Effect of Wood Acetylation with Vinyl Acetate and Acetic Anhydride on the Properties of Wood-Plastic Composites

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Chemical modifications of Scots pine (*Pinus sylvestris*) wood flour were performed with vinyl acetate (VA) and acetic anhydride (AA) in the presence of potassium carbonate as a catalyst. Scots pine wood flour samples were successfully acetylated with VA (19 wt% gain) and AA (24 wt% gain). The effect of chemical modification of the Scots pine wood flour with AA and VA on the mechanical properties of wood high-density polyethylene composites (WPC) was determined. It was observed that acetylation of wood flour allowed a significant increase in both the mechanical properties and the thermal stability of the WPCs. It was concluded that acetylation of lignocellulosic fibers improves thermal stability, dispersion in the polymer matrix, and compatibility with the polymer matrix.

Keywords: Acetylation; Acetic anhydrides; Vinyl acetate; Wood plastic composites; Scots pine

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INTRODUCTION

A composite material can be defined as the heterogeneous combination of two or more components to form a filled or reinforced matrix in which the combined effect of the components possesses superior properties compared with the individual components alone (Popa and Breaban 1995). Replacing man-made fiber with a lignocellulosic alternative offers a relatively cheaper and more environmentally friendly alternative material. The most conspicuous problem of using lignocellulosic fiber as reinforcement in a synthetic matrix is the lack of compatibility of the lignocellulosic material with the matrix. Lignocellulosic materials are hydrophilic (abundance of OH functionality), while thermoplastic (or many thermoset) polymers are hydrophobic. As a result of this divergent behavior, the adhesion between plant fibers and polymers can be very poor. The bonding between the reinforcing material and the matrix plays an important role in determining the mechanical properties of a composite material.

Various methods may be employed to improve bond quality or compatibility of lignocellulosic materials with a hydrophobic matrix. Two methods are the use of compatabilizers (silanes, isocyanates, MAPE (maleic anhydride-modified polyethylene, *etc.*)) and chemical modification of the lignocellulosic material (acetylation, epoxide modification, *etc.*) (Schneider and Brebner 1985; Maldas *et al.* 1988; 1989; Kokta *et al.* 1989; Karnani *et al.* 1997; Rowell 2006a).

For improving the bond between the matrix and the reinforcing material, coupling agents such as isocyanates and silanes (Raj *et al.* 1989; Maldas *et al.* 1989) or compatabilizers can be used because compatabilizers possess properties of both the matrix and the reinforcement in one molecule (Maldas *et al.* 1988; 1989; Felix and Gatenholm 1991; Rowell *et al.* 1997; Sanadi *et al.* 1993; 1997; Simonsen *et al.* 1997; Oksman and Clemons 1998; Oksman and Lindberg 1998).

Chemical modification of wood or natural fibers can be defined as a chemical reaction between some reactive part of a wood or fiber component and a single chemical reagent, with or without a catalyst (Rowell 2006b). All of the methods investigated to date have involved the chemical reaction between a reagent and the cell wall polymer hydroxyl groups. A number of reviews of chemical modification of lignocellulosic materials have been published (Banks and Lawther 1994; Kumar 1994; Matsuda 1996; Hon 1996; Rowell 2006a; Hill 2006). Most of the chemical modification reactions are carried out in order to improve the dimensional stability or bio-resistance of wood. Many wood modification reactions have been studied, of which the most useful are those that include reaction with epoxides, anhydrides, or isocyanates (Hon 1996; Rowell 2006b; Çetin 2000; Çetin and Özmen 2001; Çetin *et al.* 2005; Hill 2006; Özmen *et al.* 2007). Maritime pine, Scots pine sapwood, and hemp fibers have recently been successfully acetylated with a new transesterification reaction using vinyl acetate in the presence of various catalysts such as potassium acetate, potassium carbonate, and sodium carbonate (Jebrane and Sebe 2007; Jebrane *et al*. 2011; Çetin *et al.* 2011; Özmen 2012). In the literature, there are some papers dealing with acetic anhydride modified fiber reinforced polymer composites (Tserki *et al.* 2006; Lisperguer *et al.* 2007; Abdul Khalil *et al.* 2007; Luz *et al.* 2008; Mat Taib *et al.* 2010). Some authors claim that acetylation can improve the mechanical and thermal properties of WPCs (Tserki *et al.* 2006; Lisperguer *et al.* 2007; Abdul Khalil *et al.* 2007). In contradiction to these studies, it was also reported that acetylation reduced the mechanical properties of WPCs (Luz *et al.* 2008; Mat Taib *et al.* 2010).

The objective of this study was to determine the mechanical performance of acetylated and unmodified Scots pine wood flour-reinforced high density polyethylene composites. Two different approaches of acetylation (acetic anhydride and vinyl acetate) were evaluated and the results were compared with those of unmodified WPCs.

EXPERIMENTAL

Preparation of Wood Flour

For wood modification, Scots pine (*Pinus sylvestris*) sapwood was ground using a hammer mill and sieved to a size of 250 to 425 μm. Before reaction, the samples were subjected to Soxhlet extraction with deionised water for 6 h, and then with a mixture of toluene/acetone/ethanol (4/1/1, v/v) for 6 h. This was done to remove the extractive materials from the wood. The samples were then oven-dried at 103±2°C and allowed to cool to ambient temperature in a desiccator containing phosphorous pentoxide before determination of weight.

Acetylation of Scots Pine Wood Flour

500 g of the extractive-free Scots pine sapwood flour was transferred to a 2-L glass reactor containing a dimethyl formamide (DMF) solution with acetic anhydride (AA) or vinyl acetate (VA). All reactions were performed with the presence of potassium carbonate (K_2CO_3) as a catalyst at 100°C for 6 h. The acetylation reaction conditions

were derived from an earlier publication (Çetin *et al.* 2011). The treated samples were Soxhlet extracted with deionised water for 6 hours then with the toluene/acetone/ethanol mixture (4/1/1, v/v) for 6 h. This was done to remove excess unreacted chemicals and byproducts. The acetylated Scots pine wood flour was oven-dried overnight at 103±2°C, transferred to a desiccator containing phosphorus pentoxide until cool, and then weight gain levels (WPG) were determined according to Equation 1,

$$WPG\ (\%) = \frac{W_2 - W_1}{W_1}\ x\ 100 \qquad (1)$$

where W_1 is the sample weight before treatment and W_2 is the sample weight after treatment.

Infrared Spectroscopy

Infrared absorption spectra of the acetylated and unmodified wood flour were obtained using the KBr (potassium bromide) technique with a Shimatzu 8400s FT-IR spectrometer. The spectra were collected over the 4000 to 400 cm^{-1} wavenumber range, at a resolution of 4 cm^{-1} (40 scans).

^{13}C CP-MAS NMR Analysis

Solid state ^{13}C CP-MAS (Cross Polarization-Magic Angle Spinning) NMR spectra of acetylated and unmodified Scots pine wood flour were obtained at room temperature using a Bruker DPX-400 NMR spectrometer (Bruker), with MAS rates of 4 and 8 kHz and a frequency of 100.61 MHz for ^{13}C NMR. Acquisition time was 0.07 s. The pulse repetition time was 4 s and the cross polarization contact time was 1.5 s. All the spectra were run for 15 h (25,000 scans).

Thermogravimetric (TGA) Analysis

The thermogravimetric analyses of the control and acetylated wood flour-reinforced HDPE composites were performed using a thermal gravimetric analyzer (Perkin Elmer STA-6000). The sample weight was 20 mg. The measurements were carried out at a heating rate of 20°C/min in an inert nitrogen atmosphere with a flow rate of 20 mL/min. Weight loss versus temperature were recorded.

Production of Wood-Plastic Composites (WPC)

High-density polyethylene was obtained from Petkim, Turkey (HDPE; Petilen® YYS0464). Four different composites were produced: HDPE (neat polymer), W20 (20 wt% extractive free wood flour filled HDPE), AA20 (20 wt% acetic anhydride modified wood flour filled HDPE), and VA20 (20 wt% vinyl acetate modified wood flour filled HDPE). Initially, the wood flour and HDPE were mixed with a high-speed mixer for 10 min then WPC pellets were produced using a single screw extruder. The temperature setting from the hopper to die was 150/170/170/177°C, and the screw speed was 100 rpm. The pellets were dried at 70°C overnight. For injection moulding, the pellets (wood/HDPE ratio of 20/80 by weight) were melted by a single screw HDX-88 Injection Molding Machine (pressure: 100 bar, injection speed: 80 mm/sec; screw speed: 40 rpm). Then the molten material was injected into dumbbell-shaped moulds to produce the samples for tensile strength testing and into two bar-shape moulds to produce the flexural and impact specimens. After injection, the samples were rapidly cooled.

Mechanical tests were performed in order to determine the mechanical properties of the produced WPCs. Prior to testing, all samples were conditioned at a relative humidity of 65±5% and a temperature of 23±2°C for 7 days. For each WPC group, ten replicates were tested. Tensile specimens (dogbone shape (type III)) were tested with a crosshead speed of 5 mm/min. The flexural specimens (5 mm (t) x 13 mm (w) x 150 mm (l)) were tested in the three-point loading mode with a crosshead speed of 2 mm/min on a Zwick Roell Z010 Universal Testing machine. Notched impact specimens (5 mm (t) x 12.7 mm (w) x 64 mm (l)) were tested on a Zwick HIT5.5P Impact Testing machine. The notches were cut using a Polytest notching cutter by RayRan. The density, tensile, flexural, and impact properties of the manufactured samples were determined in accordance with ASTM D792 (2007), ASTM D638 (2001), ASTM D6109 (2005), and ASTM D256 (2005), respectively.

Scanning Electron Microscope (SEM) Analysis

The WPC bars were dipped in liquid nitrogen and then snapped in two to get fractured surfaces for SEM analysis. The surfaces were analyzed directly with a JEOL scanning electron microscope (Model NeoScope JCM-5000).

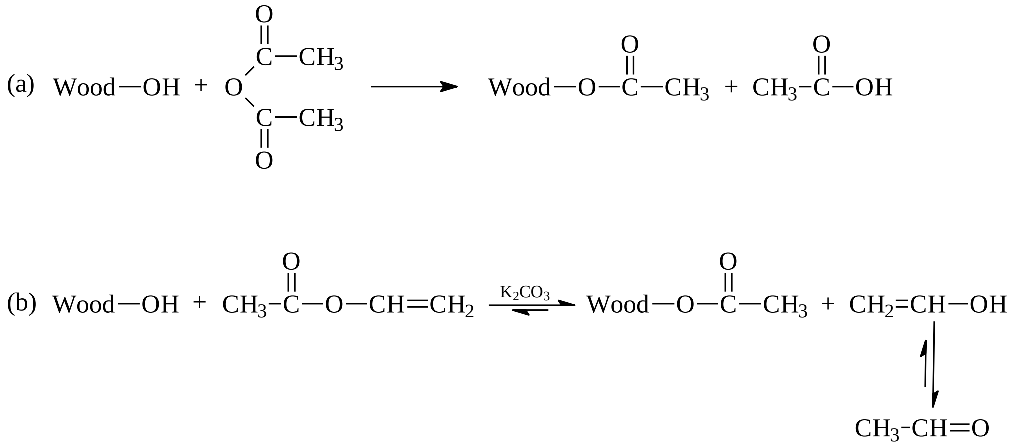
Statistical Analysis

Analysis of variance (ANOVA) was used to determine the effect of acetylation on the selected mechanical properties using Design-Expert 7.0.3. The resulting F value was compared to the tabular F value at the 95% probability level. When F tests resulted in significant differences, comparisons between means were made by Tukey test. Statistically different groups ($P<0.05$) are shown on the graphs with different capital letters.

RESULTS AND DISCUSSION

The reaction mechanism between Scots pine wood flour hydroxyl groups and acetic anhydride (AA) or vinyl acetate (VA) is shown in Fig. 1. In order to compare the classical AA modification with the new VA technique, the same reaction protocols were applied to both methods. The 24% and 19% WPG levels were achieved for 6 hours of reaction with K_2CO_3-catalyzed acetic anhydride (AA) and vinyl acetate (VA), respectively.

Figure 2 shows the FTIR spectra of AA-modified (24% WPG), VA-modified (19% WPG), and unmodified (W) Scots pine wood flour. As can be seen in Fig. 3, there was no spectral difference observed between the acetic anhydride-modified and vinyl acetate-modified samples. All modified samples showed a strong carbonyl stretching vibration (νC=O) peak in the region of 1745 cm^{-1}. Both the AA and VA-modified samples also showed a peak in the region of 1242 cm^{-1} due to the C-O stretching vibration of the acetyl moieties. The esterification reaction was also confirmed by the appearance of a new peak at 1375 cm^{-1}, attributed to the C-H bending (δs C-H) vibrations of the methyl groups introduced (Çetin *et al.* 2005, 2011; Özmen 2012).



$$\text{(a)}\quad \text{Wood—OH} + \text{O}\begin{matrix}\diagup \overset{\overset{\displaystyle \text{O}}{\|}}{\text{C}}\text{—CH}_3\\ \diagdown \underset{\underset{\displaystyle \text{O}}{\|}}{\text{C}}\text{—CH}_3\end{matrix} \longrightarrow \text{Wood—O—}\overset{\overset{\displaystyle \text{O}}{\|}}{\text{C}}\text{—CH}_3 + \text{CH}_3\text{-}\overset{\overset{\displaystyle \text{O}}{\|}}{\text{C}}\text{—OH}$$

$$\text{(b)}\quad \text{Wood—OH} + \text{CH}_3\text{-}\overset{\overset{\displaystyle \text{O}}{\|}}{\text{C}}\text{—O—CH=CH}_2 \xrightleftharpoons{K_2CO_3} \text{Wood—O—}\overset{\overset{\displaystyle \text{O}}{\|}}{\text{C}}\text{—CH}_3 + \text{CH}_2\text{=CH—OH} \rightleftharpoons \text{CH}_3\text{-CH=O}$$

Fig. 1. The reaction of (a) acetic anhydride and (b) vinyl acetate with Scots pine wood flour

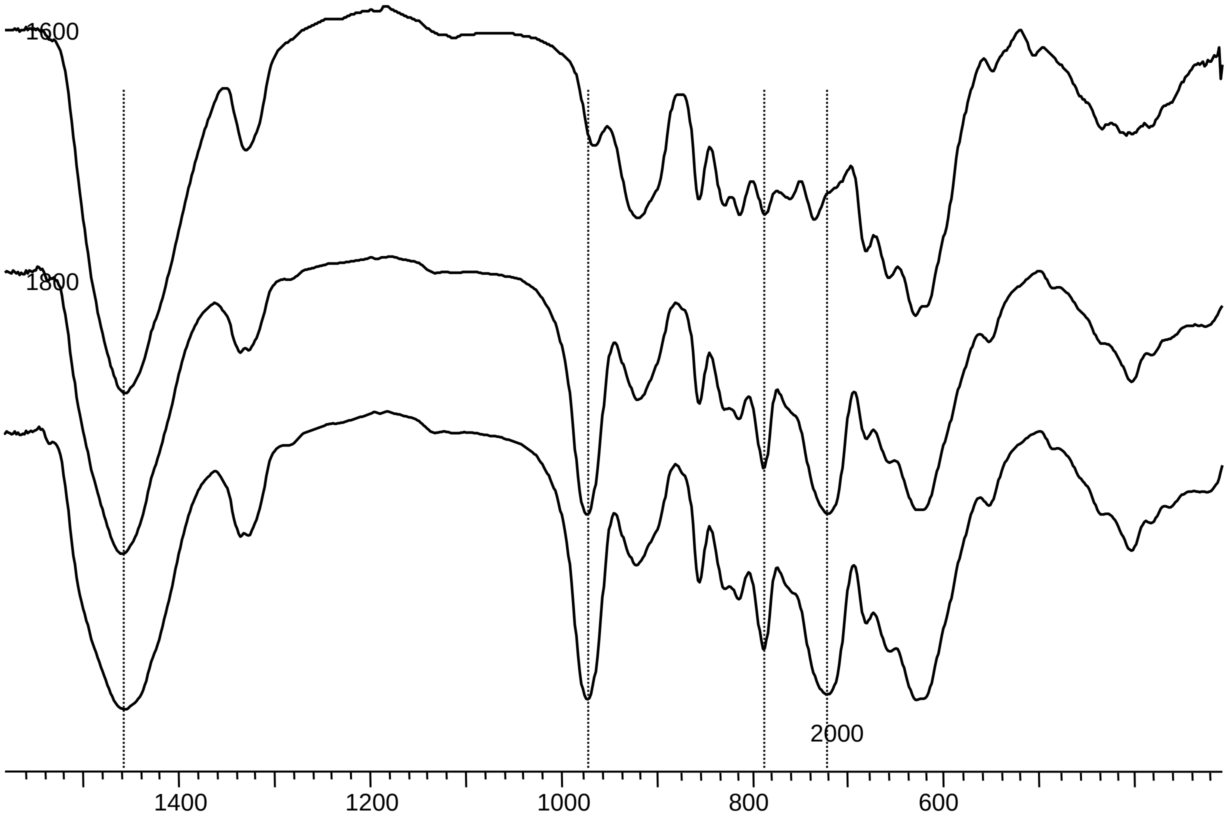


Fig. 2. FTIR spectra of untreated (W), acetic anhydride-modified (24% WPG) (W_{AA}), and vinyl acetate-modified (19% WPG) (W_{VA}) Scots pine wood flour

For further confirmation, the same samples were also characterized using ^{13}C CP-MAS NMR. The results are shown in Fig. 3. The carbon atoms of the cellulose component are assigned to the following peaks: C_1 (anomeric C) 105 δ (ppm), C_4 88 δ (ppm), $C_{2,3,5}$ 71 δ (ppm), and C_6 65 δ (ppm). Lignin, due to its heterogeneous nature, produces a broad peak at 150 δ (ppm) (Boonstra *et al.* 1996). The NMR spectra of the

AA- and VA-modified wood flour showed new peaks in the 21 δ (ppm) and 170 δ (ppm) regions due to the methyl band and the carboyxlic group of the acetyl group, respectively.

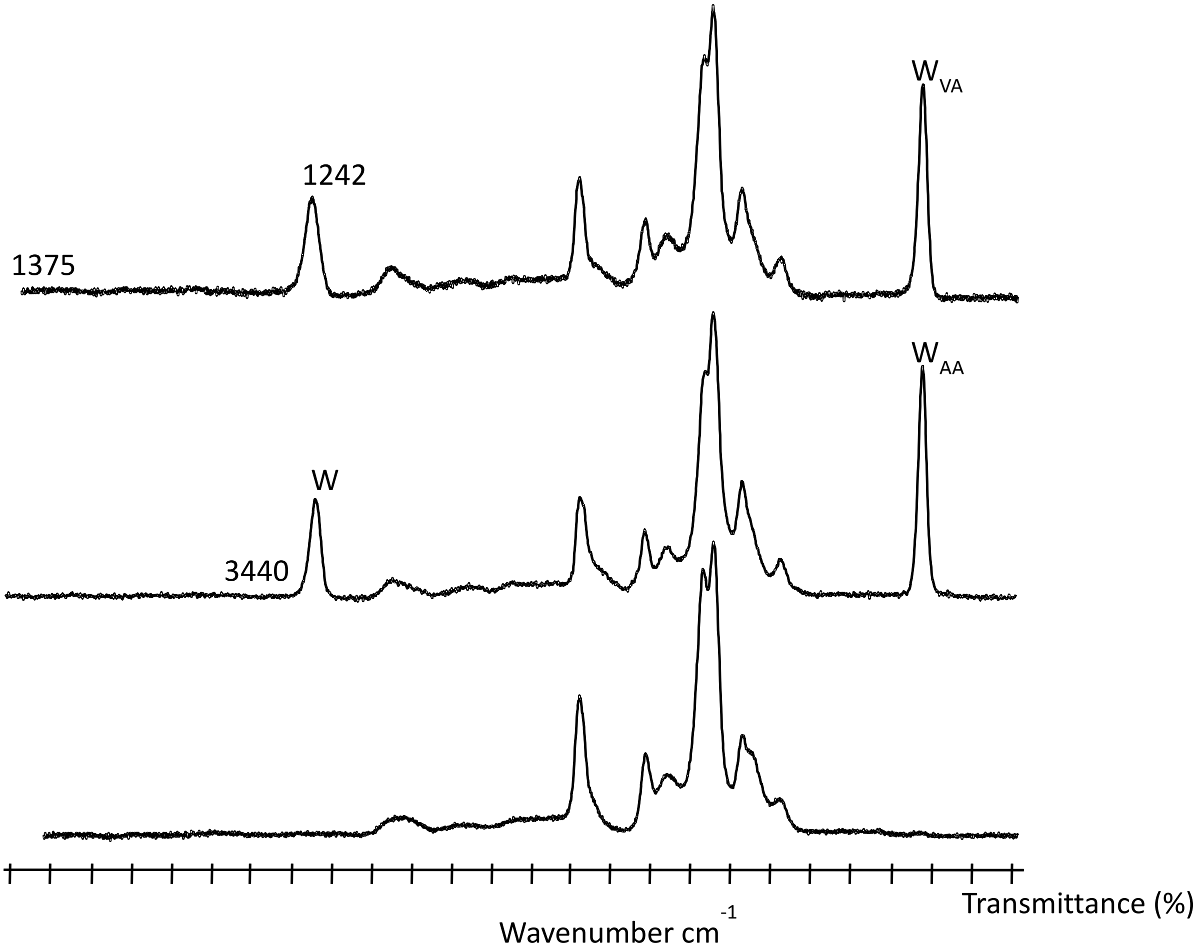


Fig. 3. ^{13}C CP-MAS NMR spectra of unmodified (W), acetic anhydride-modified (24% WPG) (W_{AA}), and vinyl acetate-modified (19% WPG) (W_{VA}) Scots pine wood flour

Figure 4 shows the density of the produced WPC groups. Statistical analysis indicated a difference between HDPE and W20. It is believed that the cellular structure of wood partially collapses during injection molding due to the high pressure, which leads to some increase in density. Especially for the injection-molded WPCs, similar results have been reported (Stark *et al.* 2004). It should also be noted that after acetylation of wood flour, the densities of the resulting composites were slightly reduced. The reason for this reduction might be that acetylated wood flour contains less lignocellulosic material than unmodified wood flour at a given weight % loading.

Figure 5 shows the tensile strengths of the HDPE, W20, AA20, and VA20 composites at 20 wt% wood flour loading. It is clear from the figure that the acetylation of Scots pine wood flour had a positive effect on tensile strength. Acetylation substitutes the wood cell wall hydroxyl groups with acetyl groups (see Fig. 1), altering the wood surface in particular, making it more hydrophobic. Since now both AA20 or VA20 and HDPE are hydrophobic, it is predicted that AA20 or VA20 might exhibit better compatibility with HDPE than W20. This would result in an increase in tensile strength of the composites as the fiber–matrix interaction is now possible to facilitate stress transfer from

HDPE to AA20 or VA20. It should also be noted that the addition of extractive-free wood flour to the HDPE polymer matrix did not reduce the tensile strength.

The tensile modulus values of the HDPE, W20, AA20, and VA20 composites at 20 wt% wood flour loading are presented in Fig. 6. The tensile modulus of the HDPE significantly increased with the addition of wood flour. This is usually explained by the rule of mixture (Matuana and Balatinecz 1998; Mengeloglu and Karakus 2008). Wood flours have a higher modulus than polymer matrixes, and as a result, their mixture produces higher modulus values compared to the polymer itself. From the figure, it is also seen that acetylation of Scots pine wood flour with VA did not affect tensile modulus values; however, acetylation of wood flour with AA had a negative effect on the tensile modulus property compared to unmodified wood flour-filled composites (W20).

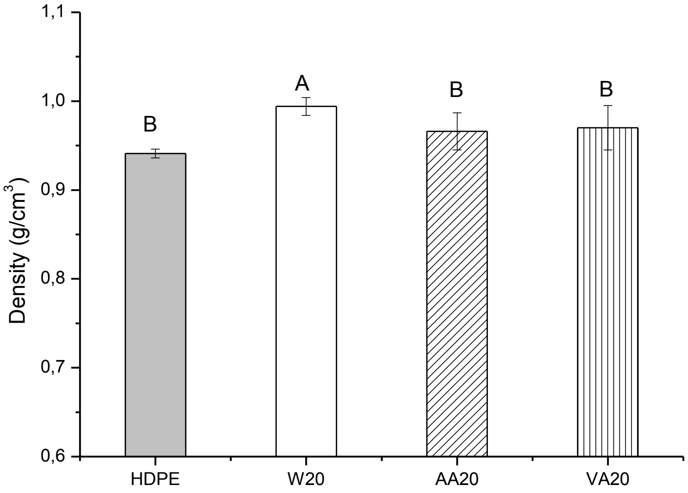


Fig. 4. Density of WPCs

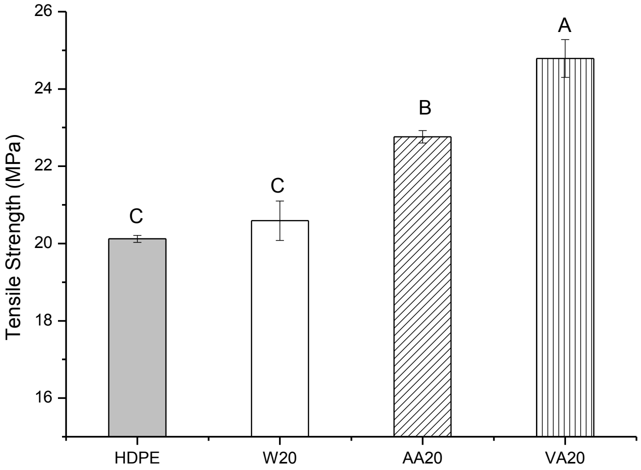


Fig. 5. Effect of acetylation on the tensile strength (TS) values of WPCs

Figure 7 shows flexural strength values for HDPE, W20, AA20, and VA20 composites at 20 wt% wood flour loading. It is clear from the Figure that the acetylation of Scots pine wood flour had a positive effect on the flexural strength. It should be noted that injection-molded WPC even without modification might give slightly higher flexural strength values (Gosselin *et al.* 2006). After acetylation of wood flour, a further increase in flexural strength was observed.

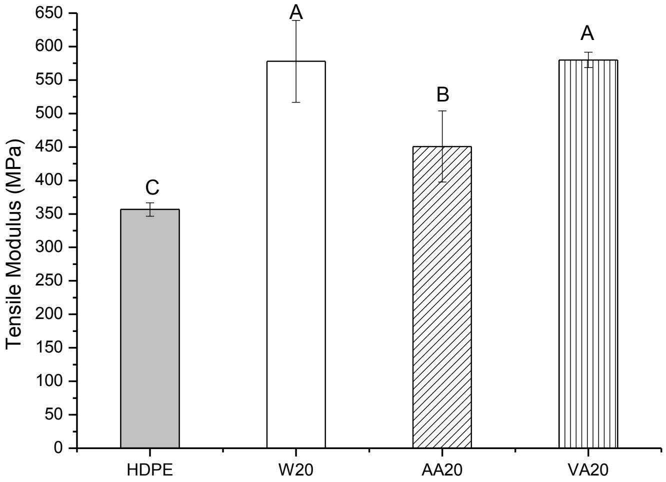


Fig. 6. Effect of acetylation on the tensile modulus values of WPCs

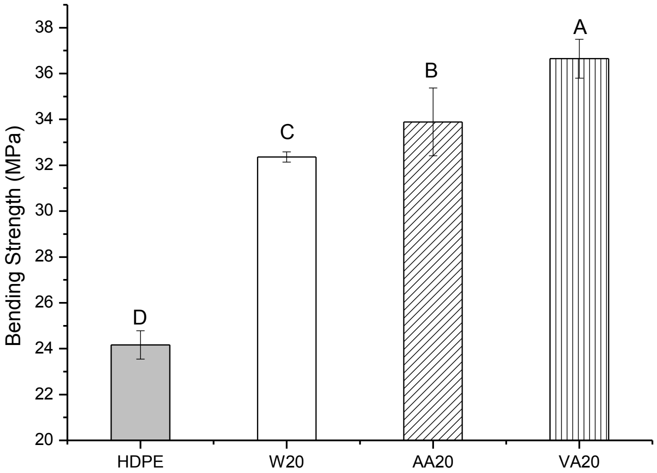


Fig. 7. Effect of acetylation on the flexural strength values of WPCs

The flexural modulus (Fig. 8), similar to the tensile modulus, was increased with the addition of wood flour to the polymer matrix. Acetylation of wood flour with AA slightly reduced these values. A possible reason for reduction of the flexural modulus that AA modified samples (24% WPG) contains 5.8% less lignocellulosic materials than unmodified wood flour at 20 wt% loading. Because after acetylation treatment, the wood flour gains weight as a result of the presence of bonded acetyl groups in the cell wall, a given weight of modified wood flour therefore contain fewer lignocellulosic materials than unmodified one (Hill 2006).

Figure 9 shows elongation at break values of the HDPE, W20, AA20, and VA20 composites at 20 wt% wood flour loading. It is clear from the Figure that compared to the unfilled HDPE (around 500%), elongation at break values of the composites were significantly lower (around 10%). It is well established that the addition of wood flour to the polymer matrix dramatically reduces the elongation at break values. It is also reported that higher modulus values usually results in lower elongation at break values for this type of composite (Mengeloglu and Karakus 2008).

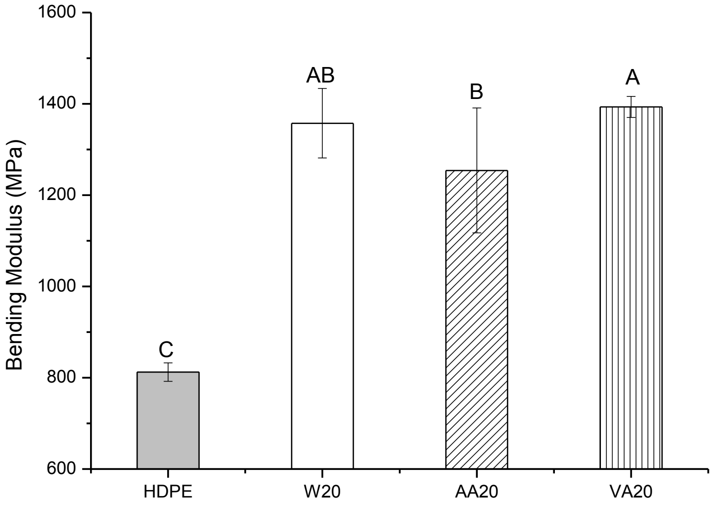


Fig. 8. Effect of acetylation on the flexural modulus values (b) of WPCs

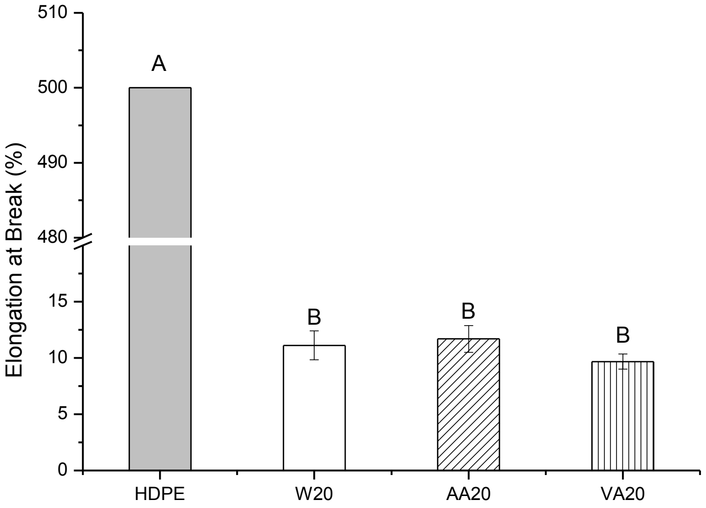


Fig. 9. Effect of acetylation on the elongation at break values of WPCs

Figure 10 presents the impact strength values of the samples. Impact strengths were significantly reduced with the wood flour addition.

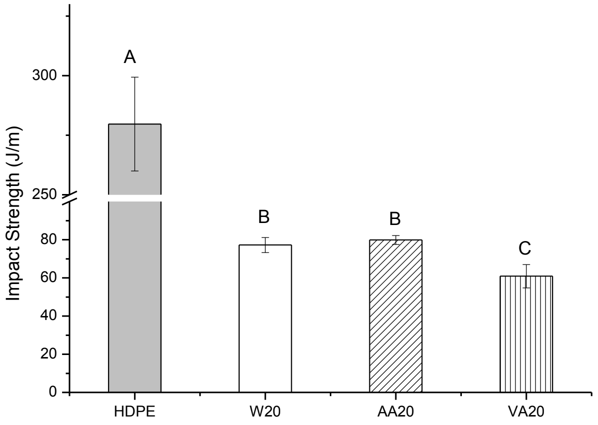


Fig. 10. Effect of acetylation on the impact strength (IS) values of WPCs

Acetylation had no effect on the impact strength. Reduction of the impact strength was reported by Mengeloglu and Karakus (2008) when the commercial coupling agent MAPE was used. This is explained by the fact that better bonding between the polymer and wood flour changed the mode of failure from fiber pullout to fiber breakage. This study was the first time VA was used, and it improved the tensile and flexural strengths as well as the modulus, but not the impact strength. Further studies will be conducted with VA modifications.

The fracture mode of the unmodified wood flour composite (W20) is shown in Fig. 11a. As shown for the freeze-fractured surface, wood fibers are debonded from and pulled out of the cavitated HDPE matrix, which indicates poor interfacial adhesion. The SEM micrographs shown in Figs. 11b and 11c display acetylated wood flour with AA or VA embedded in the HDPE matrix. The acetylated wood flour is coated with a polymer layer and shows good interaction between the two materials.

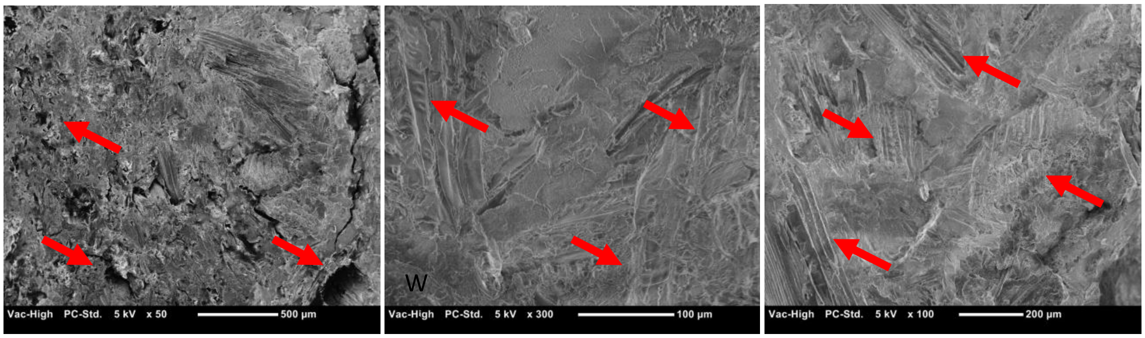


Fig. 11. SEM micrograph of freeze-fractured surface of a) W20 composite (untreated wood flour-reinforced HDPE) illustrating cavitated HDPE matrix, b) AA20 composite (acetic anhydride-modified wood flour-reinforced (24% WPG) HDPE) showing covered wood flour material connecting the wood flour to the matrix, and c) VA20 composite (vinyl acetate-modified wood flour-reinforced (19% WPG) HDPE) showing covered wood flour material connecting the wood flour to the matrix.

The composites reinforced with untreated wood flour and those treated by acetylation (AA or VA) were evaluated by thermogravimetric analysis (TGA) for verification of the thermal characteristics of the materials. This characterization allowed for evaluation of the influence of acetylation treatment of wood flour in the matrix. Figures 12 to 14 show TG curves of W20 (untreated wood flour-reinforced HDPE 20 wt%), AA20 (acetic anhydride-modified wood flour-reinforced HDPE 20 wt%), and VA20 (vinyl acetate-modified wood flour-reinforced HDPE 20wt%) composites.

For the W20 composite (Fig. 12), three stages of thermal decomposition were noticed: 25 to 150°C, 150°C to 400°C, and, 400 to 525°C, which were denoted as region I, region II, and region III, respectively. Complete decomposition of the composite occurred at 525°C. The first stage is related to the release of water or moisture. The second stage is related to the degradation of the wood components of the composite. The third region is related to degradation of HDPE. Similarly, three stages of behavior were also observed with acetylated wood flour-reinforced HDPE composites (Figs. 13 and 14).

For pyrolysis of the untreated wood flour in the HDPE matrix, the active decomposition temperature of the wood flour was determined to be 310°C. For the acetylated wood flour in the HDPE matrix, the main decomposition temperatures of the acetylated wood flour shifted to higher values: 340 and 370°C for AA (Fig. 13) and VA (Fig. 14) modified samples, respectively. It is believed that acetylation with VA enhances the thermal stability properties of lignocellulosic materials.

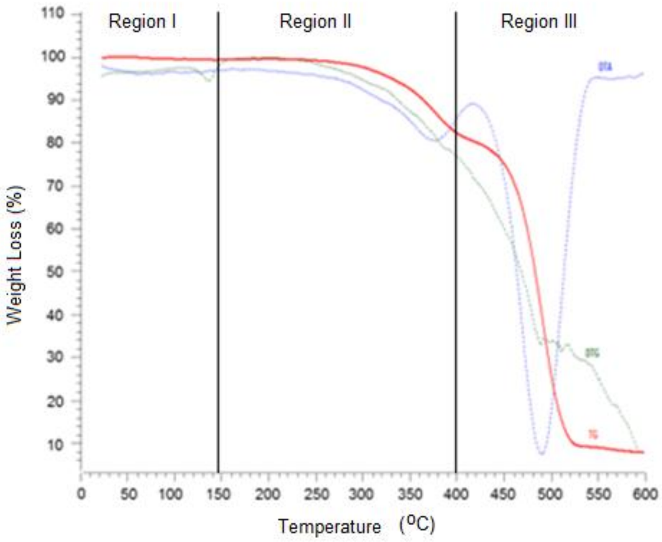


Fig. 12. TGA curves of W20 wood polymer composite

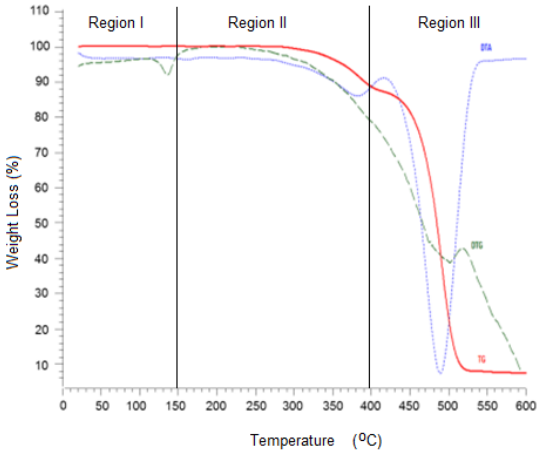


Fig. 13. TGA curves of AA20 wood polymer composite

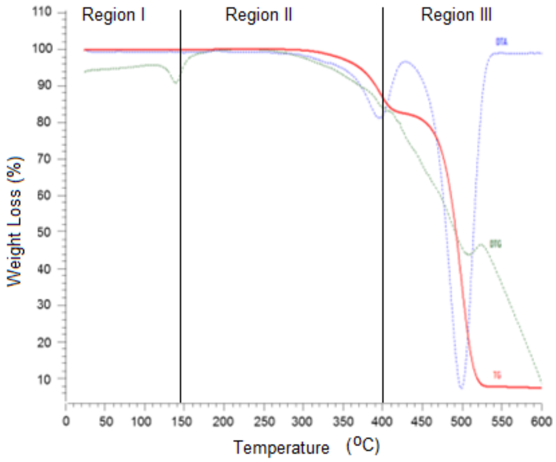


Fig. 14. TGA curves of VA20 wood polymer composite

It was reported in an earlier study that after acetylation of hemp fibers with VA (15% WPG) the active decomposition temperature shifted from 376°C to 392°C (Özmen 2012). The W20, AA20, and VA20 polymer composites consisted of around 6.9%, 5.3%, and 3.4% final ash content, respectively.

CONCLUSIONS

1. Results of AA and VA modification yielded 24% and 19% WPG, respectively. These results were obtained with AA and VA modification under the same reaction conditions.
2. The acetylation of Scots pine flour in a polymer matrix in general results in improvement in tensile strength and tensile and flexural modulus, as well as flexural strength properties compared to neat composite and extracted unmodified wood flour reinforced-composite.
3. The composites reinforced with VA acetylated wood flour exhibited better mechanical properties than the composites with AA acetylated wood flour. It would

be of great interest to investigate the effect of WPG levels of VA modification on the properties of composites in future studies.

4. The addition of wood flour or acetylated wood flour significantly reduces the impact strength compared to neat composites.
5. The composites reinforced with acetylated wood flour presented higher thermal stability than the composites reinforced with untreated wood flour. With acetylation, the maximum weight loss temperature of the wood polymer composites was increased by 30°C (for AA-modified) and 60°C (for VA-modified) when compared with untreated wood flour. Acetylated wood flour with VA exhibited better thermal stability than acetylated wood flour with AA.

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