared spectroscopy (FT-IR), indicated the impact of hemicelluloses, present both in cellulose and cellulose acetate structure, on values of mass increase, number of acetyl groups and the degree of substitution. Results of thermogravimetric analysis (TGA) later confirmed the statement that thermal properties of cellulose acetate were also dependant on hemicelluloses.

*Key words:*
wood, cellulose, acetylation, bio composite materials, FT-IR, TGA

## Introduction

The constant increase in world population directly and inevitably affects the environment in the way of creating increasing amounts of waste materials, regardless of whether they are materials of natural or synthetic origin. Therefore, in recent decades, a wide range of research has been carried out in order to develop different types of composite materials as end products with added value, whose base are the original (virgin) and/or waste (recycled) raw materials, including the biocomposite materials. Biocomposite materials are sustainable and environmentally friendly bio-based materials made from renewable raw materials with the possibility of recycling[1]. Examples of polymeric raw materials that are most often used to create biocomposites are thermoplastic starch, polyhydroxyalkanoates (PHA), polylactides (PLA), soy-based resins and epoxidized linseed oil[2]. In addition to these raw materials, biocomposite materials can also be made from wood constituents whose chemical composition is very complex. Exactly this fact makes wood

and its constituents excellent raw material for the production of biocomposite materials. It is usually necessary to isolate and chemically modify wood constituents in a way to enable the synthesis of a biomatrix, which can then additionally be filled with wood. As the concept of a biomatrix almost entirely relates to the polymeric part of the composite material, chemical modification of wood constituents should result in the synthesis of so-called bioplastic. A typical and very common example of such plastic is cellulose acetate commercially produced from high-quality wood pulp, or cellulose acetate butyrate, which is hard plastic and has applications in making handles of various tools[3,4]. However, the degradation and the inability to isolate completely pure wood pulp, limits the development of biocomposite materials. Therefore, applications of cellulose isolated from wood and its constituents in a broader scope apply almost only to the paper and textile industries or to the production of membranes for desalination, filtration and medical dialysis[5,6,7,8]. Such uses include the isolation and chemical modification of cellulose by acetylation and preparation of products by cast moulding or spinning.

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In this paper, selected chemical and thermal properties of cellulose acetates prepared from two domestic, commercially meagrely used, wood species were determined and studied from the aspect of their potential use as a polymeric base of biocomposite materials. The first phase of the experiment included determination of the chemical composition of white willow (*Salix alba*) and black alder (*Alnus glutinosa*), from which cellulose was isolated as the basis for the synthesis of cellulose acetate. In the second phase, the process of acetylation was analysed and the specifics related to the researched type of wood were specified. Cellulose acetate was analysed by means of Fourier transform infrared spectroscopy (FT-IR) in order to verify conversion of cellulose to cellulose acetate with an emphasis on the comparison of the product depending on the specific wood species. Thermal properties of synthesized cellulose acetate were determined by means of thermogravimetric analysis (TGA), which was performed in order to gain insights into the potential methods of its utilization in biocomposite materials systems.

## Experimental procedure

### Materials

White willow and black alder wood, used as basic raw materials in this study, were sampled and prepared in accordance to TAPPI T257 cm-12[9]. After sampling and air-drying of the obtained wood samples in the form of disks cut from logs, mechanical powdering, using Retsch SM 300 beater mill, and sieving by means of Cisa RP.08 laboratory sieving machine were conducted in order to prepare wood flour where particles sized between 0.5 and 1 mm were collected for further cellulose isolation and acetylation.

Ethanol, benzene, sulphuric acid, nitric acid, toluene, acetic acid, acetic anhydride, monopotassium salt of phthalic acid, sodium hydroxide, acetone, and phenolphthalein were all purchased from Kemika Ltd., Croatia. Perchloric acid and pyridine were purchased from Sigma-Aldrich, Germany. All chemicals and reagents were of analytical reagent grade. Deionised water used in all parts of the experiment was ASTM type II, and prepared using TKA MicroMed system.

### Determination of the chemical composition of the wood

The chemical composition of the wood was determined by isolation and calculation of extractives (TAPPI T204 cm-97)[10], lignin (TAPPI T222 om-11)[11] and cellulose (Kürchner-Hoffer method)[12] contents. For each wood species and for each stated

wood matter constituent, the content is expressed as the average value of four determinations with standard deviation expressed in parenthesis.

### Cellulose isolation

Prior to cellulose isolation, the wood flour was extracted according to TAPPI T204 cm-97[10] in Soxhlet apparatus using benzene/ethanol mixture (1:1 v/v %) as appropriate solvent in order to remove wood extractives. The extracted wood flour was then spread on trays and left for two days at ambient temperature in order to allow access solvent to evaporate. From thus prepared (extracted) wood flour, Kürchner-Hoffer cellulose was isolated using ethanol/nitric acid mixture (4:1 v/v %) as appropriate solvent. As nitric acid reacts rapidly with and dissolves lignin, the used method resulted in preparation of slightly degraded cellulose that still contained a small portion of the hemicelluloses[12]. Therefore, this process resulted in the preparation of a holocellulose type which has been slightly degraded. In the typical isolation process, 5 g of extracted wood flour was treated three times with, in total, 300 mL (100 mL for each step) of the stated reaction mixture (solvent) until it changed its colour to clear white, with solvent exchange after each one-hour step of the reaction. The temperature of isolation process was set at 100 °C, which was maintained through steam heating of the samples by means of Raypa BBA-6 water bath. The obtained cellulose was then filtered through G2 glass filtering crucible, washed with hot deionised water and dried overnight at 70 °C in order to remove excess water. The same process was repeated until 100 g of air-dried cellulose sample, for each wood species, was prepared.

### Cellulose acetylation

Cellulose acetate (CA) was prepared by considerably modifying the methods described in earlier studies[13,14]. Prior to acetylation, the dried cellulose samples were collected and milled using IKA A10 analytical mill in order to finely pulverize them, since pulverised samples are easier to acetylate. Cellulose (100 g) was acetylated using reaction mixture consisting of 500 mL of acetic acid, 1000 mL of toluene and 5 mL of perchloric acid as catalyst, with additional 500 mL of acetic anhydride added after 1 minute of acetylation process. Acetylation was conducted at ambient temperature and the process took 45 minutes, after which 1000 mL of deionised water was added to the reaction mixture in order to precipitate cellulose acetate (CA). Throughout the process, the reaction mixture was vigorously stirred using IKA homogeniser ULTRA TURRAX T18 paired with electromagnetic stirrer

IKA RH basic 2. The obtained CA was then vacuum filtered and washed repeatedly with 1000 mL of ethanol and 1000 mL deionised water until the prepared product became scentless. CA was then dried for 8 h at 40 °C in order to remove excess water, re-pulverised and sieved over 0.2 mm sieve. The reaction time of 45 minutes was used as earlier studies showed that the use of catalyst as perchloric or sulphuric acid induce formation of CA with higher acetyl content, the formation of which can additionally be controlled by reaction time[13,15]. Formation of CA with higher values of acetyl content and a corresponding degree of substitution (DS > 1.7) is desirable as the final product is usually not soluble in water[16,17] which is favourable from the viewpoint of the use of CA as a polymeric base of biocomposite materials.

## Characterization

*Determination of water content*

In order to gain insight into the changes in water content, since they are directly influenced by mechanical treatments during wood flour preparation and later chemical treatments (extraction, cellulose isolation and acetylation), the water (moisture) content expressed as a percentage of the total sample weight, was directly measured using Sartorius infrared moisture analyser MA 150. Using the aforementioned analyser, the water content was determined gravimetrically by heating samples weighing about 2 g at temperature of 105 °C until constant mass was achieved. Measurements were done with four repetitions and average values were calculated. The obtained values were then used for calculating absolute dry weights of samples used in determination of cellulose, lignin and extractives contents, as well as in analysis of process of cellulose acetylation. Absolute dry weights of samples were calculated according to (Eq. 1):

$$m_{ad} = m_s - (m_s \cdot [w/100]) \qquad (1)$$

where:

$m_{ad}$ – absolute dry weight of the sample (g)

$m_s$ – air dry weight of the sample (g)

$w$ – water content (%)

*Determination of acetyl content and the degree of substitution*

After acetylation, CA was analysed according to ASTM D817-96[18] in order to determine the acetyl content (% acetyl), which is a measure of the saponification value of ester and the degree of substitution (DS). Pyridine was used as the appropriate solvent for CA, and monopotassium salt of phthalic acid was used for the blanks. As pyridine was used

as solvent during the heating of the reaction mixture, great care was taken because overheating or prolonged heating could cause formation of gel-like substances, which could not be saponificated. In the properly conducted process, after pyridine addition and periodical heating/cooling of the reaction mixture, individual CA particles had swollen uniformly without any aggregate forming. The swollen individual particles were then easily saponificated after addition of acetone and sodium hydroxide solution at ambient temperature during the course of three hours. After saponification, the solutions were (re)-titrated with sulphuric acid solutions using phenolphthalein indicator to faint pink end point. Acetyl content was calculated according to (Eq. 2 and 3)[18]:

$$\% \text{ acetyl} = \{[(D-C) \cdot N_a - (B-A) \cdot N_b + P] \cdot 0.04305\} / $$
$$/W \cdot 100 \qquad (2)$$

$$P = (G \cdot H \cdot 1000) / 204.2 \qquad (3)$$

where:

D – volume of sulphuric acid required for titration of the blank (mL)

C – volume of sulphuric acid required for titration of the sample (mL)

$N_a$ – normality of the sulphuric acid solution

B – volume of sodium hydroxide solution required for titration of the blank (mL)

A – volume of sodium hydroxide solution required for titration of the sample (mL)

$N_b$ – normality of the sodium hydroxide solution

P – milliequivalents of monopotassium salt of phthalic acid

W – weight of the sample (g)

G – weight of monopotassium salt of phthalic acid (g)

H – purity factor for monopotassium salt of phthalic acid

The obtained acetyl contents were then used to calculate the degree of substitution according to (Eq. 4)[19]:

$$DS = (3.86 \cdot \% \text{ acetyl}) / (102.4 - \% \text{ acetyl}) \qquad (4)$$

As saponification and titration were performed in duplicate for CA samples and blanks, the results are expressed as average values.

*Fourier Transform Infrared Spectroscopy (FT-IR)*

Conversion of cellulose to CA was determined based on results of FT-IR analysis performed on Shimadzu FTIR 8400 S infrared spectrometer. The FT-IR spectra were obtained by direct transmission

(KBr pellet method) at resolution of 4 cm$^{-1}$ in the range from 4000 to 400 cm$^{-1}$. Standard 13 mm diameter pellets were made using PIKE press and die kit by mixing and pressing 10 mg of sample with 300 mg of dry spectroscopic grade potassium-bromide (KBr) for 5 minutes under 200 bar pressure. For each sample three measurements with 10 scans were performed, and final spectra are expressed as average of 30 scans.

*Thermogravimetric analysis (TGA)*

Thermal properties of CA obtained by modifying cellulose isolated from two wood species with emphasis on their thermal stability were determined by means of thermogravimetric analysis (TGA). Thermogravimetric (TG) curves were collected using Perkin Elmer Pyris 1 TGA analyser by heating the prior weighted powdered samples (5 ± 0.1 mg) in Pt pans from 50 to 700 °C. Experiments were done in duplicate and performed under atmosphere of synthetic air with 30 mL min$^{-1}$ flow. Derivation of TG curves in order to obtain DTG curves was done using Pyris software ver. 11.

# Results and discussion

## Chemical composition of wood

The results have shown that the examined wood species had very similar chemical composition. More precisely, average cellulose content in white willow is 54.0 % (0.7) while black alder has 50.9 % (1.0) cellulose. Also, the contents of the other two main constituents of wood matter are somewhat similar as for lignin, the experiment showed that white willow has 26.3 % (0.5) and black alder has 21.8 % (1.5) lignin. Extractives content in white willow is 2.0 % (0.1) and in black alder it is 4.9 % (0.1). Obtained results for both wood species were somewhat similar to values reported by Serapiglia *et al.*[20] who stated that in willow species (*Salix spp.*) the cellulose content may vary from 38.4 to 45.3 % with lignin content varying from 20.3 to 23.7 % depending on the specific genotype. As for white willow, Fengel and Wegener[21] reported values of 49.6 % (48.7 % in heartwood) of cellulose, 22.7 % (25.7 % in heartwood) of lignin and 3.2 % of extractives. Average cellulose content in black alder is 43.4 %

with 23.9 % of lignin and 3.8 % of extractives as reported by the latter authors. Small differences between lignin and extractives contents obtained in this study in comparison to those reported in earlier studies can be attributed to specific characteristics of the examined trees habitat. Quite large differences in cellulose content in comparison with those reported in earlier studies can be attributed to the previously mentioned presence of hemicelluloses in isolated cellulose. As hemicelluloses contents were not determined, because the effectiveness of the process of conversion wood into a polymeric base of biocomposite materials is directly influenced by extractives, lignin and cellulose contents only, the latter statement should be interpreted with caution and confirmed by additional laboratory work. Nonetheless, since the cellulose contents are rather high in both wood species, and their extractives content is very low, with relatively moderate amounts of lignin, it is possible to conclude that both species could be used as raw material for CA preparation.

## Analysis of the cellulose acetylation process

During acetylation, mass gain of final product in comparison to cellulose mass is more or less proportional to the ratio of chemicals in the reaction mixture, and it rises as the acetic anhydride content rises. In the properly conducted process, the mass gain should not be a result of residual acetic acid in the CA structure, but only a product of the conducted chemical treatment[22]. Small differences in mass gain after acetylation, between the examined wood species, could be explained with differences in weights of absolute dry cellulose samples before acetylation (Table 1). Since the cellulose and reaction mixture chemicals ratio was determined based on weights of air dried cellulose samples, in the case of black alder, a larger volume of acetic anhydride reacted with a lower mass of cellulose. However, as water reacts with acetic anhydride and forms acetic acid, the mass gain should be less emphasised in the wood species with higher initial water content of cellulose. In this case, it should be black alder, whose cellulose water content prior to acetylation was 10.5 % in comparison to white willow with 6.5 % water. The opposite tendencies of CA mass gain (Table 1) between the examined

Table 1 – *Quantitative analysis of acetylation process*

| Wood species | Mass of absolute dry cellulose (g) | Mass of absolute dry CA (g) | Mass gain (g) | Mass gain (%) | Acetyl groups* (%) | DS* |
|---|---|---|---|---|---|---|
| White willow | 93.5 | 122.5 | 29.0 | 31.0 | 38.5 | 2.32 |
| Black alder | 89.6 | 120.7 | 31.1 | 34.7 | 42.5 | 2.73 |

*Results are presented as average for duplicate runs

wood species, in correlation with cellulose water contents, suggest that mass gains are most probably additionally affected with more or less emphasised presence of hemicelluloses in isolated cellulose. As hemicelluloses and cellulose mutual adhesion is provided by hydrogen bonds[23], accessibility of cellulose OH groups is additionally restricted. Therefore, selected methods of wood extraction and cellulose isolation have not only influenced cellulose hydrophylicity and initial water content, but also CA mass gain.

During acetylation, acetic anhydride reacts both with cellulose and hemicelluloses[22]. Hemicelluloses chemical composition and structural features vary widely across wood species, subcellular location and development stages, and they usually contain acetyl- and methyl- substituted groups[23,24]. Since the acetyl content was calculated as the amount of combined acetic acid in CA, the difference between acetyl groups percentages (Table 1) could be explained with cellulose and acetic anhydride ratio. Additionally, the values of the acetyl content and resulting DS are also influenced by the presence of glucoronoxylane as the dominant type of hardwood hemicellulose. This polysaccharide backbone consists of β-D-xylopyranose units with acetyl groups at C-2 or C-3 of the xylose unit on an average of seven acetyls per ten xylose units[25]. If present, it is regularly acetylated causing the formation of xylene acetate, which is then included in saponification, leading to higher values of acetyl content and resulting DS.

Values of obtained acetyl contents and DS of CA in comparison to those of CA prepared from commercial dissolving softwood pulp are slightly higher as Loo *et al.*[26] stated that the average acetyl content of in this way prepared CA is 38.68 % with DS 2.15. The obtained values are also higher than those reported by Hu *et al.*[27] for bacterial cellulose acetylated using iodine catalyst, and somewhat similar to data reported by Cheng *et al.*[28] for iodine catalysed acetylation of cotton by-products at high reaction temperatures, where the average DS was around 2.5 depending on reaction temperature and time. Therefore, comparison of stated literature data with the obtained results further highlights the importance of cellulose purity before acetylation and the importance of proper ratio of chemicals in the reaction mixture with an emphasis on catalyst type. However, if the results, with emphasis on black alder, are interpreted through potential applications of prepared CA as a polymer base of biocomposite materials, the values of acetyl content and resulting DS are more than satisfactory, because it is proven that CA with DS > 2.4 is very resistant to biodegradation[29]. Also, as DS of CA from both species are in the range from 2.2 to 2.7, they are soluble in various solvents (e.g. acetone and dichloromethane) and therefore suitable for solvent casting of biocomposite materials[17,30].

### Results of FT-IR analysis

Cellulose conversion to CA is clearly confirmed through formation of three characteristic peaks of strong intensity, as seen in Figs. 1 and 2. The FT-IR spectra for both wood species are quite similar, with only small differences in wavenumber values of certain bands. A typical and most distinctive acetate peak is the one formed at 1757 cm⁻¹, which is associated with symmetric stretching of
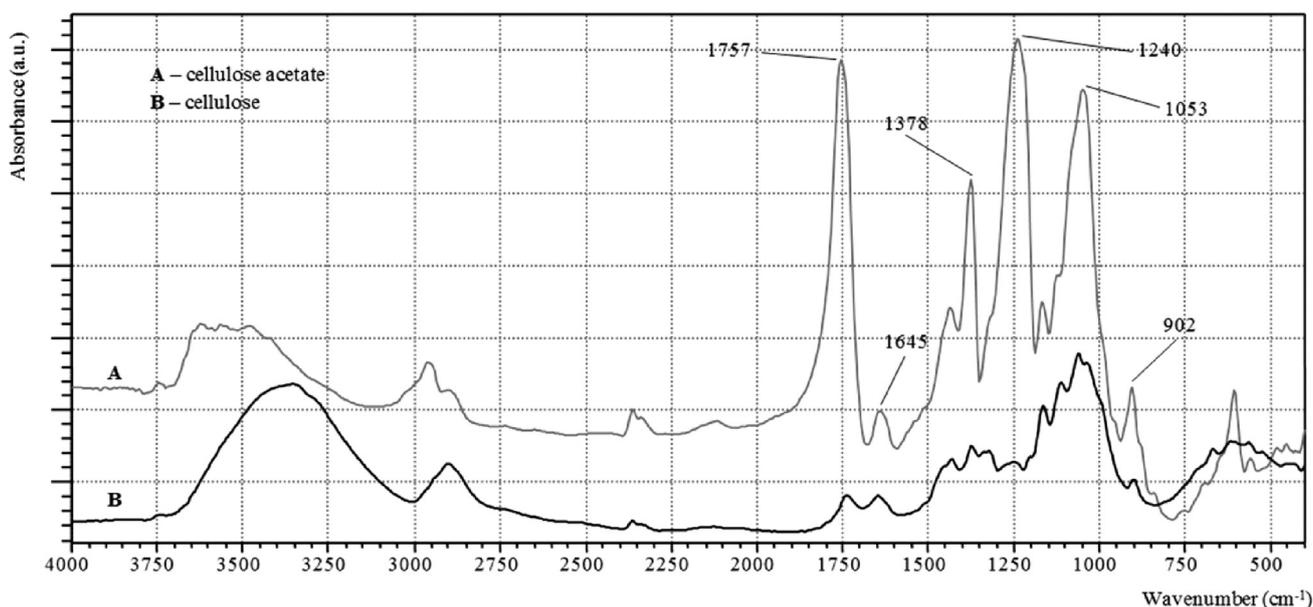


F i g .  1 – *FT-IR spectra of cellulose and CA prepared from white willow*

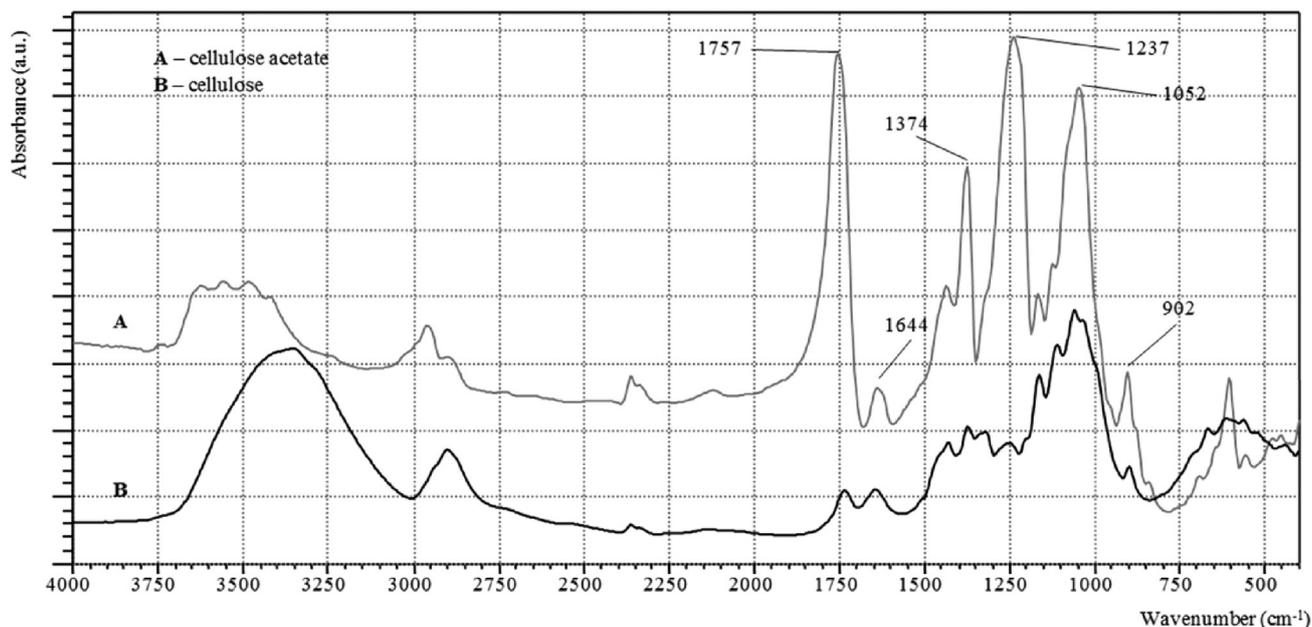F i g . 2 – *FT-IR spectra of cellulose and CA prepared from black alder*

the carbonyl group (C=O) of the acetyl group $(CH_3C(O)O–)$ in CA[31,32]. Its formation clearly indicates that some of the hydroxyl groups in the cellulose were replaced by acetyl groups.

The peak at 1374 cm^{-1} in the case of white willow (Fig. 1), and the peak at 1378 cm^{-1} in the case of black alder (Fig. 2) clearly indicate the formation of C-H bonds in methyl groups $(–CH_3)$, while those at 1237 cm^{-1} (white willow) and 1240 cm^{-1} (black alder) indicate vibrations of C–O bonds in acetyl groups[33]. The presence and very high intensities of the stated peaks inevitably confirm conversion of cellulose to CA, while the absence of peaks in the wavenumber range from 1840 cm^{-1} to 1760 cm^{-1} confirms efficient washing and complete removal of acetic acid and acetic anhydride[34]. However, the noticeable intensity increase of the peak at 902 cm^{-1} which is associated with the glycosidic bonds, indicates the degradation of the cellulose macromolecule due to prolonged chemical treatment during its isolation, which is more intensified by the use of chemicals for its acetylation (Fig. 1 and 2). Increase in intensity of peaks at 1644 cm^{-1} (white willow) and 1645 cm^{-1} (black alder) is related to the vibration of OH bonds in adsorbed water, the presence of which was determined gravimetrically.

Accuracy and good control of all acetylation parameters is best illustrated through comparison of FT-IR spectra of CA prepared from white willow and black alder (Fig. 1 and 2). Regardless of the small differences in the chemical composition of the two wood species, and the fact that cellulose isolation and its acetylation were conducted as two independent processes, the partial overlapping of spectra in means of peak positions and their intensities additionally emphasise proper choice of parameters and chemicals used for acetylation. This is related to the complex but correct and very successful process of residual acetic acid and acetic anhydride extraction from CA structure, whose presence usually causes interference during FT-IR analysis.

## Results of thermogravimetric analysis

From TG/DTG curves of CA prepared from white willow, it can be concluded that CA thermal degradation is a single stage process, where the degradation process starts at 352 °C and ends at 395 °C with maximum value at 380 °C (Fig. 3). However, in more detailed examination of DTG curve with multiple magnifications (not shown in Fig. 3), the peak of low intensity between 477 °C and 606 °C is observed, whose maximum value is at 556 °C.

Almost identical as in the case of CA prepared from white willow, TG/DTG curves of CA prepared from black alder indicate a two-stage thermal degradation process (Fig. 4). Accordingly, the formation of the peak with maximum value at 354 °C can be assigned as primary degradation, and that with maximum value at 488 °C as secondary oxidative degradation of the rest. More specifically, in the temperature range from 50 °C to 322 °C, the acetate sample loses water and other volatile components, and in the temperature range from 322 °C to 373 °C, the primary degradation occurs. Carbonisation and almost complete degradation occurs in the temperature range from 473 °C to 511 °C[35]. As thermal durability of material is determined by its onset of degradation, it can be concluded that CA prepared from white willow has greater thermal durability than that prepared
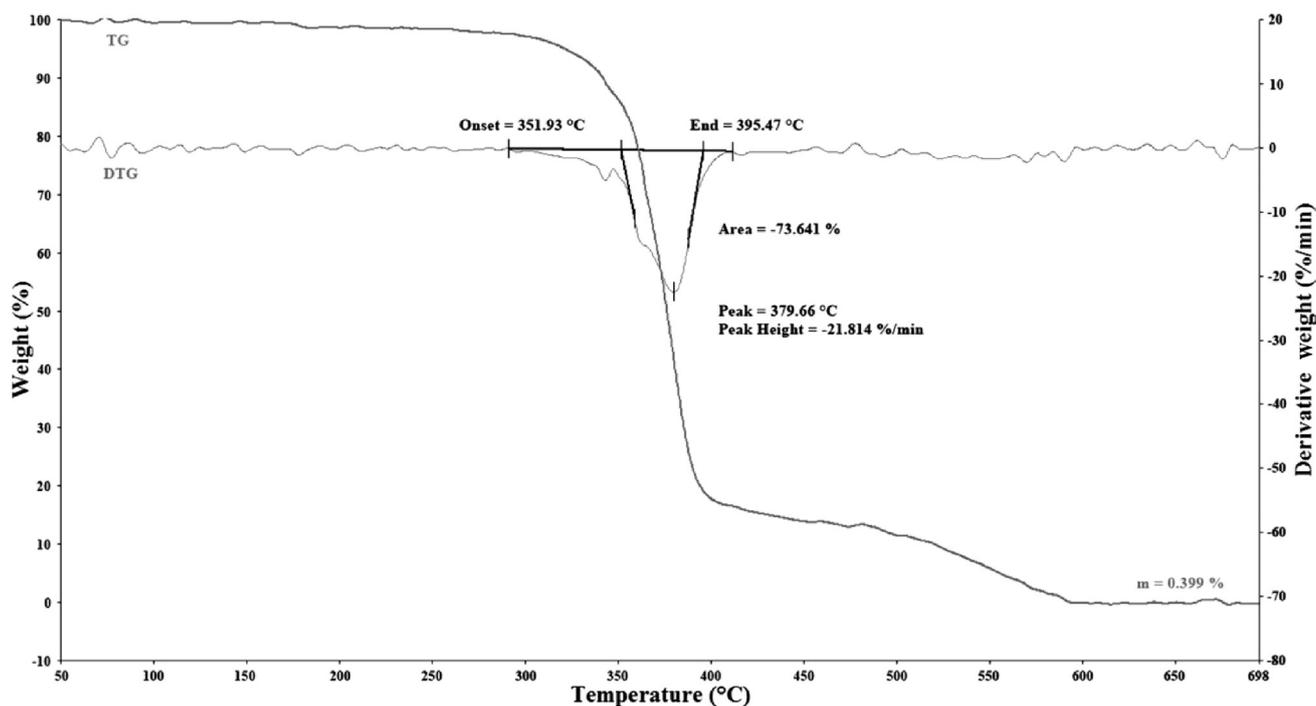
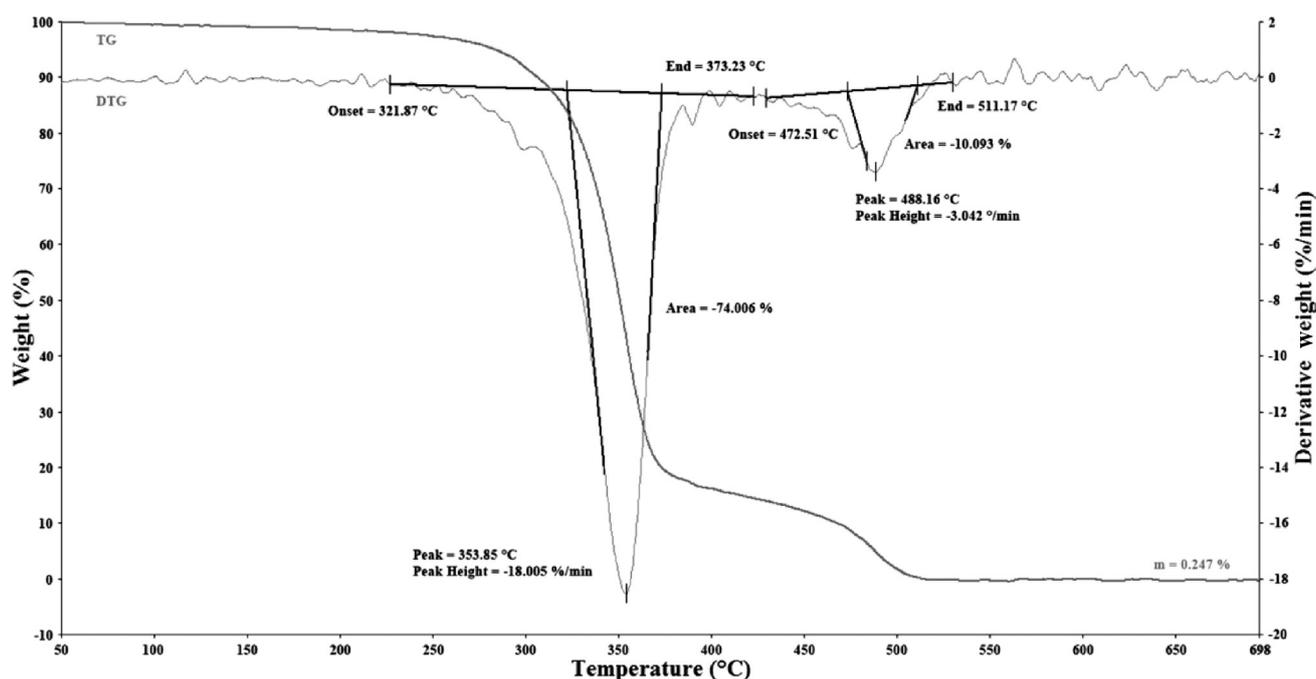F i g . 3 – *TG/DTG curves of CA prepared from white willow*



F i g . 4 – *TG/DTG curves of CA prepared from black alder*

from black alder (Fig. 3 and 4). The great difference in onset temperatures between CA from white willow (352 °C) and black alder (322 °C) is most probably gained by hemicelluloses contents in cellulose prior to acetylation. The presence of hemicelluloses significantly influences thermal stability of CA by shifting the onset temperatures to lower values as their content rises[34]. Therefore, it can be concluded that prior to acetylation, the hemicelluloses content (with

emphasis on glucoronoxylane) was higher in cellulose isolated from black alder. The obtained results additionally confirm the previously mentioned differences of acetyl contents and DS of CA prepared from the examined wood species. Char residues at 698 °C for both species can be explained by the fact that TGA analysis was performed under atmosphere of synthetic air where organic molecules burned and only inorganics ash remained.

## Conclusion

The results of this study suggest that commercially meagrely used wood species with low values of physical, mechanical and morphological characteristics can be used as raw materials for CA preparation. For that purpose the studied wood species have satisfactory chemical composition with high cellulose content, which is necessary for the effectiveness of cellulose isolation and acetylation. Regarding their chemical composition, favourable facts are also their low content of extractives and moderate lignin content. However, as results have shown, the more or less emphasised presence of hemicelluloses is exactly what determines CA chemical and thermal properties. In order to gain detailed insight into hemicelluloses role as a wood constituent that directly influences the examined properties, their contents and types should be determined in future research. The obtained results could then be used for more precise determining of effectiveness of the process of conversion of wood cellulose into a polymeric base of biocomposite materials. Nonetheless, based on the obtained results, it can be concluded that CA prepared in the described manner could be used as a polymeric base of biocomposite materials, e.g. they can be used for production of everyday household items by means of solvent casting. This is additionally confirmed by the results of FT-IR analysis, which indicated that, in such prepared CA, there is no potentially harmful free acetic acid and/or acetic anhydride.

### Nomenclature

DS        – degree of substitution

% acetyl – acetyl content, %

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