

Effect of chemical modification of wood flour on the mechanical properties of wood-plastic composites

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Abstract. The poor compatibility between the highly hydrophilic wood fibres and the hydrophobic polymers is associated with a loss of mechanical properties. Therefore, to improve the interfacial adhesion between the polymer matrix and wood flour (WF), a chemical modification of WF is an appropriate solution. This study analyzes the influence of different chemical modifications of WF on the mechanical properties of wood-plastic composites (WPCs). WPC test samples were prepared from birch (*Betula*) WF with a mesh size of 0.63 mm as the filler material and polypropylene (PP) as the matrix material. WF was chemically modified by six different methods to increase its adhesion to, and compatibility with, the polymer matrix. The six chemical methods used were: alkaline (NaOH) modification, polyvinyl alcohol (PVA) modification, silane treatment with 3-aminopropyltriethoxysilane (APTES), acetylation with acetic anhydride, cyanoethylation, and wood fibre esterification. The composites were produced using a twin-screw extruder and the test samples were prepared by injection moulding. The composites' mechanical properties (three-point bending test), Charpy impact strength and thermal properties were tested. In addition, SEM micrographs of WPC surfaces were generated. WF as a filler material enhanced the flexural properties, while impact strength decreased, making the material more rigid and brittle. The test results revealed that the chemical modifications of WF improved the mechanical properties and crystallinity of WPC materials, while the melting temperature decreased. However, the influence of the chemical modification on the mechanical and thermal properties of WPC varied by method.

Key words: wood-plastic composite, wood flour, chemical modification, mechanical properties, thermal properties.

INTRODUCTION

In recent years, wood-based renewable composites have garnered much attention, both scientific and commercial, due to their light weight, eco-friendliness and low cost, as well as worldwide environmental awareness. Natural fibres are considered potential alternatives to glass or carbon fibres in fibre-reinforced thermoplastic composites because of their nature-friendliness, recyclability, biodegradability and low cost compared to mineral fillers (Ashori, 2008; Lu et al., 2008). According to previous research, natural fibres are less abrasive than inorganic mineral fillers and therefore cause little damage to moulding and mixing equipment (Acha et al., 2006).

However, the usability of natural fibres in composite materials is still limited due to their hydrophilic nature, which leads to poor compatibility with the hydrophobic

polymer matrix. This may also result in composites with poor mechanical properties and decreased durability. Here, chemical modification of wood is used to alter its structure, enhancing interfacial adhesion between the polymer matrix and wood fibres and thus improving the physical and mechanical properties of the composite material (Gwon et al., 2010b; Těšínová, 2011). The chemical modification of wood flour (WF) has been studied by many authors. It has been reported that chemical modification can clean the wood fibre surface, stop the moisture absorption process, and increase the surface roughness. Different chemical modification techniques have been used, such as alkaline treatment, benzylation, silylation, peroxide, acetylation, esterification, maleated coupling, etc. (Kalia et al., 2011). With alkaline treatment, the amount of crystalline cellulose is increased, impurities and swelling of the wood fibres are reduced, resulting in a smaller number of hydroxyl groups. The swelling of the wood fibres depends on the alkali concentration (Kim et al., 2011). Silanes efficiently connect with the superficial hydroxyl groups of the wood fibres and induce hydrolysis, condensation, and bond formation, producing chains between the polymer matrix and wood fibres. It is reported that silane modification enhances the properties of composite materials (Farsi, 2010; Kim et al., 2011).

Acetylation of wood has been widely used for modifying wood with acetic anhydride, which results in the esterification of accessible hydroxyl groups in the cell wall with acetyl groups. Previous research has shown that acetylated wood fibre based WPC materials exhibit enhanced mechanical properties, decreased moisture content and an improved resistance to brown-rot decay compared with unmodified WPC materials (Khalil et al., 2002; Segerholm et al., 2005). Generally, these chemical modification methods all improve the overall properties of WPC materials compared with unmodified composites. Based on previous studies it is also believed that the interfacial adhesion between the polymer matrix and the chemically modified WF is significantly increased (Gwon et al., 2010a).

The aim of this study was to investigate the influence of the chemical modification of WF on the interfacial strength of WPC. Therefore, WF was modified with six different chemical agents. Chemically modified WF was compounded with polypropylene (PP) resin and WPC test specimens were prepared by injection moulding. The mechanical behaviour of these composites was evaluated after the flexural and impact test.

MATERIALS AND METHODS

Materials

In this study, PP was used as a matrix material for WPCs. The PP obtained from the company Borealis Polymers OY is a heterophasic copolymer (block copolymer) with a density of 0.905 g cm^{-3} and a melt flow index (MFI) of $3.5 \text{ g } 10 \text{ min}^{-1}$. The wood filler from hardwood (birch (*Betula*)) chips was supplied by the firm UPM Kymmene Otepää AS and then refined to a mesh size of 0.63 mm using the disintegrator device DS-A. For a chemical modification of the WF, a reagent grade sodium hydroxide (NaOH), 98%; polyvinyl alcohol (PVA); 3-aminopropyltriethoxysilane (APTES), 98%; acrylonitrile, 99%; dimethylformamide (DMF), 99%; and acetone, 99.5%, were purchased from Sigma Aldrich Chemical Co. For acetylation, acetic anhydride (AA), 98.5%, acquired from Merck Millipore chemicals, vinyl acetate (VA), 99%, from Fluka Chemical Corp, toluene from LACH-NER, s.r.o. and ethanol were used.

Alkaline modification of WF

Different concentrations of NaOH were selected based on previous studies (Doczekalska & Zborowska, 2010; Doczekalska et al., 2014) to investigate the effect of removing impurities and increasing crystalline cellulose content on the mechanical properties of WPCs. The chosen concentrations of NaOH for WF treatment were 5 wt% and 17.5 wt% (based on the mass of the WF). WF was treated in the chosen solutions of NaOH at room temperature (25 °C) for 90 min. The NaOH solution was prepared in the laboratory by dissolving NaOH granules in water and the solution was then poured onto the WF. After activating, the WF was rinsed with distilled water to neutralize the excess NaOH and then oven-dried at 60 °C for 24 h.

Polyvinyl alcohol modification of WF

PVA has excellent adhesive properties and therefore could be used for cross-linking wood fibres to polymer matrix. In this experimental method, an aqueous solution was prepared with 5 wt% of PVA (based on the mass of the WF) to compare it with other modifications. WF was treated with the PVA solution at room temperature (25 °C). The PVA solution was prepared in the laboratory by dissolving PVA powder in distilled water and then poured onto the WF. After treatment the WF was oven-dried at 60 °C for 24 h.

Silane modification of WF

For silane modification, the WF was treated at room temperature (25 °C) with an aqueous APTES solution. The concentration of APTES chosen for comparison with other modification methods was 5 wt%. On the basis of previous research in WF modification (Gwon et al., 2010a), 5 wt% of APTES (based on the mass of the WF) was added, prior to treatment, for the purpose of hydrolysis in a solution of ethanol/distilled water at a ratio of 9:1 (where ethanol is highly volatile and the objective was to obtain fast-drying WF) and at a pH value of 5. The stirring time was 10 min. A silane solution was then poured onto the WF and treated for 2 h; after the treatment the WF was oven-dried at 60 °C for 24 h.

Acetylation of WF

The acetylation of WF was carried out by two different methods to compare acetylation by boiling and acetylation using a co-solvent and a catalyst to increase the reaction rate. The effect of the two different acetylation methods and using the catalyst on the mechanical and physical properties of WPCs were investigated. The first method, based on a previous study (Ibach & Clemons, 2006), was straightforward and consisted in boiling the WF in AA. The WF was boiled in AA in a 1 l round-bottom flask with a stirrer for 4 h. The modified WF was then washed with distilled water and oven-dried at 60 °C for 24 h.

In the second method (Cetin et al., 2011), the WF was transferred to a round-bottom flask with a condenser containing a DMF solution with AA. The reaction was carried out using potassium carbonate (K_2CO_3) as a catalyst for 1.45 mmol g^{-1} dry wood. The amount of AA used in the solution was 70 mmol g^{-1} dry wood. The reaction was performed at 100 °C for 4 h. After the reaction, the modified WF was Soxhlet extracted by means of distilled water for 6 h and then by means of toluene/acetone/ethanol solution

(at a ratio of 4:1:1 vol/vol) for 6 h to remove unreacted chemicals and by-products. After extraction the WF was oven-dried at 60 °C for 24 h.

Esterification of WF

WF esterification was carried out at the conditions established in a previous study (Wei et al., 2013). WF was weighed into a 3-neck round-bottom flask fitted with a condenser, an overhead stirrer and a thermometer. WF was reacted with VA at an amount of 12.5 mmol g⁻¹ dry wood, 15 g of K₂CO₃ and 600 ml of DMF. Heat was then applied using sand as the heating medium because of the high temperature; the reaction mixture was stirred continuously at 120 °C for 6 h. After this, the reaction mixture was filtered to remove any excess reagents and the WF was then washed with distilled water and rinsed with acetone. After washing, the WF was oven-dried at 60 °C for 24 h.

Cyanoethylation

WF was cyanoethylated according to a method found in previous research (Ghali et al., 2011). Prior to cyanoethylation, the WF was treated with a NaOH solution (5 wt% based on the mass of the WF) for 2 min at room temperature to about 90% wet pickup. After the alkaline treatment, the WF was put into a round-bottom flask containing acrylonitrile/toluene solution (at a ratio of 50:50). The reaction was performed at 60 °C for 60 min. When the reaction was finished, the WF was thoroughly washed with 5% acetic acid solution and then with distilled water. After washing, the WF was oven-dried at 60 °C for 24 h.

Composite processing

After modification, the WF was weighed and the composite mixtures for all the samples were calculated at a ratio of 65% polymer and 35% WF. The mixture of the composites is shown in Table 1. The composites were compounded in a twin-screw extruder Brabender Plasti-Conder PLE 651 at 195 °C at a screw speed of 40 rpm. The compounded materials were then ground to produce granules. Test samples were prepared by injection moulding (Battenfeld BA 230 E) using the previously made granules according to standard ISO 178:2010. The conditions for injection moulding were as follows: temperature 170–185 °C from feed zone to die zone; injection pressure 7 MPa; screw speed 40 rpm; cooling time 15 s. The molten mixture was injected into two-bar shape moulds to produce flexural and impact test samples. The dimensions of the test samples were 63 x 10 x 4 mm.

Table 1. Make-up of the composites

Sample	PP (wt%)	WF (wt%)	Modification	Modification (wt%)
1	100	0	–	–
2	65	35	–	–
3	65	35	NaOH	5
4	65	35	NaOH	17.5
5	65	35	PVA	5
6	65	35	APTES	5
7	65	35	AA	5
8	65	35	AA and DMF	5
9	65	35	VA and DMF	5
10	65	35	Acrylonitrile	5

Mechanical properties

The flexural properties were determined with the three-point loading system Instron 5866 according to ISO 178:2010. The testing was carried out at room temperature 20 °C, at a crosshead speed of 20 mm min⁻¹ and a test span of 60 mm. Five samples were used for each composite. For each composite, its flexural strength and modulus of elasticity (MOE) were calculated. In addition, Charpy impact strength was determined for single-notched samples according to ISO 179-1. Notched impact strength was tested with a Zwick 5102 pendulum impact tester at room temperature 20 °C and nominal pendulum energy of 4 J. The energy absorbed by breaking the test sample was measured and Charpy impact strength was calculated.

Differential scanning calorimetry

WPC samples were tested by differential scanning calorimetry (DSC) to measure the thermal transition of the composites. DSC was performed by means of the Mettler Toledo FP900 Thermosystem with FP90 Central Processor (control and evaluation unit) and FP85 Measuring Cell fitted with cooler system using a nitrogen atmosphere at a flow rate of 20 mL min⁻¹. WPC samples were weighed at about 10 mg, placed in a small aluminium crucible and subjected to a temperature program. The heating and cooling conditions for WPC samples were 30 to 250 °C and 250 to 30 °C with heating and cooling rates of 10 °C min⁻¹, respectively. For each WPC sample its melting temperature (T_m), melting enthalpy (ΔH_m), crystallization temperature (T_c), crystallization enthalpy (ΔH_c) and crystallinity (X_c) were determined.

Scanning electron microscopy

The unmodified and modified composite surfaces and cross-sections were evaluated microscopically by means of the field emission scanning electron microscope (FE-SEM) ZEISS Ultra-55 with GEMINI In-lens SE detector. The acceleration voltage used was 20 kV. Samples were prepared by cutting and mounting a microtomed cross-section. After that, the samples were coated with gold.

RESULTS AND DISCUSSION

Flexural properties

The flexural strength of WPCs with different wood modifications is presented in Fig. 1. The results show that the addition of WF to the PP matrix increased the flexural strength; this effect is enhanced by different chemical modifications of the WF, which make the material more rigid and brittle. However, some chemical modifications demonstrated a decrease in the flexural strength compared to unmodified WF composites. 5% NaOH, PVA and AA modified PP/WF composites showed the lowest values of flexural strength (33.1 MPa, 33.3 MPa, and 33.4 MPa, respectively), which indicates poor interfacial adhesion between the PP matrix and WF. Adding 35% WF to the PP matrix increased the flexural strength of the composites by about 10% with unmodified WF. A similar increase in flexural strength with 30–40% unmodified WF has also been noted in previous studies (Stark & Rowlands, 2003; Karmakar et al., 2007; Ndiaye et al., 2012). However, these previous studies also show that when adding a maleic anhydride grafted polypropylene (MAPP) coupling agent to the composite mixture the increase in flexural strength is significantly higher. The best flexural strength values were obtained by the WF esterification method (38.5 MPa), which increased flexural strength by about 7% compared to unmodified WF (36.2 MPa). The conclusion here is that interfacial adhesion between PP and WF improved with the esterification of WF.

As seen from Fig. 1, an increase in the NaOH concentration from 5% to 17.5% results in a 12% higher flexural strength (from 33.1 MPa to 36.9 MPa, respectively). Alkaline treatment increases the fibre surface roughness and possible reaction sites on the fibre surface, which helps to improve the mechanical properties of WPC through mechanical interlocking and chemical bonding (Gwon et al., 2010a). The mechanical properties of WPC materials are influenced by removing impurities from WF. Based on the results presented in Fig. 1, it can be concluded that at an increased alkaline content the mechanical properties of WPC are also enhanced. However, previous research has shown that at an alkaline content increased to more than 10 wt%, the flexural strength starts to decrease slightly as a result of corrosive interactions between wood fibres in the composites caused by excessive alkali that weakens the WF surface (John et al., 2008; Gwon et al., 2010a). Therefore it is important to choose an optimum amount of NaOH to achieve strong mechanical properties of WPCs.

Two different methods of WF acetylation were also tested and the mechanical properties were compared. The flexural strength results in Fig. 1 show that just boiling the WF in AA even decreases the flexural strength of WPC compared to unmodified WF-based composites. However, another method using the solution of AA and DMF with a catalyst (K_2CO_3) gave better results, increasing the flexural strength slightly, by 2%, compared with unmodified WF (from 36.2 MPa to 37.1 MPa, respectively) and by 11% compared with acetylation by boiling in AA (from 33.4 MPa to 37.1 MPa, respectively). Therefore, acetylation with the AA and DMF solution with a catalyst (K_2CO_3) was found more effective with regard to enhancing the mechanical properties of WPCs. An enhanced acetylation of wood in the presence of a catalyst and an improvement in the mechanical properties of WPCs has also been shown in previous studies (Cetin, et al., 2011; Özmen et al., 2013). Acetylation replaces the OH groups of

wood cell wall polymers with acetyl groups, so that they become hydrophobic and thus compatible with thermoplastics.

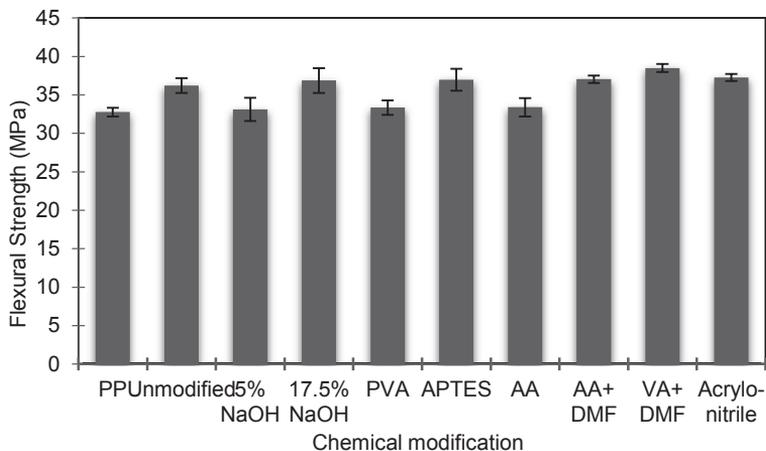


Figure 1. Flexural strength of chemically modified and unmodified WF/PP composites.

With acrylonitrile and APTES modification of WF, the flexural strength was also higher than with unmodified WF composites. With cyanoethylation, the wood OH groups are modified with acrylonitrile and wood is made hydrophobic and compatible with polymers. With acrylonitrile, the composites' flexural strength (37.3 MPa) was increased by 3%, and with APTES (37.0 MPa), it was 2% higher than with unmodified WF composites. However, previous research (Kim et al., 2011) has shown a significantly higher improvement in flexural properties with APTES modified PP/WF composites (about 80% compared to unmodified composites) when the WF is modified with NaOH prior to silane modification. The increase in flexural properties with APTES modification is explained by a stronger interface between WF and PP compared to unmodified composites. This enhances flexural stress distribution in the composites. Silane-reactive chemical groups provide covalent bonding with the OH groups of wood fibres and another chemical group connects with the polymer by creating interfacial adhesion between the polymer and WF.

The flexural MOE values of different composites are shown in Fig. 2. The results demonstrate that significantly higher values of flexural MOE were achieved by four different chemical modifications: 5% NaOH, PVA, APTES and AA. APTES gave the highest flexural MOE value (2.6 GPa) and compared to unmodified WF composites, the value increased from 1.00 GPa to 2.56 GPa, respectively, making the composite stiffer. On the other hand, WF esterification gave the lowest values of flexural MOE (0.91 GPa).

Therefore, it can be concluded from the flexural properties that most of the chemical modification methods tested in this study improved the flexural strength values, which indicates that interfacial adhesion between WF and PP was increased. The increase in bonding between WF and PP may be due to the fact that chemical modification reduces the number of hydroxyl groups in WF and modification with NaOH leads to the removal of extractives and hemicellulose from the WF.

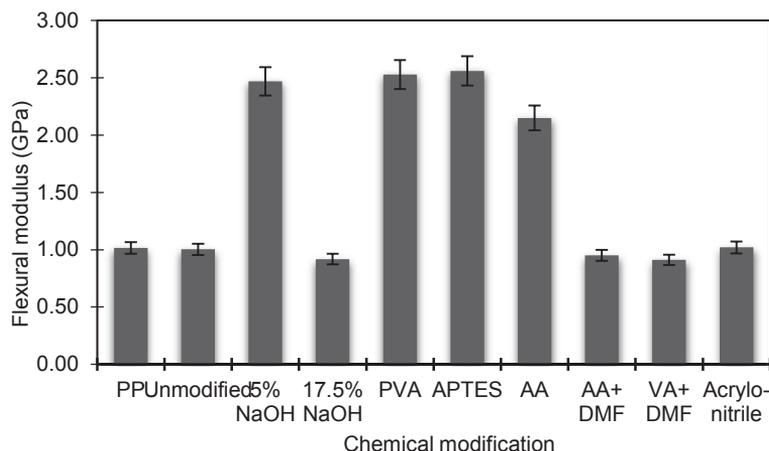


Figure 2. Flexural modulus of chemically modified and unmodified WF/PP composites.

Impact strength

The Charpy impact strength of single-notched specimens of unmodified and modified WPC samples is shown in Fig. 3. The single-notched impact test was chosen because the pendulum impact tester did not provide sufficient energy to break unnotched PP samples due to the high elasticity of the PP matrix. This is the reason why many other researches have also previously used the single-notched impact test for WPC impact testing. With all the composites, the addition of WF to the PP matrix lowered the impact properties significantly (about threefold) compared to pure PP; this is also in accordance with previous research (Bledzki & Frauk, 2004; Bledzki et al., 2009). When incorporating WF in the PP matrix, impact strength is decreased due to the stress concentration regions in WPC that require less energy to break the composite, making the material more brittle. The results show that only the PVA and acrylonitrile modifications of WF had a slightly higher impact strength (4.72 kJ m^{-2} and 4.56 kJ m^{-2} , respectively) compared with unmodified WF composites (4.44 kJ m^{-2}). All the other modified composites exhibited a lower impact strength compared with the unmodified ones. The lowest impact strength was demonstrated by APTES modified WF composites (3.56 kJ m^{-2}) – 25% lower than that of unmodified WPC samples. APTES silanol groups can create strong bonds with the hydroxyl groups of WF and thus improve interfacial adhesion between WF and the polymer matrix.

The chemical modification of WF improves the interaction between WF and the polymer matrix, resulting in strong bonding, and therefore the breaking of the composites needs relatively low impact energy. Composites with weaker interfacial bonding have higher impact strength because micro-cracks can occur in the impact test, propagating along the fibre/matrix interface and causing debonding, which leads to a higher energy-absorption capacity of the WPC (Ray et al., 2001; Nourbakhsh & Ashori, 2010). Therefore, an impact test shows the effect of chemical modification on the interfacial bond in the composites, which also affects the mechanical properties of WPC materials.

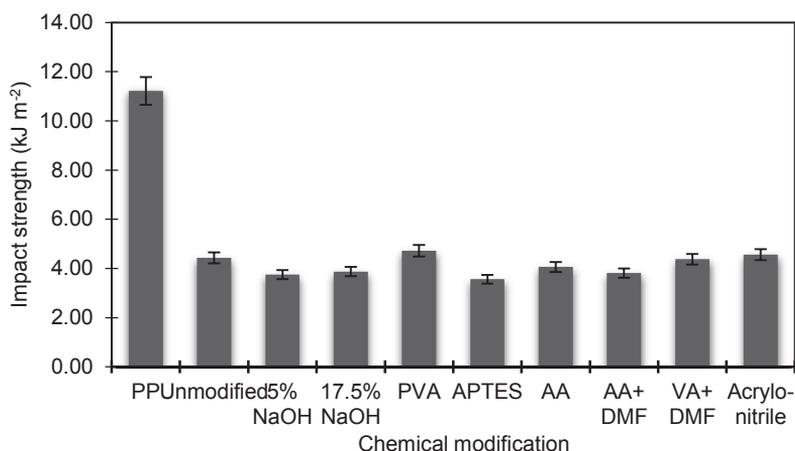


Figure 3. Impact strength of chemically modified and unmodified WF/PP composites.

Differential scanning calorimetry

All the WPC samples (unmodified and modified) were measured with the DSC system and the data of the composites is shown in Table 2. Thermal analysis demonstrates that the addition of WF to the polymer matrix decreased the T_m by 1.3–4.3 °C. The addition of 35% unmodified WF to the polymer matrix decreased the T_m by 1.7 °C, while the largest decrease, by 4.3 °C, was provided by NaOH (17.5 wt%) modified WF composites. ΔH_m values decreased significantly when WF was added to the polymer matrix. It was interesting that PVA modified WF composites gave only 14.1 J g⁻¹ of ΔH_m compared to pure PP (54.6 J g⁻¹ of ΔH_m) and therefore a lot less energy is required to melt the composite. With WPC samples, the highest ΔH_m was obtained with APTES – it was just 17% lower than pure PP. Therefore, the APTES modification of WF requires a lot more energy than other modifications to melt the composite. The same trend was also noted in a previous study (Kim et al., 2011).

The T_c of the WPCs with PVA and NaOH (5 wt%) modified PP/WF composites was higher than with other modifications and unmodified composites, indicating a better nucleation ability of PVA and NaOH (5 wt%) modified WPCs. Accordingly, these act as nucleating agents, increasing the rate of crystallization of polymers and thereby also the crystallization temperature (Ayrilmis et al., 2014). Other WF modifications show lower T_c values (0.6–5.8 °C), which indicates a weakened nucleation ability with these modified WF composites, resulting in a better interfacial adhesion between PP and WF. Wood consists of cellulose with a crystalline structure, and hemicellulose and lignin with an amorphous structure, thus reducing the crystallinity of composites. Therefore, the improved interfacial adhesion in these composites is explained by the hindered movement of PP chains, decreasing the crystallization rate of PP in the WPCs (Ndiaye & Tidjani, 2012).

All WPC samples except AA+DMF modified WF composites show a decrease in the ΔH_c results compared to pure PP. Most of the WF modifications decreased the ΔH_c compared to unmodified composites. However, APTES, AA and AA+DMF modified composites increased the ΔH_c by 7%, 1%, and 36% respectively, compared to unmodified WPCs. Previous research (Ayrilmis et al., 2014) has shown that the

modification of WF can increase the ΔH_c by inducing a formation of crystals in heterogeneous nucleation spots. This increases the crystallization rate in the WPCs.

The crystallinity X_c of all the composites was reduced with the addition of WF to the polymer matrix. The lowest X_c was obtained with the PVA modified composite of only 6.2% crystallinity. Most of the modified composites increased the X_c compared to unmodified composites. The highest X_c was achieved with APTES ($X_c = 21.3\%$) and 17.5% NaOH ($X_c = 20.2\%$) modified composites – just 19% and 26% lower than pure PP, respectively. The decreased crystallinity of WPCs shows that the formation of polymer crystals is hindered by WF in the composites. However, the higher crystallinity of APTES modified composites may be explained by the better interfacial adhesion between WF and the PP matrix. Previously it has been reported that APTES modification provides the highest increase in X_c (Kim et al., 2011).

Table 2. DSC results of the unmodified and modified WPC samples

Sample	PP/WF (wt%)	Modification	Modification (wt%)	T_m^a (°C)	ΔH_m^b (J g ⁻¹)	T_c^c (°C)	ΔH_c^d (J g ⁻¹)	X_c^e (%)
1	100/0	–	–	173.0	54.6	107.5	1,950	25.4
2	65/35	–	–	171.3	32.6	107.6	1,760	15.3
3	65/35	NaOH	5	171.7	36.0	109.2	1,420	18.9
4	65/35	NaOH	17.5	168.7	40.5	102.4	1,380	20.2
5	65/35	PVA	5	169.5	14.1	116.3	868	6.2
6	65/35	APTES	5	171.5	46.7	103.3	1,880	21.3
7	65/35	AA	5	171.3	40.4	107.5	1,780	19.2
8	65/35	AA and DMF	5	172.1	22.6	106.9	2,400	10.5
9	65/35	VA and DMF	5	170.1	38.2	101.7	1,620	19.0
10	65/35	Acrylonitrile	5	169.6	34.5	103.8	1,520	15.4

^aMelting temperature; ^bmelting enthalpy; ^ccrystallization temperature; ^dcrystallization enthalpy; ^ecrystallinity

Scanning electron microscopy

SEM pictures of the surfaces and cross-sections of modified and unmodified WPC samples are shown in Fig. 3. With a chemical modification of WF there is a better dispersion of wood and adhesion with the polymer matrix. With unmodified composite samples (Fig. 4a and 4b) cavities and voids are present in the composite surfaces. Also PVA modified composite surfaces (Fig. 4g and 4h) reveal voids and separate wood particles, representing a non-compatible system. Therefore, these composites have poor interfacial adhesion between WF and the PP matrix. With modified composites, micrographs show fewer cavities and voids and more homogenous surfaces, which also indicate an improved interfacial adhesion between WF and the PP matrix. Smooth and uniform surfaces with a good dispersion of WF in the PP matrix can be seen in Fig. 4m, 4n, 4q and 4r, which shows a strong compatibility between WF and the PP matrix with AA+DMF and Acrylonitrile modifications. With other chemical modifications, minor cavities and voids are present on the surfaces of WPCs, reducing the interfacial bonding of PP and WF. These SEM observations clearly explain the enhanced mechanical properties of modified WPCs, so that the stronger interaction between WF and PP also improves the mechanical properties of WPCs.

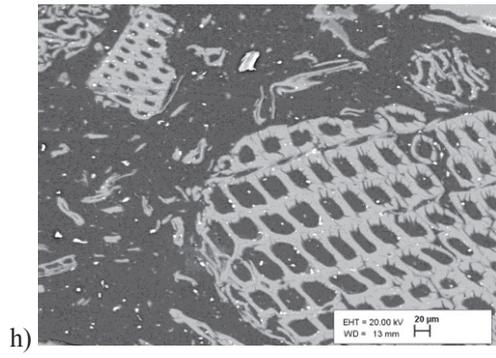
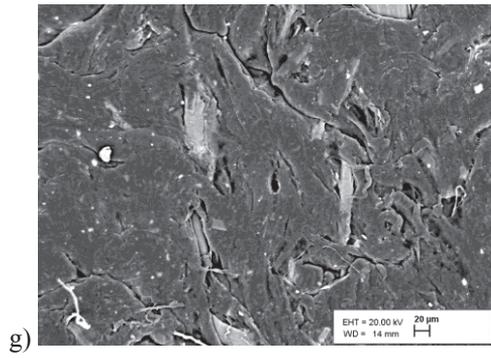
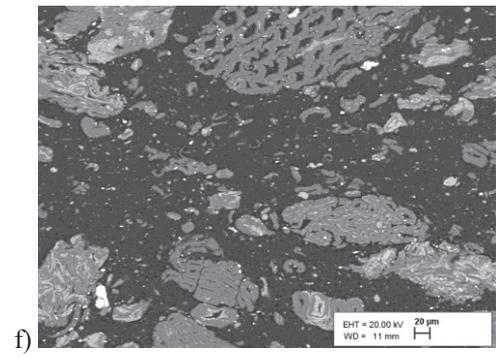
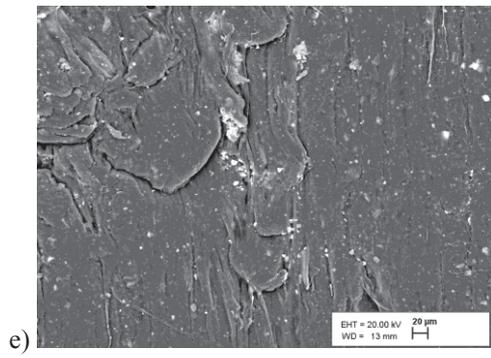
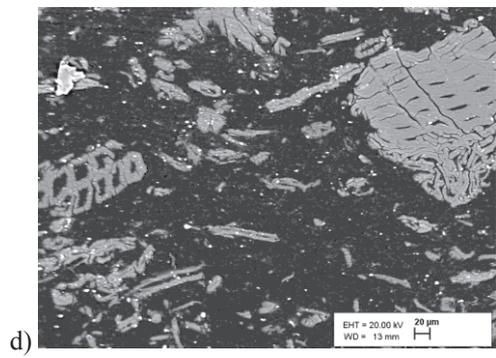
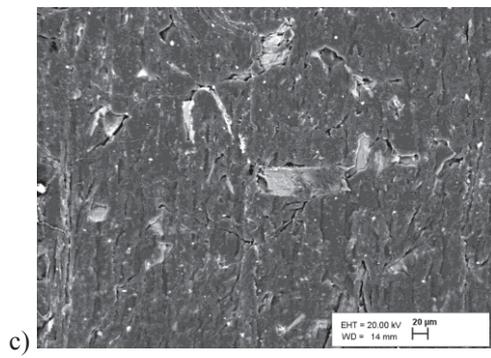
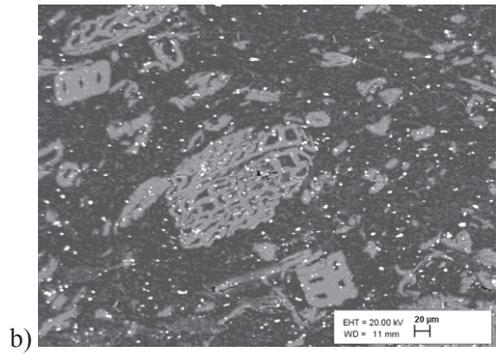
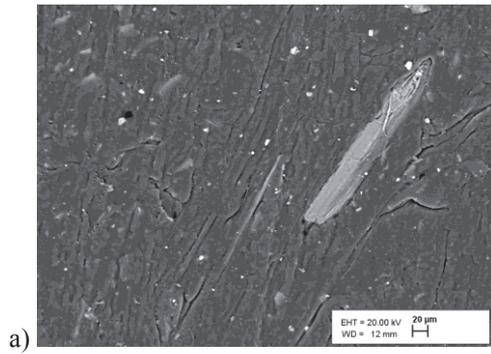


Fig.4 (continued)

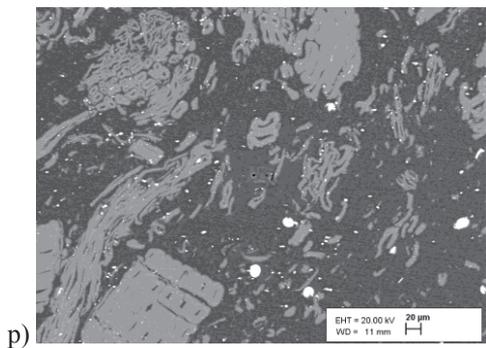
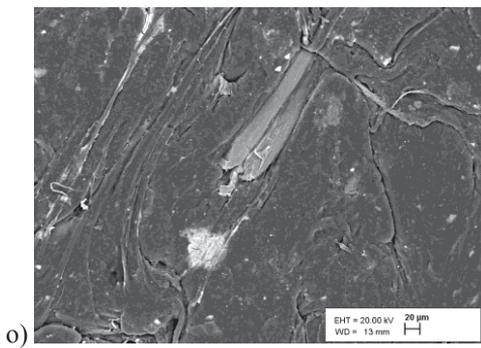
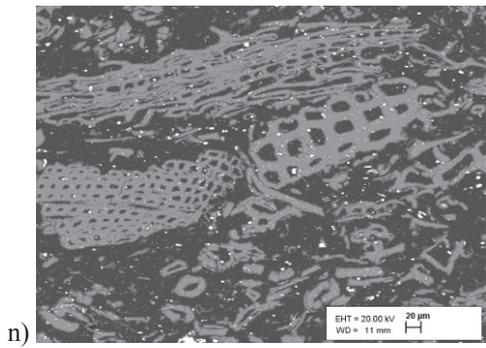
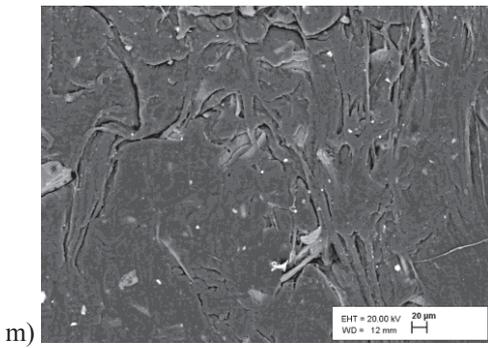
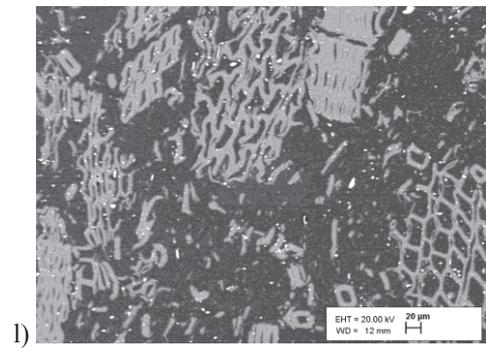
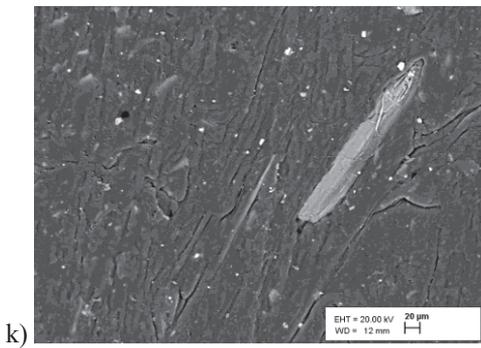
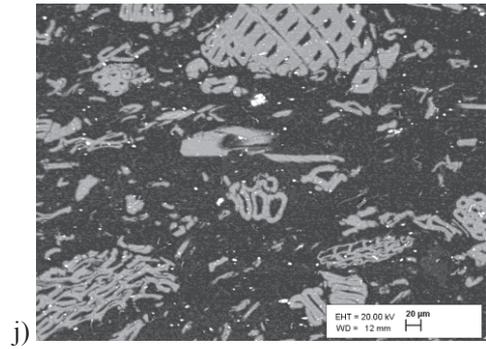
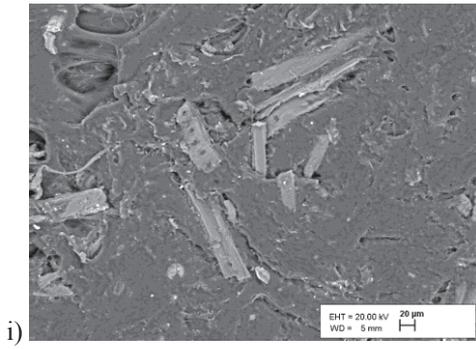


Fig.4 (continued)

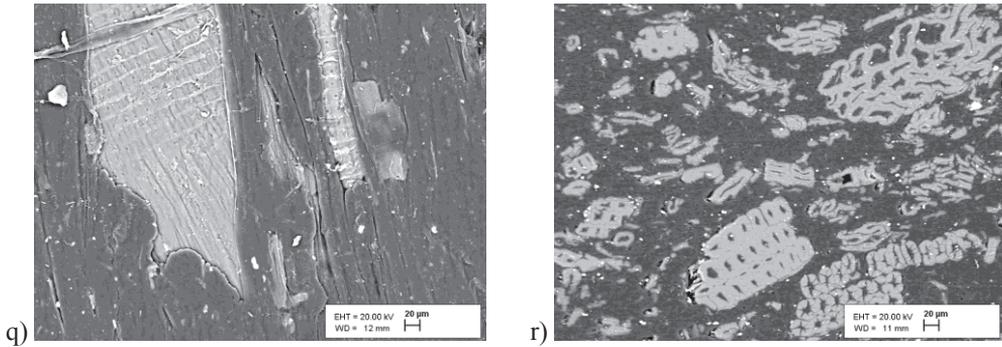


Figure 4. SEM micrographs of the surfaces and cross-sections of unmodified and modified composites: a) unmodified WPC surface; b) unmodified WPC cross-section; c) 5% NaOH modified WPC surface; d) 5% NaOH modified WPC cross-section; e) 17.5% NaOH modified WPC surface; f) 17.5% NaOH modified WPC cross-section; g) PVA modified WPC surface; h) PVA modified WPC cross-section; i) APTES modified WPC surface; j) APTES modified WPC cross-section; k) AA modified WPC surface; l) AA modified WPC cross-section; m) AA+DMF modified WPC surface; n) AA+DMF modified WPC cross-section; o) VA+DMF modified WPC surface; p) VA+DMF modified WPC cross-section; q) Acrylonitrile modified WPC surface; r) Acrylonitrile modified WPC cross-section.

CONCLUSIONS

This study focused on the influence of WF modification on the mechanical properties of WPC. The chemical modification of WF with seven different chemicals was evaluated. It was found that chemical modification enhances the flexural properties of WPC materials due to an improved compatibility between WF and the polymer matrix. WF esterification showed the best flexural properties, indicating strong interfacial adhesion between WF and the PP matrix. The results of an impact strength test showed that the chemical modification of WF lowers the impact strength needed for breaking the WPC material. This is due to the fact that the debonding effect of the WF/PP matrix absorbs more impact energy with modified composites than with unmodified ones. The largest decrease in impact energy was observed with APTES modified composites. It can be concluded that the chemical modification of WF results in improved mechanical properties of WPCs. The results varied slightly by method but it is possible to choose an optimal modification method for the best mechanical performance of the composites.

In the DSC analysis, T_m , ΔH_m and X_c decreased with chemically modified composites. Most of the composites with chemical modifications showed higher values of X_c compared to unmodified composites, suggesting better interfacial adhesion between WF and PP. SEM micrographs showed that the surfaces of the modified composites had fewer voids and cavities, resulting in a more homogeneous material with improved mechanical properties.

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