Chemical and Physical Parameters of Different Modifications of Rape Straw (*Brassica napus* L.)

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Material alternatives to wood, such as rape straw, are needed for the production of composite materials. This study performed an analysis of rape straw as a composite material source for production. There were three types of rape straw particle modification: untreated particles as reference variant, boiling in water, and soaking in sodium hydroxide (NaOH) solution. The pH and calorific value were highest for the variant soaked in NaOH. The total elemental content and the elements on the rape straw surface varied between variants. The modification method chosen influenced the pH, calorific value, elemental composition, and contact angle.

Keywords: Modification of rape straw; Brassica napus; Physical and agrochemical parameters; Scanning electron microscopy

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INTRODUCTION

Recently there has been an effort to develop new composite materials using alternative sources of raw materials. This trend is largely explained by population growth, which contributes directly to a limited supply of natural resources, as well as wood shortage in all wood processing industries (Galor and Weil 2000; Bektas *et al*. 2005; Seintsch 2011; Lauri *et al.* 2012). One alternative source of raw materials is post-harvest rapeseed crop residue (Mohanty *et al*. 2002; Dziurka *et al.* 2015). As a prospective raw material, rapeseed has many advantages, as it is available in large quantities and is not yet used in other products with high added value (Bečka *et al*. 2007; Dukarska *et al*. 2017). However, waxy and siliceous substances are present on the surface of winter rape stems, which prevents the formation of quality adhesion between particle and adhesive (Grigoriou 2000). This is the main disadvantage of particles from annual plants compared to wood particles. The chemical composition differs between internal and external areas of the stem because of cuticles and epicuticular waxes (Wiśniewska *et al.* 2003; Trischler, and Sandberg 2014). The surface has a strong impact on the water contact angle, which deteriorates the wetting of particles by adhesives, since adhesives used in particleboard production are mainly water-based (Wiśniewska *et al.* 2003). Therefore, it is necessary to pre-treat these particles from annual plants before the production of the composite material itself (Mahlberg *et al*. 1999; Cao *et al.* 2017). This modification can be done in various ways (Pelaez-Samaniego *et al*. 2013; Trischler and Sandberg 2014). Boiling in water is regarded favorably as a treatment due to its ease of implementation (Bekhta *et al.* 2013). An alternative is alkaline treatment, which breaks ester linkages between wax and lignocellulose, as well as dissolving wax and lignin (Binod *et al.* 2010; Wan *et al.* 2011). In this study, winter rape chips were modified by applying hydrothermal and chemical (soaking in sodium hydroxide) processes (Xie *et al*. 2010; Bekhta *et al*. 2013). It is assumed that the modification destroys the waxy, siliceous substances on the surface of the chips and consequently improves adhesion in the composite product. This study characterized the physical and chemical properties of raw and modified rapeseed particles to measure the effects of modification on particle properties. This information on the effect of the various particle modifications on particle properties will promote the utilization of this waste material in particleboard production.

EXPERIMENTAL

Materials

Chipped rape straw (*Brassica napus* L.) particles were treated by one of two processes. In the chemical treatment, the particles were soaked in 2% sodium hydroxide solution (NaOH) at 20 °C for 45 min. Alternatively, a hydrothermal treatment was carried out by boiling in water for 45 min. After both modifications, particles were carefully flushed with water and then oven-dried to 6% moisture content. A portion of each sample was dried at 40 °C and milled for determination of the total element content, calorific value, and percentage of volatile solids. Representation of the individual fractions in chopped rape straw is stated in Table 1.

Table 1. Representation of the Individual Fractions in Chopped Rape Straw

Fraction [mm]	0-0.25	0.25-0.5	0.5-0.8	0.8-1.6	1.6-2	2-3.15	3.15-8
Representation [%]	0.3	0.6	5.2	39.9	20.9	23.8	9.3

Methods

The goal of this study was to determine the effects of different particle pre-treatment methods on particle properties. In order to estimate this effect and to determine what happened and changed in the particle after modification, the following characteristics were observed: equilibrium moisture content, pH value, calorific value, total element content, elemental composition of the surface, water contact angle, and microstructure of the particle surface.

Chemical analysis of rape straw

Moisture content was determined by measurement at 105 °C by a ML-50 Moisture Analyzer (A&D Company, Elk Grove Village, IL, USA). The pH was measured in samples mixed with deionized water (1:5 w/v wet basis) using a WTW pH 340 I device (GeoTech, Denver, CO, USA), according to BSI EN 15933 (2012). Total element contents were determined through decomposition in an enclosed microwave, using an Ethos 1 system (MLS GmbH, Leutkirch im Allgäu, Germany). Elemental concentrations were determined using inductively coupled plasma optical emission spectrometry (ICP-OES; Varian VistaPro, Mulgrave, Australia) with axial plasma configuration. The calorific value of the material and the percentage of volatile solids were determined using the Laget MS 10A dry calorimeter (Laget, Staufen im Breisgau, Germany). The sample was burned in a 100% oxygen atmosphere, according to ČSN ISO 1928 (2010).

Scanning electron microscopy (SEM) and elemental analysis

The surface of the rape straw particles was observed with a MIRA 3 electron microscope (Tescan Orsay Holding, Brno, Czech Republic) with a secondary electron detector operated at 15 kV acceleration voltage. When rape straw is washed with water, the elements can be changed on the surface, as well as when straw soaked in NaOH. The elemental compositions of the surface were examined by an energy dispersive spectroscopy system (Bruker XFlash X-ray detector, Karlsruhe, Germany, and ESPRIT 2 software).

Contact angle

Contact angle analysis is widely used to determine the wettability of solid materials (Walinder and Ström 2001; Aydin 2004). To determine wetting characteristics of modified particles, the contact angle of the water and particle surface was measured using a DSA 30E goniometer (Krüss GmbH, Hamburg, Germany). Straw particles have both interior and exterior surfaces. However, due to a pith on the interior of the particles, the contact angle of the water droplet could not be measured on the inside, and therefore only the exterior contact angle was measured. Static contact angle was measured for 30 measurements for each straw modification. In order to minimize the influence of variable of straw surface, a new particle was used for each droplet. The volume of distilled each water droplet was 5 µL with the measurement taken 5 s after the application. Contact angle was measured using image analysis software.

Statistical Analysis

All results from the agrochemical analysis represent the mean values of three replicates. Analysis of normality and homogeneity and one-way analysis of variance (ANOVA) were performed with STATISTICA 12 software (StatSoft, Tulsa, OK, USA). ANOVA was based on a 95% confidence level in accordance with Tukey's range HSD (honest significant difference) test.

RESULTS AND DISCUSSION

In each modification, the pH value of the rape straw was different. The lowest pH value was in the sample modified through maceration in H_2O (6.58), and conversely, the highest pH value was in the sample modified through maceration in NaOH (9.44) (Table 2). This result suggests that the straw was not well washed after soaking in the NaOH solution as there was the highest total content of Na present. Both in this variant and the reference variant, there was a high content of calcium (Ca) on the surface of the straw, which was seen in the elemental analysis (Fig. 2a, c). The equilibrium moisture content was very low in all samples, with no statistically significant difference. The highest moisture content was in the sample modified with H_2O 7.7% (Table 2).

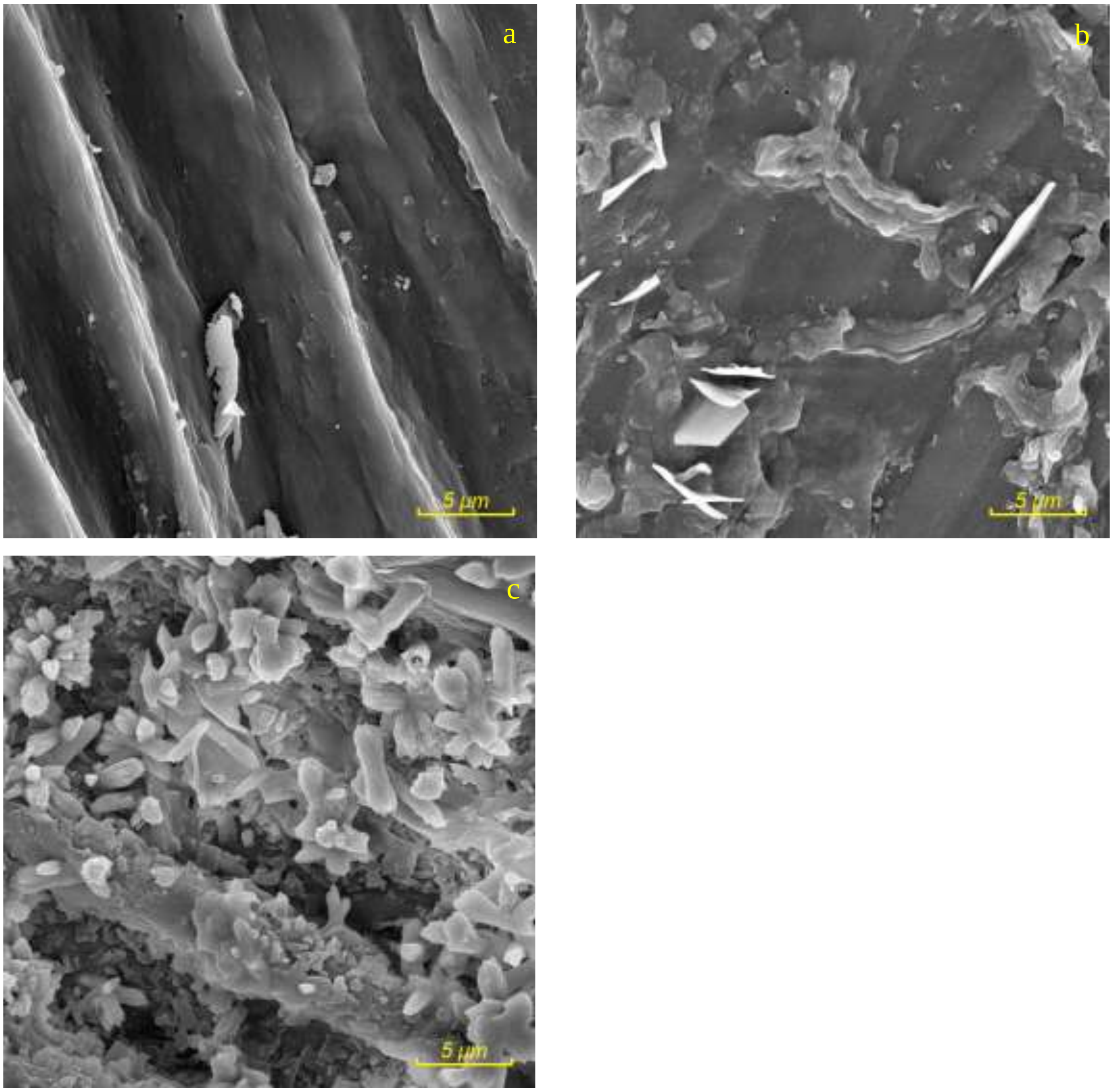

Fig. 1. Electron micrographs of rape straw surfaces (magnification 10000x). (a) Reference variant, (b) variant modified by cooking in H_2O, and (c) variant modified in NaOH solution

Table 2. pH and Moisture Content in Modified Rape Straw

Modification	pH/H_2O	Moisture (%)
Ref.	7.86 ± 0.08 ^{a}	7.6 ± 0.46 ^{a}
H_2O	6.58 ± 0.07 ^{b}	7.7 ± 0.10 ^{a}
NaOH	9.44 ± 0.56 ^{c}	6.9 ± 0.32 ^{a}

Values are the means ± SD (n = 3). Different letters (in superscript) in a column indicate significant differences (Tukey's HSD test, $P < 0.05$).

The percentage of volatile solids present in all modifications was relatively high. The highest value of volatile solids was found in the modification with H_2O (96.97%) (Table 3). It appeared that the H_2O dissolved in the compounds into an improved combustible form. This variant had the highest value of volatile solids, but also the lowest calorific value. In contrast, the variant with NaOH had the highest calorific value of 18.4 MJ.kg^{-1} but the lowest value of volatile solids. The calorific value can be influenced by the content of carbon (C) or sulfur (S) present (Erol *et al*. 2010). As the elemental analysis showed, the highest C content was found in the variant with NaOH (Fig. 2c), explaining the high calorific value of this variant. Total S content was the highest in the reference variant and the lowest in variant with H_2O (Table 4), again explaining its calorific value.

Table 3. Volatile Solids and the Calorific Value of Modified Rape Straw

Modification	Volatile Solids (%)	Calorific Value (MJ.kg^{-1})
Ref.	95.52	17.9
H_2O	96.97	17.6
NaOH	94.60	18.4

Table 4. Elemental Analysis of Modified Milled Rape Straw

Element / Modification	Reference	H_2O	NaOH
Al (mg/kg)	45.30 ± 4.1 ^{a}	59.73 ± 0.95 ^{b}	61.93 ± 8.95 ^{b}
B (mg/kg)	11.01 ± 0.52 ^{a}	7.85 ± 0.2 ^{b}	7.94 ± 0.9 ^{b}
Ca (mg/kg)	6941.9 ± 99 ^{a}	5858.5 ± 41.6 ^{b}	5705.2 ± 657.7 ^{b}
Cd (mg/kg)	0.08 ± 0.01 ^{a}	0.09 ± 0.01 ^{a}	0.09 ± 0.02 ^{a}
Cr (mg/kg)	0.23 ± 0.0 ^{a}	0.25 ± 0.02 ^{a}	0.25 ± 0.04 ^{a}
Cu (mg/kg)	1.03 ± 0.07 ^{a}	0.82 ± 0.03 ^{b}	0.67 ± 0.07 ^{c}
Fe (mg/kg)	42.67 ± 11.8 ^{a}	46.97 ± 1.39 ^{a}	50.83 ± 8.42 ^{a}
K (mg/kg)	5036,8 ± 198 ^{a}	1026.1 ± 34.5 ^{b}	732.8 ± 88.3 ^{c}
Mg (mg/kg)	998.8 ± 18.38 ^{a}	739.1 ± 11.72 ^{b}	1089.8 ± 107.9 ^{a}
Mn (mg/kg)	8.09 ± 0.3 ^{a}	6.71 ± 0.05 ^{b}	4.80 ± 0.57 ^{c}
Ni (mg/kg)	0.33 ± 0.13 ^{a}	0.10 ± 0.05 ^{b}	0.19 ± 0.1 ^{ab}
P (mg/kg)	248.9 ± 29.72 ^{a}	217.5 ± 9.3 ^{a}	210.3 ± 24.84 ^{a}
S (mg/kg)	1340 ± 45.6 ^{a}	431.5 ± 13 ^{b}	323.4 ± 27 ^{c}
Zn (mg/kg)	1.26 ± 0.08 ^{a}	1.68 ± 0.27 ^{a}	2.50 ± 0.45 ^{b}
Na (mg/kg)	245.5 ± 49.5 ^{a}	663.8 ± 29.1 ^{a}	4187.8 ± 508.5 ^{b}

Values are the means ± SD (n = 3). Different letters (in superscript) in a column indicate significant differences (Tukey's HSD test, $P < 0.05$).

An extensive analysis of element concentrations was performed, including an analysis of the total element content (Table 4) and an analysis of particle surfaces using SEM (Fig. 1a-c; Fig. 2a-c). The total content of arsenic (As) and lead (Pb) were below the detection limit. The total contents of cadmium (Cd), chromium (Cr), and nickel (Ni) were very low and therefore were not statistically different. None of the above elements were found on the surface of the rape straw.

The total contents of copper (Cu), zinc (Zn), manganese (Mn), boron (B), iron (Fe), and aluminum (Al) were low but statistically significant. Specifically, the total content of Mn and Cu was the highest in the reference variant, almost twice as high as in the variant with NaOH (Table 4). Significant differences were not found in the total content of Fe. None of these elements were detectable using SEM (Fig. 2a-c).

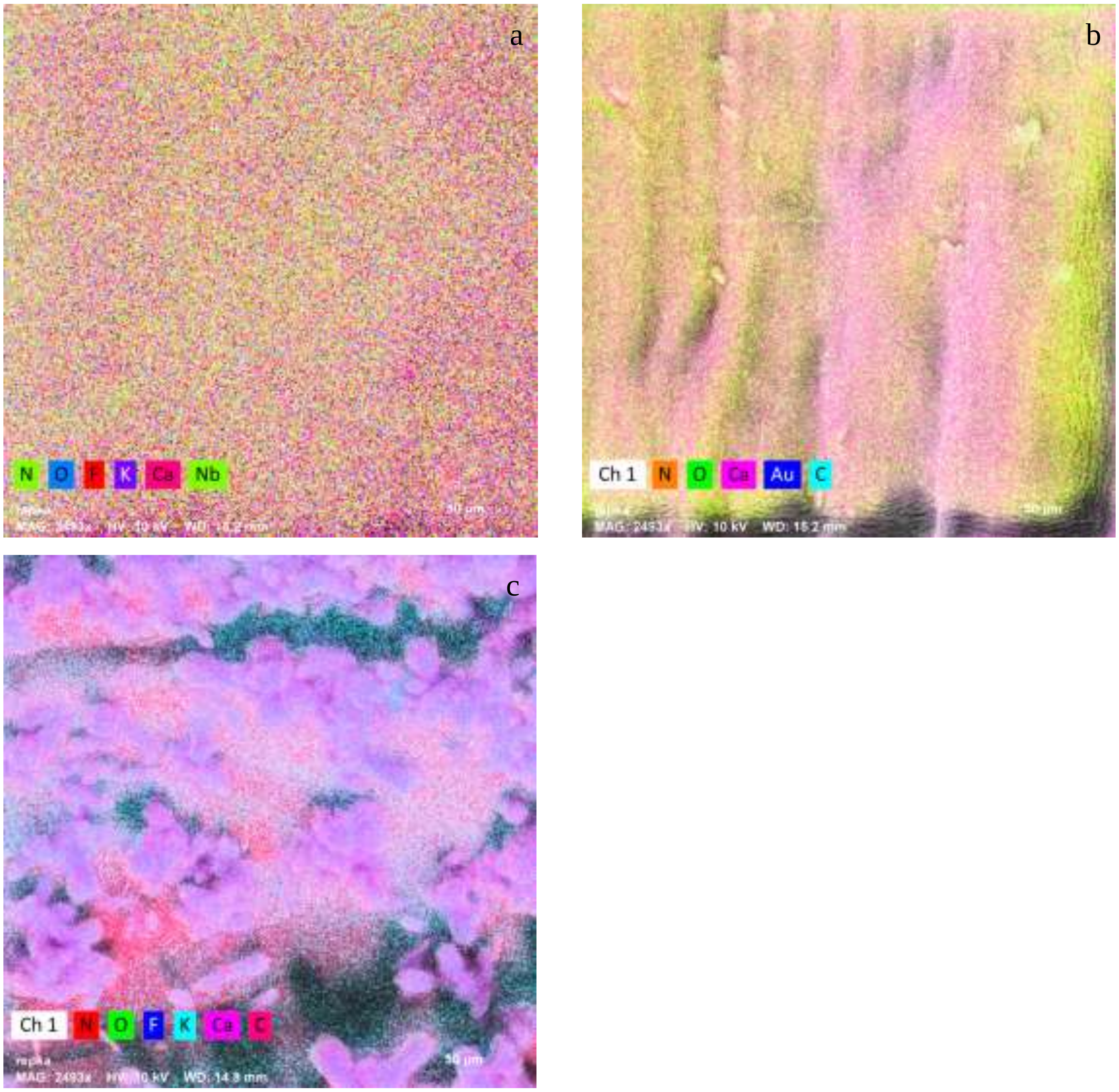

Fig. 2. Elemental content of rape straw surface taken by SEM. (a) Reference variant, (b) variant modified by cooking in H_2O, and (c) variant modified in NaOH solution

The total phosphorus (P) content was over 200 mg/kg in all variants, and no significant differences were found. However, a significant difference was found in the total content of Na. The total content of Na was 17 times higher (4187.8 mg/kg) for the variant with NaOH compared with the reference variant (245.5 mg/kg). As Na was only found on the exterior surface of this variant, it can be assumed that the large amount of Na present was probably caused by poor washing of the NaOH solution.

The total S content of the reference variant was four times higher than in variant with NaOH, which further confirming the calorific value of this variants. Potassium (K) was found only on the surface of the reference variant and the variant with NaOH, as shown in pictures taken by SEM (Fig. 2a-c). In the variant with H_2O, K could have been washed away from the surface. In the variant with NaOH, K could have precipitated on the surface. Total K content was the highest in the reference variant (5037 mg/kg) and was almost 7 times higher in the reference variant than in the variant with NaOH (733 mg/kg).

The lowest magnesium (Mg) content was found in variant with H_2O (739 mg/kg). However, Mg on the surface of the rape straw was found only in the variant with H_2O. The total Ca content corresponds to the content found on the rape straw surface by SEM analysis. The hydroxide precipitated Ca on the surface of the variant with NaOH (Fig. 2c). This Ca deposit created crystals that were observed also by SEM, as can be seen in Fig. 1c. There were no Ca crystals on the surface of reference particles or the particles modified by cooking. Only dust was found on the surface of these particles (Fig. 1a, b). The pith of the rape straw particles was observed also. Figure 3a shows the undisturbed pith of the reference sample. Both hydrothermal and alkaline modification destroyed the pith, which is shown in Fig. 3b and Fig. 3c, respectively.

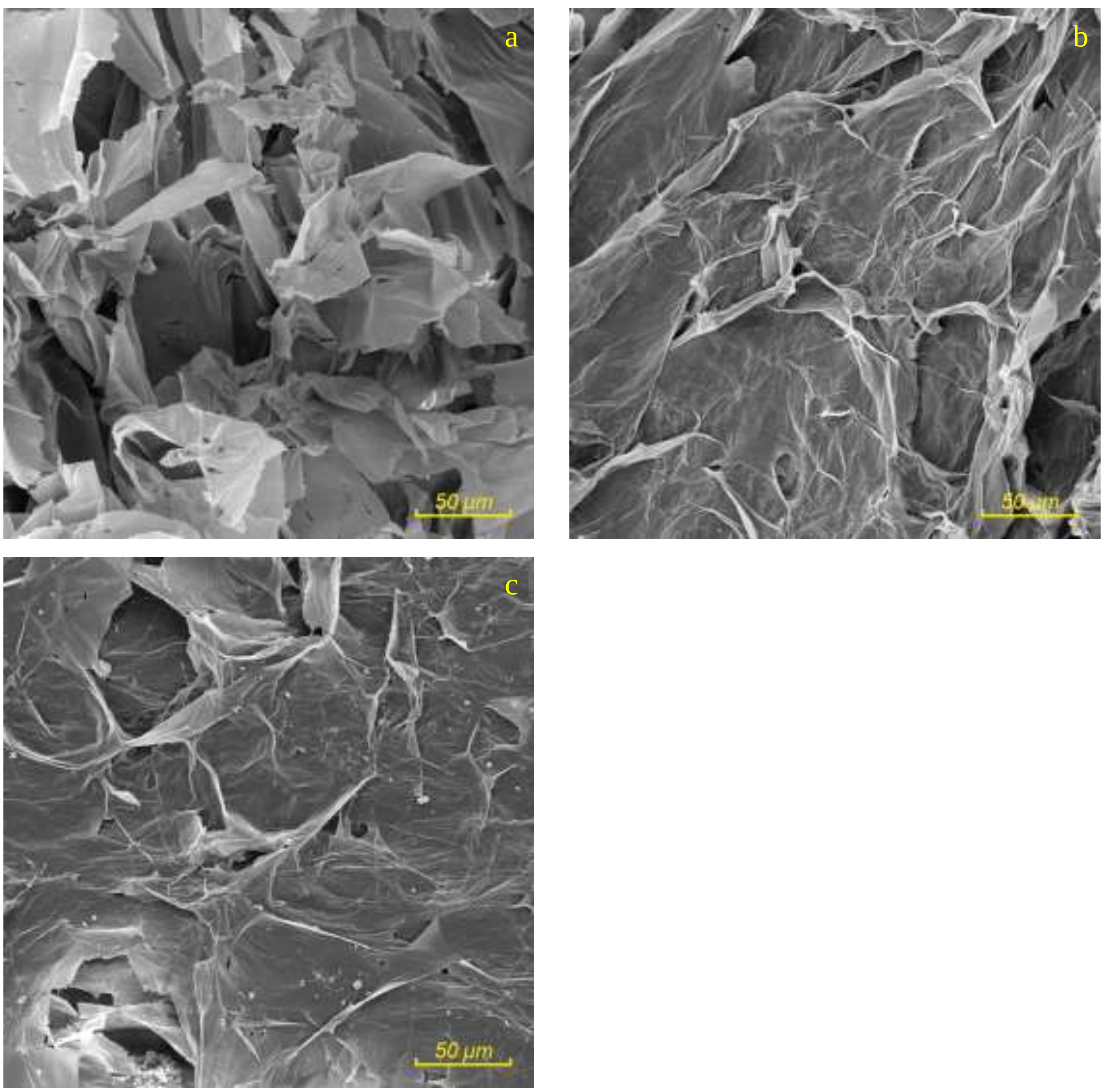

Fig. 3. Electron micrographs of rape straw pith (magnification 1000x). (a) Reference variant, (b) variant modified by cooking in H_2O, and (c) variant modified in NaOH solution

Figure 4 depicts the analysis of contact angle between water droplet and straw particle surface. The vertical columns depict 95% confidence intervals. Both modifications caused the desired decrease in water contact angle, while the contact angle was different for each modification. The largest contact angle was found in the reference variant, with a mean of 94.1° and the lowest mean, 82.7°, was seen in the modification with H_2O. A smaller contact angle is better for the strength of a glued joint (Banea and Silva 2008; Moghadamzadeh *et al*. 2011). The variant with H_2O exhibited a significant difference from the others, but there was no significant difference between the reference and NaOH variants. The alkaline modification resulted in the lowest variability of water contact angle (Fig. 4).

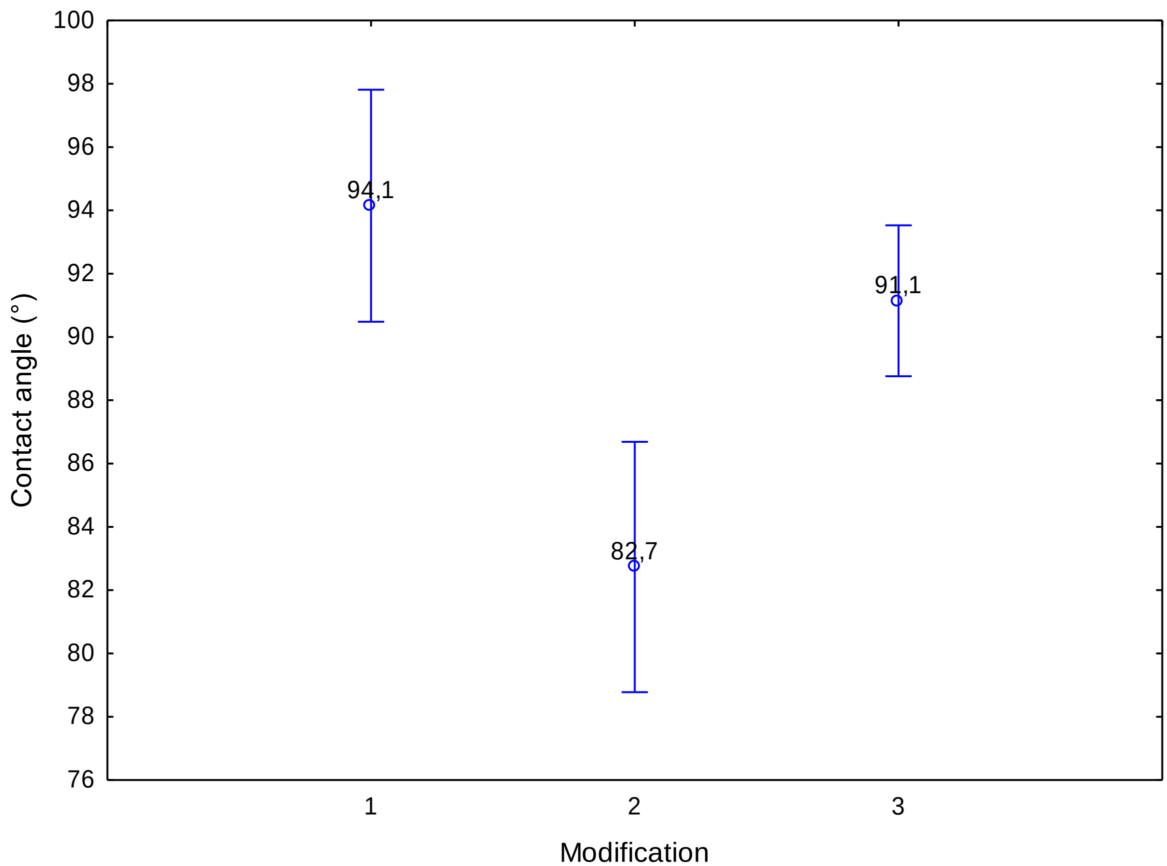

Fig. 4. Influence of modification technique on contact angle: 1-reference variant, 2-variant modified by cooking in H_2O, 3-variant modified in NaOH solution

CONCLUSIONS

1. The elemental composition of surface and the total element content of rape straw are highly influenced by the type of modification.
2. A variant modified with H_2O exhibited the highest value of volatile solids and the

lowest calorific value, but a variant modified with NaOH had the highest calorific value and the lowest value of volatile solids.

3. A disadvantage of soaking rape seed straw particles in NaOH is that it is not possible to rinse out all of the hydroxide. Therefore, the variant modified with NaOH had the highest pH value.
4. Contact angle is also dependent on the type of modification. The variant with the best strength for a glued joint was modified with H_2O.
5. Moisture content is not dependent on the type of modification, as there were no significant differences.

ACKNOWLEDGMENTS

This work was supported by the Czech University of Life Sciences Prague under the CIGA project No. 20174306.

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Article submitted: August 25, 2017; Peer review completed: October 8, 2017; Revised version received and accepted: November 1, 2017; Published: November 6, 2017.
DOI: 10.15376/biores.13.1.104-114