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Aluminium Trihydrate-filled Poly(methyl methacrylate) (PMMA/ATH) Waste Powder Utilization in Wood-plastic Composite Boards Bonded by MUF Resin

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An alternative approach to producing a wood-plastic composite (WPC) from wood particles, aluminium trihydrate-filled poly(methyl methacrylate) (PMMA/ATH) waste powder, and melamine-urea-formaldehyde (MUF) resin is described. The surface of PMMA/ATH powder was modified with ureido- and amino-functional silane coupling agents at four different degrees of modification: 0.3%, 0.5%, 1.0%, and 2.0%. An X-ray photoelectron spectroscopy (XPS) analysis was executed on a silane-modified PMMA/ATH material, and the results revealed the presence of chemically bonded silanes on the PMMA/ATH surface. Contact angle measurements were also performed to calculate the surface free energies of the modified powders. Water contact angles of modified powders slightly decreased as surface free energy increased with the degree of surface modification. Mechanical tests of the composites showed that different degrees of surface modification had a significant influence on modulus of elasticity (MOE) and modulus of rupture (MOR) of the composite boards. However, there were no significant differences between the silanes used.

INTRODUCTION

Composite materials containing industrial and agricultural waste have attracted a great deal of interest in research and development departments in recent decades. The main intention of the researchers is to produce alternative, environmentally friendly, and sustainable materials that can compete with traditional materials on the market. The wood industry has turned its attention to the research and manufacture of wood-plastic composites (WPC), primarily in response to the need for moisture-durable wood-based materials (Wolcott 2003), but also to utilize residues from the wood industry, paper industry, and other biomass fibre-producing industries (Rowell *et al.* 1991). The general idea in producing WPCs is to combine wood particles or wood flour with predominantly thermoplastic resins, but the use of thermoset resins and naturally derived resins may also be applied. Many different techniques of producing WPCs have been documented and can be sorted into three main categories: extrusion, injection moulding, and flat-pressing technologies. The latter can be considered as a straightforward and cost-effective alternative to manufacturing WPC (Wolcott 2003; Ayrilmis and Jarusombuti 2010; Shalbafan *et al.* 2013).

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In this article, the production and mechanical properties of flat-pressed alternative WPC boards are presented. This study aimed to utilize the industrial aluminium trihydrate-filled poly(methyl methacrylate) composite (PMMA/ATH) waste powder into a WPC-type composite. The PMMA/ATH waste powder represents a potential raw material for new products, because its global production is estimated to be approximately 85000 tons per year (Vovk *et al.* 2019). Combining PMMA/ATH waste with renewable natural resources, such as wood, would thus contribute to the more sustainable use of materials. This was the authors' main motivation behind the concentrated research of the PMMA/ATH waste use in alternative WPC.

The production, composition, and chemical reactions of PMMA/ATH during the synthesis, as well as the diverse application of the composite along with the possibilities of recycling, are well-described elsewhere (Vovk *et al.* 2017). The characteristics of the PMMA/ATH powder form have also been determined and presented (Vovk *et al.* 2019). Mechanical and surface characteristics of the PMMA/ATH powder offer the possibility of utilizing the powder as an asphalt concrete additive (Sustersic *et al.* 2013; Tusar *et al.* 2014) as well as combining PMMA/ATH with wood (Vovk *et al.* 2017, 2019; Wallenhorst *et al.* 2015, 2018). Air plasma-treated PMMA/ATH composite plates have been bonded with wood using melamine-urea-formaldehyde (MUF) resin (Vovk *et al.* 2018). Although no significant differences occurred between untreated and plasma-treated samples, the results showed the potential of utilizing MUF resin to combine PMMA/ATH with wood-based materials. Furthermore, atmospheric pressure plasma powder deposition is also used to apply PMMA/ATH powder waste as a coating on wood (Wallenhorst *et al.* 2015), and the addition of phenol-formaldehyde to the coating system results in outstanding bonding to wood (Wallenhorst *et al.* 2018).

To overcome the differences in surface characteristics between wood and PMMA/ATH material, different approaches to the surface treatment of the PMMA/ATH powder were applied in this article. Grinding the powder was the first approach, as it is documented that ground particles have lower water contact angles and slightly higher surface energy (Vovk *et al.* 2019), which could be beneficial in composite systems with water-based resin, such as MUF, which was used in this study. The second approach was to coat the PMMA/ATH particles' surfaces with silane coupling agents and thus induce chemical changes at the surfaces of the particles to make them more compatible with the selected adhesive. Silanes with ureido- and amino- functional groups have been chosen as suitable for the MUF resin, as their effect was already proven in similar urea-formaldehyde (UF) resin (Han *et al.* 1998; Zuo *et al.* 2013). Successful attachment or deposition of aminofunctional and ureidofunctional silanes on different kinds of surfaces such as cellulose fibres, magnesium hydroxide, $CaCO_3$, palygorskite clay, and E-glass fibres, has already been demonstrated by other researchers (Acres *et al.* 2012; Demjen *et al.* 1997; Salon *et al.* 2005; Watson *et al.* 2001; Luo *et al.* 2008; Zuo *et al.* 2013).

EXPERIMENTAL

Materials

The PMMA/ATH waste powder was provided by Kolpa d.d. (Metlika, Slovenia). Detailed characterization of the powder is documented by Vovk *et al.* (2019). For the purposes of this paper, the same powder was used, particularly the non-ground and ground PMMA/ATH powder with average particle diameters of 75.6 µm and 14.1 µm,

respectively. The Brunauer-Emmett-Teller (BET) specific surface area was also determined to be 2.15 m²/g for non-ground powder and 3.17 m²/g for ground powder. Other characteristics, such as morphology, surface free energy, and thermal stability, are also described by Vovk *et al.* (2019).

Industrial aluminium trihydrate-filled poly(methyl methacrylate) (PMMA/ATH) plate, white (colour 108), 3-mm-thick, was also provided by Kolpa d.d. (Metlika, Slovenia) and used to execute the X-ray photoelectron spectroscopy (XPS) analysis of the chemical composition of its silane-modified and unmodified surfaces.

Silanes Dynasylan® SIVO 214 (γ-aminopropyltriethoxysilane, APTES) and Dynasylan® 2201 EQ (γ-ureidopropyltriethoxysilane, UPTES) were used as PMMA/ATH surface modifiers (Evonik, Essen, Germany). The main differences between the two are their reactive functional organic groups, as silane APTES contains the amino- group and UPTES contains the ureido- group.

Wood fibres were provided by Lesonit d.o.o. (Ilirska Bistrica, Slovenia) and consisted of 80% fir (*Abies alba* Mill.) and 20% European beech (*Fagus sylvatica* L.) fibres. The fibres were subjected to a drying process for 72 h at 50 °C.

Wood powder was prepared from beech wood, cut to smaller dimensions (5 mm × 5 mm × 40 mm) and ground with a Retsch SM 2000 (Retsch, Haan, Germany), using the 4 mm × 4 mm mesh. Wood fibres and wood powder were stored at 50% relative air humidity and at 21 °C for at least 10 days. One day prior to their use, both were additionally dried at 70 °C for 18 h and afterwards kept in sealed plastic bags as they cooled down. The moisture content of wood fibres and wood powder after drying and prior to the application was 3.3% and 1.9%, respectively.

Meldur H97 melamine-urea-formaldehyde (MUF) resin was provided by Melamin d.d. (Kočevje, Slovenia). According to the manufacturer, MUF resin consisted of 62 ± 2% dry content, viscosity (as per SIST EN ISO 2431 (2019) φ4, 20 °C) was 80 s to 200 s and consisted of maximum 0.5% free formaldehyde.

Methods

Contact angle measurement and surface free energy calculation

The PMMA/ATH powder samples with different degrees of surface modification were pressed with a hand press (Graseby, Specac, Orpington, United Kingdom) to form round plates, measuring 13 mm in diameter, which were used for the contact angle measurements. Conditions of the pressing procedure are described in Table 1. A DSA100 drop shape analyzer (Krüss, Hamburg, Germany) was used to determine the contact angles of distilled water and diiodomethane drops on un-modified and modified PMMA/ATH powder. The volume of drops applied was 1 μL to 2 μL. The process of applying drops on substrates was recorded in video format, and each drop was subsequently analysed with a circle-fitting method from which the contact angle was calculated. A minimum of 10 and a maximum of 15 drops were analyzed for each sample. Surface free energies of the samples were determined using the drop shape analyzer with an integrated Owens, Wendt, Rabel, and Kaelble (OWRK) algorithm (Owens and Wendt 1969), which was based on Young's equation,

$$\gamma_{SG} = \gamma_{sl} + \gamma_{LG} \cos \theta \qquad (1)$$

where γ_{SG} is the interfacial energy (*mNm^{-1}*) between the solid and the gas, γ_{LG} is the interfacial energy (*mNm^{-1}*) between liquid and the gas, and γ_{SL} is the interfacial energy between the solid and liquid (*mNm^{-1}*).

According to the OWRK, the total energy γ^{tot} is the sum of polar γ_s^p and disperse γ_s^d part: $\gamma^{\text{tot}} = \gamma^P + \gamma^D$. Distilled water ($\gamma_l^p = 51\ mNm^{-1}$, $\gamma_l^d = 21.8\ mNm^{-1}$ at 20 °C) and diiodomethane ($\gamma_l^p = 0\ mNm^{-1}$, $\gamma_l^d = 50.8\ mNm^{-1}$ at 20 °C) were used to analyze contact angles and determine their surface energy.

Table 1. Conditions for the Plate Formation and Contact Angles Analysis

Pressing Time	10 s
Pressure	739.46 N/mm^2
Sample Mass	275 ± 5 mg
Wetting Time	3 s
Environmental Humidity	35 ± 2%
Environmental Temperature	22 ± 1 °C

Surface modification and XPS analysis

Silane mixtures were prepared prior to their application to the non-ground PMMA/ATH powder. Distilled water was acidified with acetic acid to pH 4 (pH value was measured with a SevenEasy pH Meter S20; Mettler Toledo, Columbus, OH, USA) and added to silanes in a 1:1 molar ratio for APTES and a 1:3 molar ratio for UPTES. This mixture was stirred for 1 min to enable the hydrolysis of silanes. After the hydrolysis, non-ground PMMA/ATH powder was silanized using a high-shear mixer 4M8-TriX (ProCept, Redwood City, CA, USA) with a FM4000 4-L glass container, and then 400 g of PMMA/ATH powder was put into the container and mixed. The impeller speed was set at 400 rpm, and the chopper speed was set at 1200 rpm during the addition of silane mixtures, which were applied to the PMMA/ATH powder with an intensity of 2 mL/min as the powder was mixed. After the addition of silane mixtures, impeller and chopper speeds were raised to 600 rpm and 2000 rpm, respectively, and mixed for 5 min to increase the shear forces between the powder particles, raise the temperature, and enable even spreading of the silane mixtures on the particles. The degree of surface modification was determined by the amount of silane mixtures added to the PMMA/ATH powder with respect to the ATH content in the powder. Therefore, the different degrees of surface modifications were 0.3%, 0.5%, 1.0%, and 2.0%. The surface-modified powder was stored in glass vessels and put in the convection oven for 45 min at 80 °C. After that, it was left overnight to cool down and used to make the composite boards the next day.

The XPS spectrometry was used to determine whether the APTES and UPTES silanes bonded to the PMMA/ATH surface. The PMMA/ATH plate was hand-ground on one side with rough abrasive paper (p40) to obtain a rough surface where ATH particles were to be exposed. Grinding the surface attended for silane modification, the authors attempted to simulate the powder structure of PMMA/ATH with exposed ATH particles, as described by Vovk *et al.* (2019), which provided –OH$^-$ groups as active sites for silanes to attach to. The PMMA/ATH plate was cut into five specimens with dimensions of 20 mm $\times$ 20 mm $\times$ 3 mm. Approximately 3 mL of the same silane mixtures, as described above, were applied to rough surfaces of the specimens and carefully spread with cotton cloth to obtain a thin layer of coating. Five different specimens were obtained, as shown in Table 2. The reference specimen (REF-S) had an un-modified surface. Two specimens had surfaces modified with silane UPTES, one of which was additionally exposed to a temperature of 80 °C in a convection oven for 45 min (specimen US80) and the other was left at a room temperature at 20 °C (specimen US20). The last two specimens had surfaces

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modified with silane APTES, one of which was also exposed to 80 °C for 45 min (specimen AS80) and the other was left at 20 °C (specimen AS20). Specimens with modified surfaces and a reference specimen were carefully stored in closed glass vessels and left overnight. The next day, each specimen was separately immersed in a 50:50 mixture of distilled water and ethanol and placed into an ultrasound bath for 15 min. Afterwards, the specimens were carefully sealed in glass vessels to avoid contamination. A model TFA XPS spectrometer (Physical Electronics, Inc., Chanhassen, MN, USA) was used to perform the XPS analysis on the surfaces of specimens. The analysis was executed in an ultra-high vacuum at 10^{-7} Pa, using Al-monochromatized source of x-rays. A non-modified PMMA/ATH plate specimen was analysed on both sides (non-ground and ground) as a reference. The diameter of the analysing surface was 0.4 mm. The XPS spectres were recorded, chemical elements were defined, and their concentration was calculated. The calculation was performed in a way that the measured intensities were divided by the relative sensitivity factors, which were provided by the spectrometer manufacturer.

Table 2. Conditions for the Plate Formation and Contact Angles Analysis

Pressing Time	10 s
Pressure	739.46 N/mm^2
Sample Mass	275 ± 5 mg
Wetting Time	3 s
Environmental Humidity	35 ± 2%
Environmental Temperature	22 ± 1 °C

Board production

For each board produced, 240 g of materials were used. The shares of materials were as follows: 50 wt% of PMMA/ATH powder, 35 wt% of wood powder, 5 wt% of wood fibres, and 10 wt% of MUF (dry content). Materials were mixed with high shear mixer 4M8-TriX (ProCept, Redwood City, CA, USA) with an FM4000 4-L glass container. The speed of the impeller and chopper was set at 600 rpm and 1800 rpm, respectively. It was established in preliminary tests that mixing the components with more than 5% of wood fibres was not possible, as fibres became stuck between the impeller and the glass container, which caused high torque, or the whole mixture circled along with the impeller and therefore failed to mix at all. Mixtures of PMMA/ATH powder, wood powder, and wood fibres were mixed for 2 min prior to addition of MUF resin. While the mixtures were being mixed, MUF resin was manually added with a 30-mL syringe with the speed of 25 mL/min and mixed for an additional 1 min. The temperature of the product mixture (PMMA/ATH powder, wood powder, wood fibres, and MUF resin) was 36 ± 2 °C. The product was placed into a steel mould with interior dimensions of 180 mm × 180 mm × 50 mm and manually spread across the surface. A 3-mm-thick steel plate was placed at the bottom of the mould and covered with a 50-mm-thick lid that enabled the transfer of temperature and pressure from the hot press (MICRO-MOULD 100kN, JBT Engineering & Consultancy Ltd, Altrincham, Great Britain). The mould, plate, and lid were kept in the hot press before the insertion of the product to keep them at the appropriate temperature until the product mixture was ready. The steel mould with the product mixture was thus put into hot press and pressed at 150 °C with maximum pressure of 3.03 N/mm² and the

lowest pressure was 0.15 N/mm². To avoid blistering of the boards, caused by the evaporating water from the resin, pressure had to be adjusted as presented in Fig. 1.
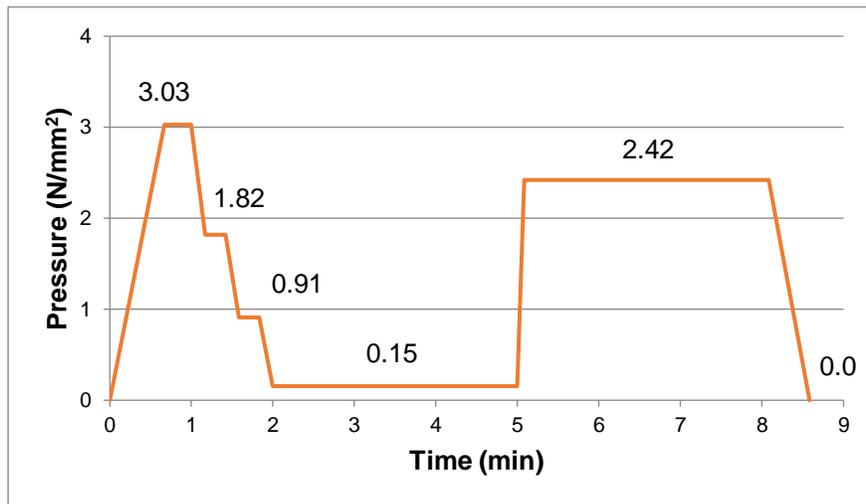
Fig. 1. Pressing regime during the production of composite boards

The purpose of pressing the boards in a mould was to simulate the industrial conditions, in which the dimensions of boards are much larger and therefore water evaporates with difficulty. Altogether 10 series of board production were completed, and three boards per series were made. All WPC boards produced were labelled according to the degree of surface modification and silanes used (Table 3). It must be pointed out that the degree of the silane modification was relative to the ATH content. Therefore, in composites of 0.3% degree of modification, there was only 0.09 wt% actual content of silane mixture in the whole WPC, as shown in Table 3.

Table 3. Labels of Produced Boards

Variety of PMMA/ATH Powder	Label	Silane Surface Modification Degree (%)	Silane Mixture Content in WPC (%)
Non-grinded PMMA/ATH	Ng_PMMA/ATH	0	0
Grinded PMMA/ATH	G_PMMA/ATH	0	0
APTES-modified PMMA/ATH	APTES_0.3	0.3	0.09
	APTES_0.5	0.5	0.15
	APTES_1.0	1.0	0.30
	APTES_2.0	2.0	0.60
UPTES-modified PMMA/ATH	UPTES_0.3	0.3	0.09
	UPTES_0.5	0.5	0.15
	UPTES_1.0	1.0	0.30
	UPTES_2.0	2.0	0.60

Determination of WPC boards' mechanical properties

Four specimens from each board were cut and conditioned at 65% relative humidity (RH) and 20 °C to determine the modulus of elasticity (MOE) and modulus of rupture (MOR) according to the standard SIST EN 310 (1996). Specimens were tested on a Zwick Z005 universal testing machine (Zwick Roell Group, Ulm, Germany). Static bending tests in dry conditions were conducted on 170-mm-long, 25-mm-wide, and approximately 6-mm-thick specimens. A three-point bending test over an effective span of 100 mm was performed. All results of MOE and MOR were standardized with the specific gravity of the WPCs.

Three specimens (50 mm × 50 mm × 6 mm) were cut out from each board to determine the density profile. The specimens were conditioned for 2 weeks at 65% RH and a temperature of 20 °C. Density profile was measured using an X-ray densitometer (MGP 201, Jožef Stefan Institute, Ljubljana, Slovenia) MGP-20 at intervals of 0.1 mm through the thickness of the specimens.

Statistical analysis of differences between the composite boards was executed in "R" software environment for statistical computing (R, Free Software, The R Foundation R-2.14.1 for Windows (32/64 bit)). When Comparing more than two different series of data, homogeneity of variances was tested with Levene's test. Analysis of variances (ANOVA) test was executed on data with homogeneous variances. When comparing two different data series, the F-test was used for testing the homogeneity of variances. If variances were indeed homogeneous, a t-test for independent samples was used to compare mean values. If variances were not homogeneous, Welch's t-test was used.

RESULTS AND DISCUSSION

XPS and Surface Energetics

The XPS analysis of the reference specimen REF_S showed no difference between the non-ground and ground side of the PMMA/ATH plates. Therefore, only results of the ground side of the plates are shown in Table 3. The presence of C, O, Al, N, and Si was detected with relative contents of 60.7%, 32.7%, 5.2%, 1.1%, and 0.3%, respectively. The C, O, and Al were attributed to the main constituents of the PMMA/ATH (PMMA and ATH), whereas the presence of N and Si could be assigned to several possible additives in the plates. The use of diverse additives in PMMA/ATH are described in patents by Osborn *et al.* (1981), Hayashi and Kameda (1990, 1992), and Otremba *et al.* (1998), among others. Concentrations of C, O, and Al were relatively the same at all specimens' surfaces. The surfaces of modified and heated specimens, US80 (Fig. 2) and AS80, showed noticeably higher relative concentrations of N, while non-heated specimen US20 showed the same value as the reference. It seemed that the thermal treatment of the specimens caused higher fixation rates of silanes and, therefore, also amino and ureido groups on the PMMA/ATH substrate. A non-heated specimen AS20 showed slightly lower concentrations of N, compared to the reference, which confirmed the previous statement. However, concentrations of Si showed the greatest differences between unmodified and modified specimens. Reference specimen REF_S had 0.3% relative content of Si on its surface, which could be the consequence of the additives used in the production of the PMMA/ATH material. Silane-modified specimens had three (AS20) to seven times (US80) higher concentrations of Si on their surfaces, which indicated that silane molecules were indeed attached to the PMMA/ATH during the surface modification treatment. Again, the relative

content of Si on the silane-modified specimens also indicated that thermal treatment enhanced the chemical reaction and fixation of silanes as both US80 and AS80 showed higher concentrations of Si than specimens US20 and AS20, respectively. A small concentration of S was also detected at the surfaces of UPTES-treated specimens US20 and US80. The authors cannot give a clear explanation of the occurrence of S at these surfaces because both PMMA/ATH and UPTES silane should not have any sulfur-containing molecules. Therefore, the authors can only speculate that there could have been slight contamination of these specimens, or that the UPTES silane mixture contained additives with sulfur-containing molecules.

Table 4. Relative Element Content (%) of Unmodified and Silane-modified PMMA/ATH Surface

Specimen	C	O	Al	N	Si	S
REF_S	60.7	32.7	5.2	1.1	0.3	
US80	58.0	32.5	4.9	2	2.2	0.4
US20	58.2	33.4	5.7	1.1	1.5	0.1
AS80	59.1	32.6	5.1	1.7	1.5	
AS20	59.6	33.4	5.1	0.8	1.1	
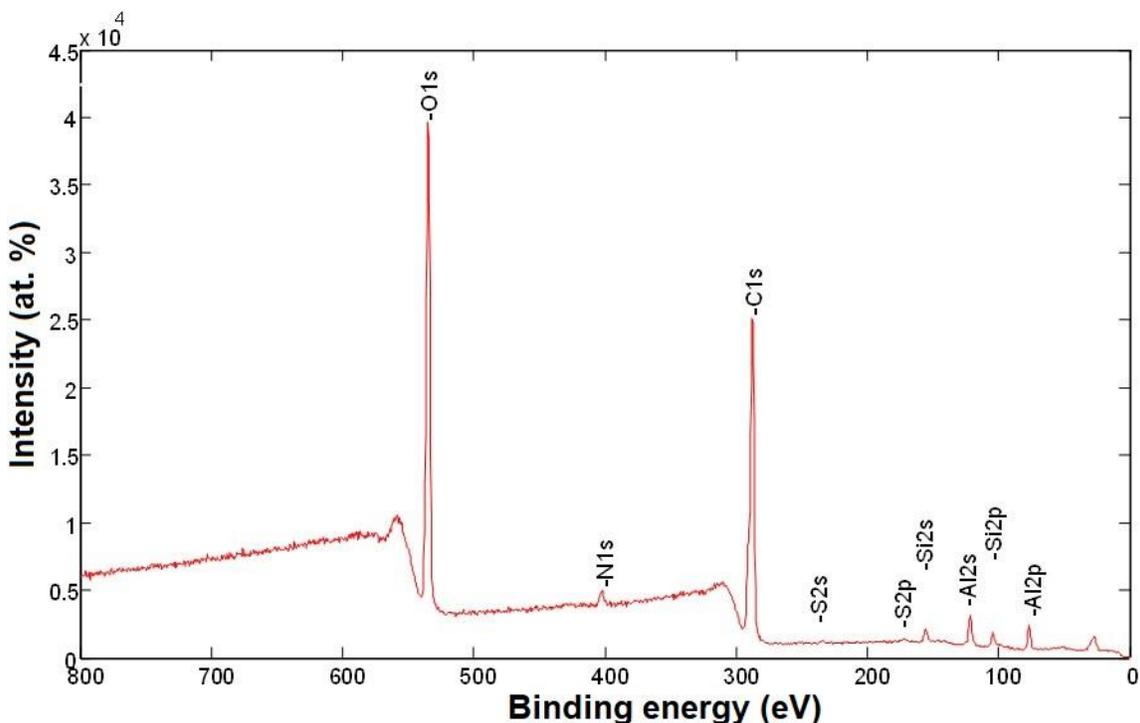
Fig. 2. XPS spectra of UPTES-modified PMMA/ATH surface, specimen US80

Figures 3 and 4 show surface energies with their dispersive and polar parts of APTES- and UPTES-modified PMMA/ATH powder, respectively. The results showed a slight increase in surface energy of APTES-modified powder, where the lowest degree of

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modification caused an increase of polar part by 36% of APTES_0.3 (from 8.6 mN/m to 11.7 mN/m) and total surface energy increased 8% (from 49.3 mN/m to 53.3 mN/m). Further increase of the silane APTES concentration did not result in further increment of surface energy, compared to the 0.3% degree of modification. The UPTES-modified PMMA/ATH powder showed similar increase of surface energies up to a 1.0% degree of surface modification. However, the polar part remarkably increased roughly 150% (from 8.6 mN/m to 21.6 mN/m) on specimen UPTES_2.0 with a 2.0% degree of modification, and surface free energy increased 26% (from 49.2 mN/m to 62.0 mN/m). Similar behaviour of silane-modified PMMA/ATH powders' surface was mirrored in water contact angles (Fig. 5). A 2% degree of PMMA/ATH surface modification of specimen UPTES_2.0 resulted in major decrease of water contact angle by 35% (from 66.9° to 43.4°), which should have resulted in improved wetting of the powder with a water-based adhesive, such as MUF, that was used in this study.
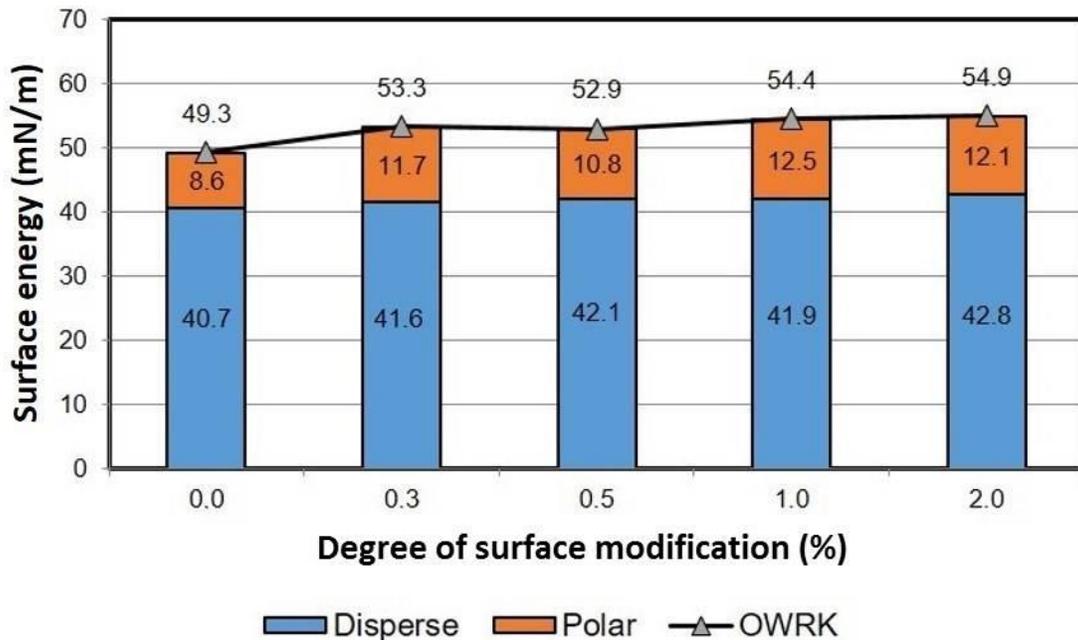
Fig. 3. OWRK surface free energy with its disperse and polar part of PMMA/ATH powder, modified with silane APTES
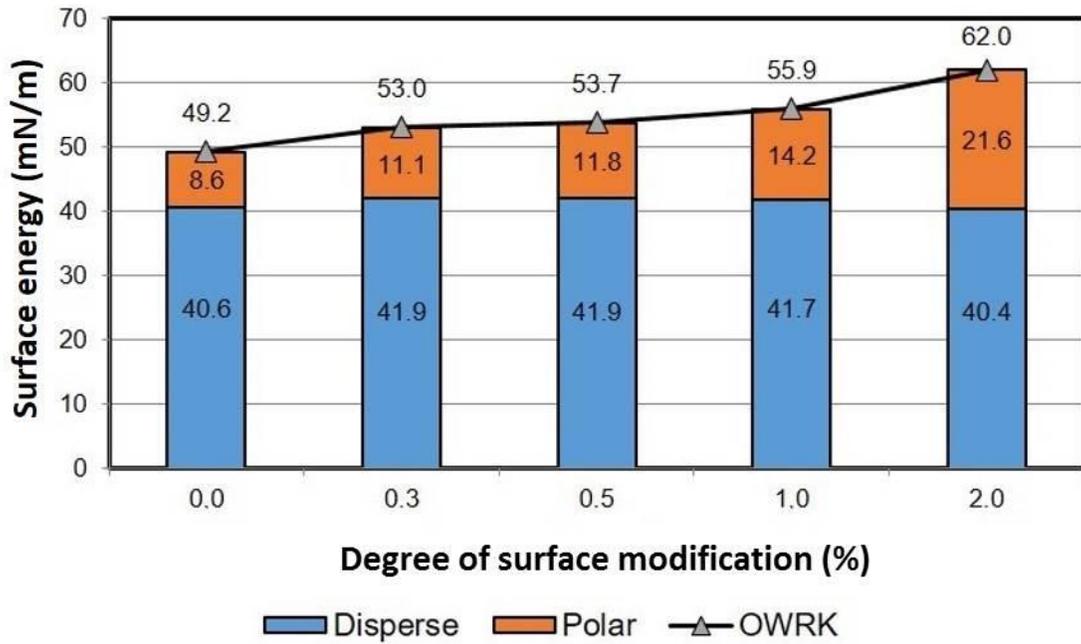
Fig. 4. OWRK surface free energy with its disperse and polar part of PMMA/ATH powder, modified with silane UPTES
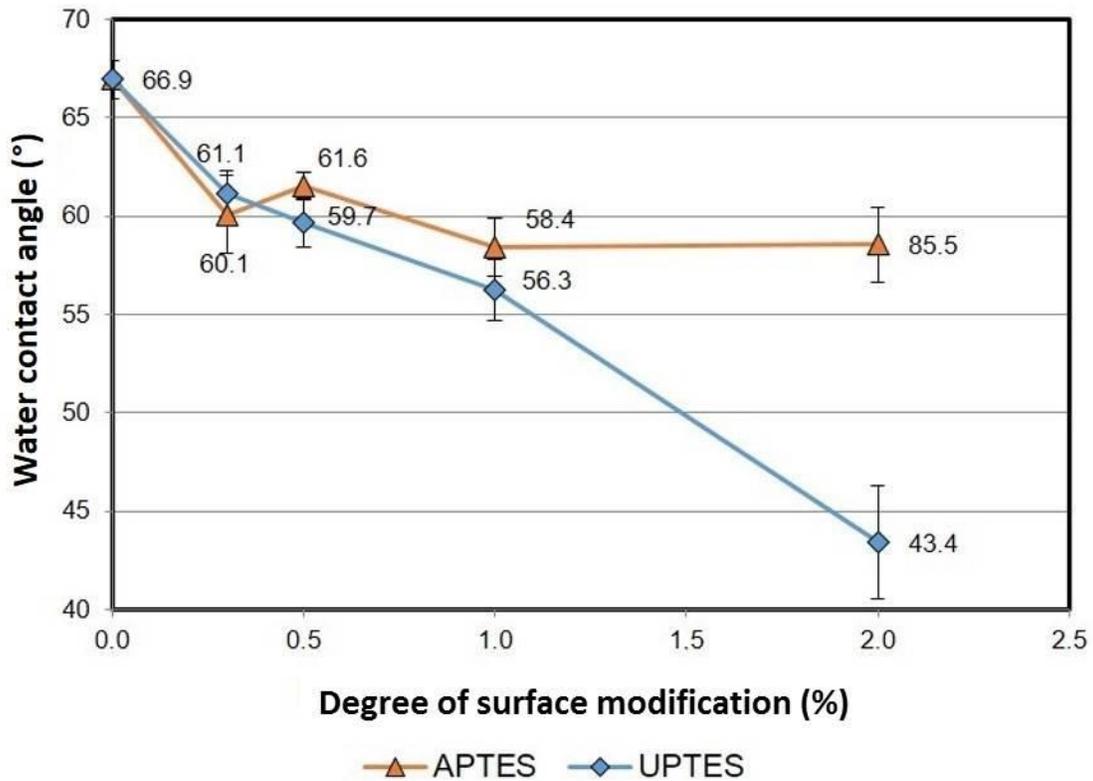
Fig. 5. Comparison of water contact angle values of PMMA/ATH powder surfaces modified with different concentrations of silanes APTES and UPTES

Mechanical Properties of the Boards

All produced composite boards had an average density of 1.20 ± 0.02 g/cm³. Figures 6 and 7 show the density profile variations through the thickness of the composite boards. It was evident that the density was highest in the middle of the boards' thickness, while it was noticeably reduced at the bottom and top of the boards' surface. That effect was most probably caused by the vapour pressure that gathered on both surfaces of the board during the hot-pressing process, which caused the congestion of particles in the middle of the board. Another reason for this kind of density profile was the board production process in which one single layer of material was spread into the mould. Furthermore, it was also evident that the density at the bottom of the board (from 0 mm to 1 mm of board thickness) was higher than the density on the top of the board (from 4.5 mm to 5.5 mm thickness of the board), where the bottom and top sides of the board were defined by their actual position in the press. Therefore, Fig. 6 also showed that composite particles had obviously migrated towards the bottom of the board's thickness during the insertion of material into the mould and during the hot press process. The density profile shown in Fig. 6 was the opposite of the particleboard or fibreboard's density profiles in the wood industry, in which the intention is to have the highest densities at the board's surface, which is why the finest wood particles are layered on the bottom and the top of the boards.

Different degrees of surface modification had no influence on the density profile variation of the boards, as shown in Figs. 6 and 7. The same figures also showed the comparison of the density profile variation of boards containing PMMA/ATH powder with modified surface (modification from 0.3% to 2.0%) with the reference board Ng_PMMA/ATH (0.0% modification). The figures showed that there were no clear differences in density profiles between the reference board and boards containing surface-modified PMMA/ATH powder.
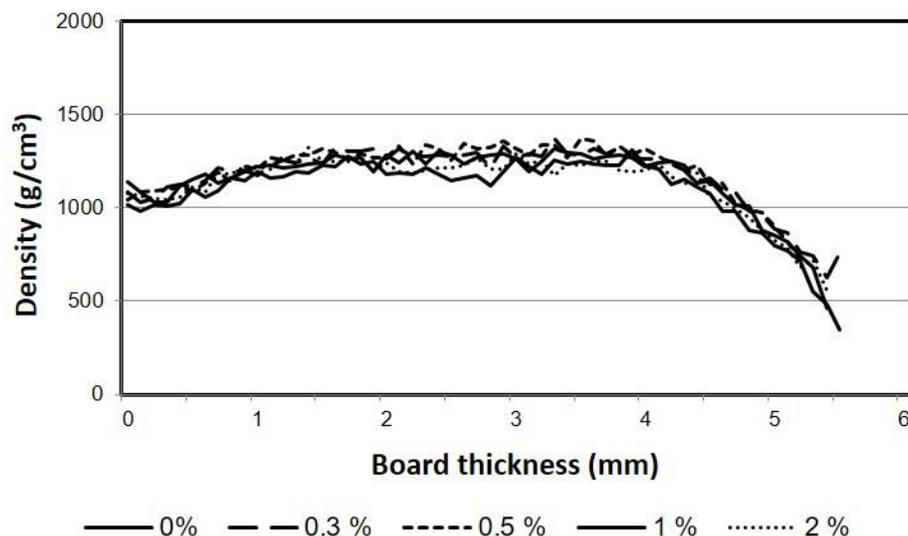
Fig. 6. Density profiles of boards with different degrees of PMMA/ATH powder modification with silane APTES; average curves of three measured specimens are shown. Density profile of Ng_PMMA/ATH (0% modification) is given as a reference.
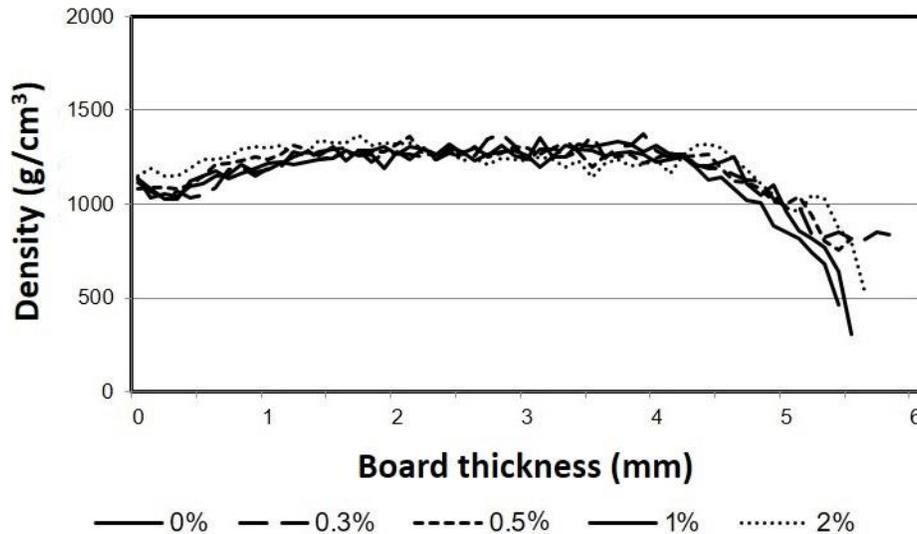
Fig. 7. Density profiles of boards with different degrees of PMMA/ATH powder modification with silane UPTES; average curves of three specimens are shown. Density profile of Ng_PMMA/ATH (0% of modification) is given as a reference.

MOE and MOR

The mechanical properties of the composite boards are shown from Fig. 8 to Fig. 10, where the influence of PMMA/ATH average particle size and different degrees of powder surface modifications are presented. It was already shown in a previous article that grinding the PMMA/ATH powder to smaller average particle sizes increased its surface free energy and decreased the water contact angle (Vovk *et al.* 2019), which was the reason to test the properties of composite boards with different average particle size powders used in them. The results shown in Fig. 9 indicated that there were no differences in MOR between the composites containing ground and non-ground PMMA/ATH powder. Statistical analysis showed significant differences between the MOE measured in the two composites, as composite G_PMMA/ATH reached 2250 N/mm², which was 32.6% higher than the Ng_PMMA/ATH composite. This result was attributed to slightly higher surface free energy and its polar part of ground PMMA/ATH powder particles, which resulted in increased wetting of particles by MUF resin.
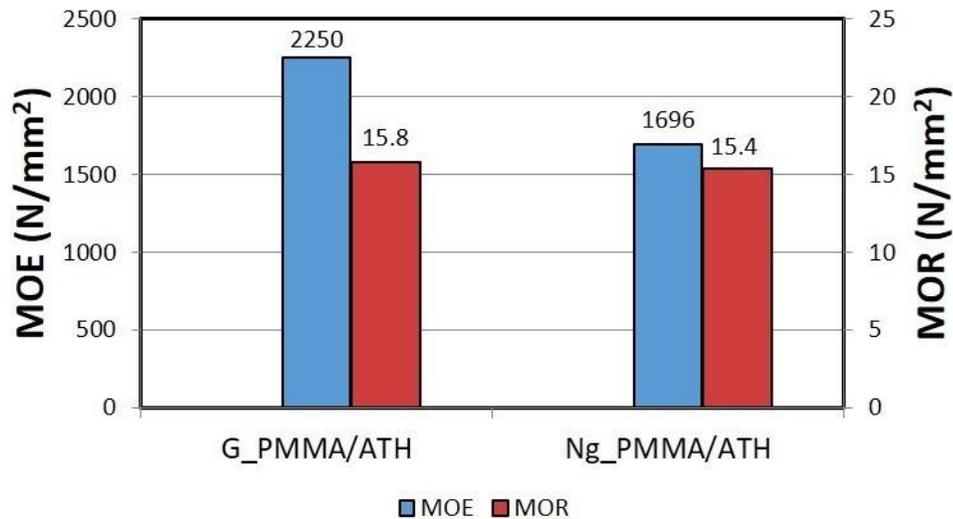
Fig. 8. Comparison of MOE and MOR between composite boards containing ground (G_PMMA/ATH) and non-ground PMMA/ATH (Ng_PMMA/ATH); results are normalized by the specific gravity of the composites

The influence of PMMA/ATH powder surface modification on composite MOE is shown in Fig. 9. It was evident that both silanes APTES and UPTES caused the increase of MOE. Even the lowest degree of surface modification caused statistically significant increases of MOE of 33% and 29% in composites APTES_0.3 and UPTES_0.3, respectively, compared to the reference composite Ng_PMMA/ATH with the un-modified surface of PMMA/ATH powder. Increasing the degree of surface modification to 0.5% caused a decrease of MOE in both cases, but further increment of the degree of modification to 1.0% caused an increase of MOE by 36% and 42% for APTES_1.0 and UPTES_1.0 composites, respectively, compared to Ng_PMMA/ATH. Increasing the degree of modification further to 2.0% had no significant impact on the MOE change, compared to the 1.0% of PMMA/ATH powder modification. Nevertheless, values were slightly higher and reached 2480 N/mm² in APTES_2.0 and 2501 N/mm² in UPTES_2.0 and were approximately 47% higher than reference composite Ng_PMMA/ATH. Statistical analysis of variances confirmed that the degree of surface modification of PMMA/ATH powder had a significant influence on MOE of the composite boards. However, there were no significant differences between the silanes APTES and UPTES. The given results suggested that even the lowest degree of PMMA/ATH powder surface modification (0.3%) gave satisfactory MOE, which was comparable to wooden composites such as particleboards and fibreboards.
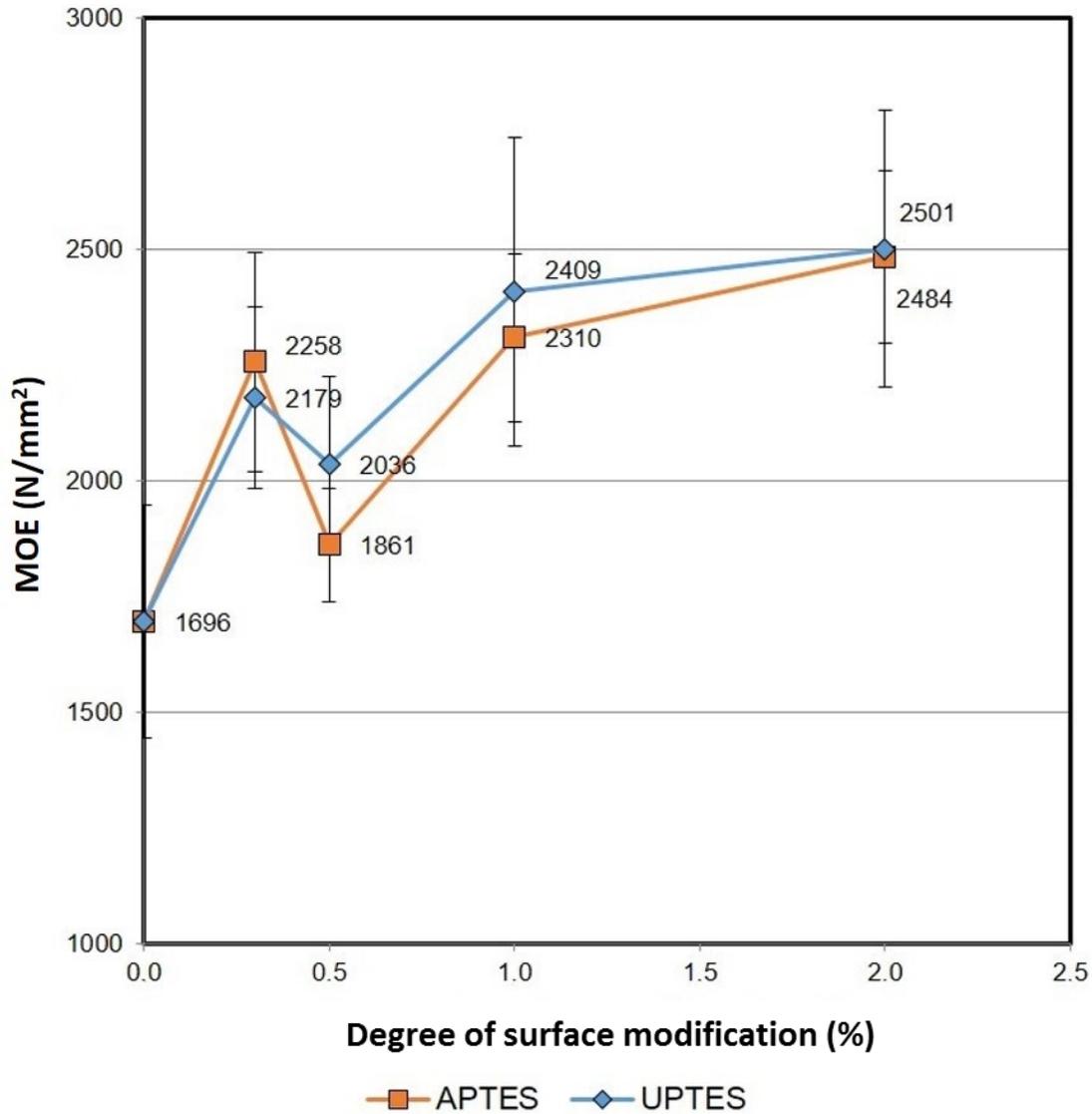
Fig. 9. MOE of composite boards depending on different degrees of PMMA/ATH powder surface modification with silanes APTES and UPTES; results are normalized by the specific gravity of the composites

The results of the MOR tests are shown in Fig. 10. Reference board Ng_PMMA/ATH was measured to have a MOR of 15.4 N/mm². Lower degrees of PMMA/ATH powder surface modification (0.3% and 0.5%) resulted in slight increases of MOR for composites APTES_0.3, UPTES_0.3, APTES_0.5, and UPTES_0.5, but the increase was not statistically significant in comparison to the reference board. However, when the modification degree was increased to 1.0%, MOR increased to 20.0 N/mm² in APTES_1.0 and 21.2 N/mm² in UPTES_1.0, which were 30% and 37% higher than in composite Ng_PMMA/ATH, respectively. Further increase of surface modification to 2.0% gave similar results to the 1.0% modification; the differences between the two were negligible. Statistical analysis of variances confirmed that the modification degree had a statistically significant impact on MOR of the composites, while there were no statistically significant differences between the silanes APTES and UPTES.

Similar findings concerning the utilization of silane coupling agent for the enhancement of mechanical characteristics of the composite were reported by Santiagoo *et al.* (2011) where aminosilane treated rice husk powder (RHP) in polypropylene/recycled acrylonitrile butadiene rubber biocomposite exhibited comparatively higher tensile strength and much higher tensile modulus when compared to the untreated RHP. Another example of effective aminosilane use was presented by Han *et al.* (1998) in urea-formaldehyde bonded wheat straw particleboards, where the mechanical properties of wheat board were also greatly improved by adding aminosilane.
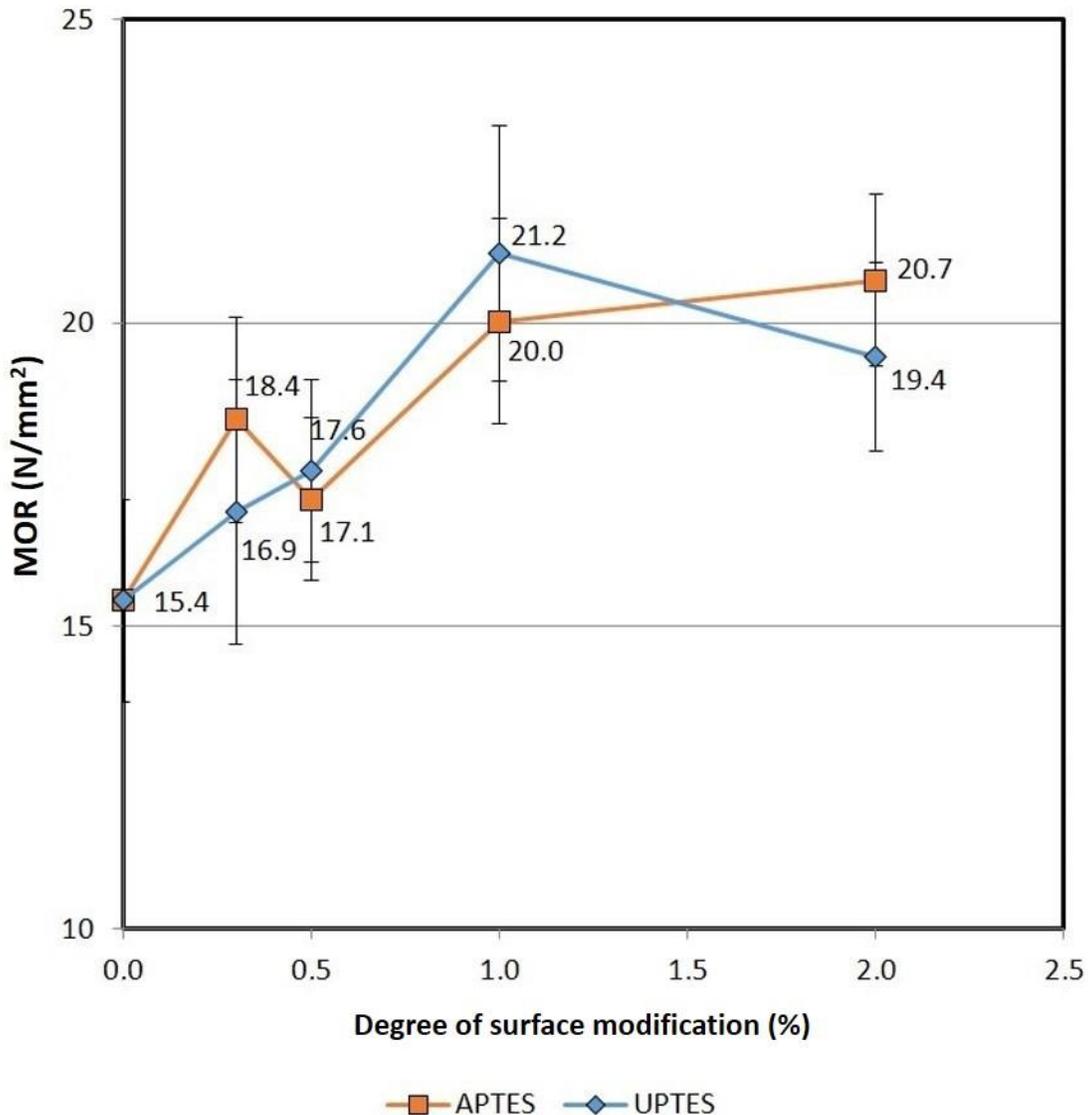
Fig. 10. MOR results of composite boards depending on different degrees of PMMA/ATH powder surface modification with silanes APTES and UPTES (results are normalized by the specific gravity of the composites)

The use of silane coupling agents is uncommon in WPC production. Other coupling agents, such as maleic anhydride, are applied more often because of the predominant use of thermoplastic materials in WPCs. Such examples are shown in research by Najafi and

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Khademi-Eslam (2011), Liu *et al.* (2013), and Tisserat *et al.* (2017). However, for this research, the presence of OH⁻ groups on ATH particles offered an opportunity to attach silanes APTES and UPTES on the surface of PMMA/ATH and therefore modify its surface so that it could be chemically compatible with MUF resin. The authors found this to be an alternative approach to producing WPCs. With the given results of mechanical properties of the boards, one could be convinced that silanes used in this research had a positive impact in increasing the MOE and bending strength of the boards when MUF was used as an adhesive in a WPC system containing PMMA/ATH powder and wood particles. However, there were no significant differences between APTES and UPTES silanes used for powder surface modification. The XPS results suggested that both silanes had made a chemical bond to PMMA/ATH, although covalent bonds are not necessary to form water-resistant oxane bonds (Plueddemann 1970). Although there were differences between silanes shown in contact angle measurements and surface free energy of the modified PMMA/ATH powder particles, these differences were not mirrored in the mechanical properties of the boards. Because the behaviours of MOE and MOR were similar when using APTES and UPTES silanes, it seemed that the increase of the mechanical properties was more likely due to the chemical composition of the silanes, which was in line with the general behaviour of silane coupling agents. All coupling agents for duromeric resins must be reactive with the resin, as there are no correlations between the polarity of silanes or wetting of silane-modified surfaces and effectiveness of silane coupling agents (Plueddemann 1970). The APTES and UPTES have amine- and ureido-functional groups, respectively, which probably entered the condensation reaction of MUF adhesive, using the formaldehyde to make a chemical bond between the adhesive and PMMA/ATH powder particles.

CONCLUSIONS

1. The PMMA/ATH waste powder was suitable for production of an alternative WPC in a system with wood particles and MUF resin.

2. The thermal stability of PMMA/ATH made it suitable for flat-pressing technique.

3. The PMMA/ATH powder particles were suitable for chemical surface modification with silane coupling agents.

4. Silane coupling agents UPTES and APTES were effective in improving mechanical characteristics of alternative WPCs made of wood particles, PMMA/ATH waste powder, and MUF resin. Reactivity of silanes with MUF resin was crucial for adhesion.

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