

Mechanical and physical properties of thermally modified wood flour reinforced polypropylene composites

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Abstract. Heat treatment of wood helps to lower the hydrophilicity and polarity of wood fibres used in wood-plastic composites. By means of heat treatment it is possible to reduce the access to wood hydroxyl (OH) group, which causes hydrophilic and polarity of wood fibres. Therefore improving compatibility between the wood and polymer matrix. In this research, the effect of wood flour (WF) heat treatment and chemical modification with 3-aminopropyltriethoxysilane (APTES) were investigated. WPC test samples were prepared using alder (*Alnus incana*) WF with mesh size of 0.05 mm as a filler material and polypropylene (PP) as the matrix material. WF was chemically modified with NaOH and APTES to increase the adhesion and compatibility of WF to polymer matrix. The composites were manufactured using a twin-screw extruder and the test samples were made by injection molding. The composites mechanical properties were tested using three-point flexural test and Charpy impact test. The composite physical properties were investigated with Fourier transform infrared spectroscopy (FTIR). The effect of silane (APTES) and NaOH modification on thermally treated and untreated WF was examined with contact angle measurement. Comparisons were made between the untreated WF and thermally treated WF. Also the effect of NaOH and silane (APTES) modification on the properties of thermally modified and unmodified WF composite were investigated. Using WF as a filler material increased flexural strength, while impact strength decreased thus making the material more rigid and brittle. The test results revealed that there was no significant difference in the mechanical properties between thermally treated and untreated composites. However, chemical modification improved the mechanical properties of the composites.

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

INTRODUCTION

The use of lignocellulosic fillers has received considerable interest from academics and industry for its environmental and economic benefits. Natural fillers have many advantages over inorganic fillers such as: renewable nature, availability, low cost and

density, high specific strength and moduli etc. Despite many advantages they have a big disadvantage – they are incompatible with the polymer matrix due to the polarity of the natural fillers and non-polarity of the polymer matrix. Many solutions have been proposed to overcome this problem for instance adding a coupling agent has been a successful way of aiding compatibility (Krzysik & Youngquist, 1991; Gatenholm et al., 1993; Kazayawoko et al., 1999; Lu et al., 2000; Kaboorani et al., 2008). Presently, the use of coupling agents such as silane, maleic anhydride grafted polypropylene, alkali treatment, acetylation have been the most common ways to increase the compatibility of the hydrophilic natural fibers and the hydrophobic polymers (Luo et al., 2013).

Heat treatment is a relatively simple method for modifying wood. This method improves hydrophobicity, dimensional stability and biological resistance. During heat treatment, significant changes take place in the chemical composition of the wood filler including decomposition of hemicellulose which is hydrophilic. Heat treatment also has some drawbacks including the reduction of mechanical properties and unwanted color and odor (Adyembir et al., 2015). With heat treatment the adsorption of water into wood decreases which results in lowered swelling or shrinkage behavior compared to untreated wood. It is noted that moisture is absorbed by the hydrophilic wood fibers into the composite which leads to degradation of the interfacial adhesion quality and therefore decreases the strength of the composite. Thermal modification reduces the polarity of wood fibers and thereby improves their compatibility with hydrophobic thermoplastics and increases interfacial strength. Therefore, these materials provide the needed properties for such uses as decking, railing, cladding and under the hood applications in the automotive industry (Follrich et al., 2010).

Thermal treatments use no chemicals thus making it an environmentally friendly process (Eslam et al., 2011). Wood can be degraded and finally burn at high temperatures. The initial degradation can start at temperatures as low as 117 °C depending on the heating period, atmosphere and wood species. Thermal stability is a critical factor in the processing time and temperature (Kaboorani & Faezipour, 2009). In theory, adding heat treated wood in which some components have been decomposed should lead to an improvement in thermal stability (Kaboorani & Faezipour, 2009).

The aim of this research was to explore the use of thermally modified wood as a filler material for wood plastic composites as thermal treatment potentially reduces the polarity of wood and makes it more compatible with thermoplastic polymers. The task of this project is to investigate the effect of chemically treated, thermally treated and untreated wood on the mechanical and physical properties.

MATERIALS AND METHODS

Materials

In this research, PP was used as the matrix material for making WPCs. The PP (BC245MO) obtained from the Borealis Polymers OY company is a heterophasic copolymer (block copolymer) with a density of 0.905 g cm⁻³, and melt flow index (MFI) of 3.5 g 10 min⁻¹. Thermally treated (170 °C) hardwood (alder (*Alnus incana*)) boards were supplied by HA SERV OÜ. Thermally modified boards were then comminuted into a fine flour with mesh size of 0.05 mm using a disintegrator device DS-A. As a coupling agent 3-aminopropyl-triethoxysilane (APTES) from Sigma-Aldrich was used. The molecular weight of the substance is $M_w = 221.37 \text{ g mol}^{-1}$ and the boiling point at

atmospheric pressure is 217 °C. A reagent grade sodium hydroxide (NaOH), 98% was also used and glycerine in some samples.

Wood flour modification

Preparation of the composites started with modification of wood flour (WF). Firstly, WF was weighed in a stainless steel vessel. According to the previous research (Gwon et al., 2010), optimum concentration of alkali for the treatment is 10 wt% and above, so that the mechanical properties may slightly decrease. Therefore, in this study a 10 wt% (based on WF mass) aqueous solution of NaOH was prepared in the laboratory by dissolving NaOH granules in water. WF was immersed in 10 wt% NaOH solution at room temperature (25 °C) for 90 min. The WF was then rinsed with distilled water to neutralise the excess NaOH and dried in the oven at 60 °C for 24 h.

WF silane modification according to a previous research (Kim et al., 2011) was used. For silane modification, 5 wt% (based on WF) APTES was taken. APTES was immersed in a solution of ethanol/distilled water (6:4 ratio) for 1 h in order for it to be hydrolyzed and the pH of the solution was adjusted to the value of 4–5 with acetic acid. Then silane solution was poured on the WF was left at room temperature (25 °C) for 2 h. After the silane treatment the WF was dried in the oven at 60 °C for 24 h.

The usage of glycerine in WPC-s was similar to a previous research (Sanadi & Caulfield, 2008) which showed that adding 2% glycerine resulted in the best properties. Glycerine was used as a processing aid and added to the modified WF in the amount of 2% of the mass of WF. Glycerine was weighed and 500 ml of water was added to it so that the mixing process would be easier. Table 1 illustrates the composition of the composites.

Composite processing

The test specimens were prepared in Tallinn University of Technology, Department of Polymer Materials. The first operation was the modification of WF and then the compounding and granulation of the obtained mixtures. The last step was to produce test specimens by injection molding method.

After the modification, the WF was weighed and mixed with polymer granules maintaining the ratio of 65% polymer and 35% WF for all the samples. The composition of the mixtures are shown in Table 1. The mixtures were compounded using twin-screw extruder Brabender Plast-Corder PLE651. The barrel had four heating zones. The melting zone temperatures were set at 180 °C, 185 °C and 190 °C, and 185 °C for die zone. The rotation speed of the twin-screw was 60 rpm. The extruded material was cooled with ventilators and granulated with a Brabender granulator. The test samples were made by injection moulding (Battenfeld BA 230 E) according to standard ISO 178:2010. Depending on the material the temperature and pressure was suitably adjusted. Conditions for injection moulding were: temperature: 170–185 °C from the feed zone to the die zone, injection pressure: 7 MPa, screw speed 40 rpm, cooling time 15 s. The mixture was injection moulded into bar shape specimens for flexural and impact tests. Dimensions of the specimens were 63 x 10 x 4 mm.

Table 1. Composition of the composites

| Sample | PP (wt%) | WF (wt%) | NaOH (wt%) | APTES (wt%) | Glycerine (wt%) |
|--------|----------|----------|------------|-------------|-----------------|
| 1 | 100 | – | – | – | – |
| 2 | 65 | 35 | – | – | – |
| 3 | 65 | 35 | 10 | 5 | – |
| 4 | 65 | 35 | 10 | 5 | 2 |
| 5 | 65 | 35* | – | – | – |
| 6 | 65 | 35* | 10 | 5 | – |
| 7 | 65 | 35* | 10 | 5 | 2 |

* – thermally treated WF

Mechanical properties

Flexural properties were tested by means of three-point loading system Instron 5866 according to ISO 178:2010. Testing was carried out at room temperature 20 °C, crosshead speed of 20 mm min⁻¹, test span of 60 mm. Five specimens were used for each composite. For each composite, flexural strength and modulus of elasticity (MOE) were calculated. Also, the 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 specimen was measured and Charpy impact strength was calculated.

Fourier transform infrared spectroscopy (FTIR)

The efficiency of the chemical modification was verified using Fourier transform infrared spectroscopy (FTIR). FTIR spectroscopy measurements were performed using Interspectrum FTIR spectrometer (model Interspec 200-X) with KBr disc method. The spectral resolution was 4 cm⁻¹ and the spectra were recorded in the range of 1,800–800 cm⁻¹ using. Thin wafers were cut from the previously produced flexural test specimens using a scalpel. The thin wafers were placed under a clamp and the spectra were measured under ambient conditions.

RESULTS AND DISCUSSION

Flexural properties

The flexural strength of WPCs with thermally treated and untreated, silane modified and unmodified WF is presented in Fig. 1 The addition of WF has increased the flexural strength by 9–21% (from 32.76 MPa to 41.47 MPa), thus making the composites more rigid and brittle. The results show very slight differences in flexural strength between different composites. In order to achieve better mechanical properties, chemical modification of WF was used to gain better adhesion and better dispersion of the filler in the composite but unfortunately the results show little difference between modified and unmodified WF based composites. Chemical modification of WF slightly decreased the flexural strength (about 10%) compared to unmodified WF based composites. The decrease of flexural strength of modified WF based composites may be due to the excessive alkali that weakens the surface of WF and causes the effect of corrosive interactions between wood fibers in the composites (John et al., 2008; Gwon et al., 2010).

However, there were no significant differences between thermally treated and untreated WF based composites. This can be explained by the fact that WF was ground to very fine flour with mesh size of 0.05 mm and therefore modifications have no effect on the composite properties anymore. WF with mesh size of 0.05 mm acts just as a filler in the PP matrix and not as a reinforcing fiber. WF with mesh size 0.05 mm was chosen to be similar with wood dust in sawmill and furniture industries and to find usage for this wood dust in WPCs. As can be seen from Fig. 1, there is almost no difference between modified, thermally treated or untreated WF used in WPCs. The differences of the results between all the composite remain fit within the boundaries of measurement uncertainty. However, previous researches have shown increase in flexural properties with APTES modified WF/PP composites (Kim et al., 2011; Kallakas et al., 2015). For some WPC samples, glycerine was used as processing aid. The results show (see Fig. 1) that there was no effect of using glycerine on the flexural properties.

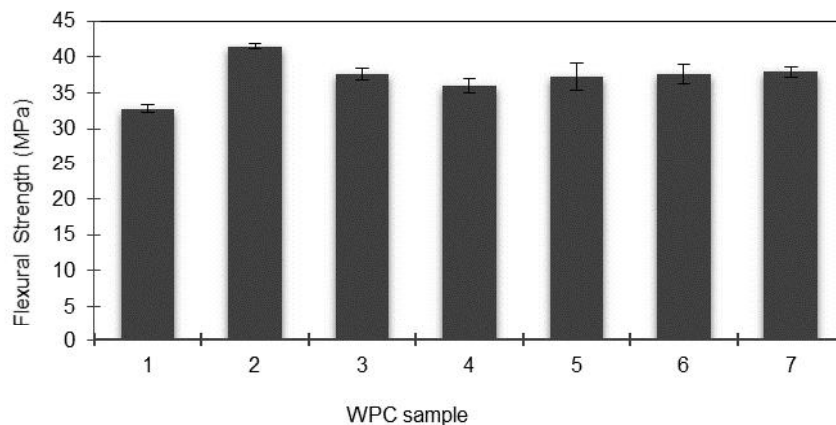


Figure 1. Flexural strength of chemically and thermally modified and unmodified WF/PP composites.

Modulus of elasticity (MOE) shows the materials ability to withstand deformation. The results derived from the flexural test show the stiffness of the composite (see Fig. 2). Comparing the results to the MOE of pure PP (1.01 GPa) the stiffness of the composite is significantly higher (over 200%). The increased stiffness can be explained by the stress transfer from the polymer matrix to the filler (Ndiaye & Tidjani, 2012). The results show that chemically unmodified composites have slightly, about 10% higher MOE values than modified composites. When comparing thermally treated and untreated WF composite, it can be seen from the results (see Fig. 2) that there is no difference. The results show a slight effect on MOE values when glycerine was used. MOE decreased by 50% with untreated WF composites where glycerine was used as a processing aid since it is likely that the small molecules of glycerine could act as a plasticizer/lubricant.

Therefore, from the flexural properties, it can be concluded that chemical or thermal modification has minimal or no effect on the flexural properties of WPCs when fine WF with mesh size of 0.05 mm is used.

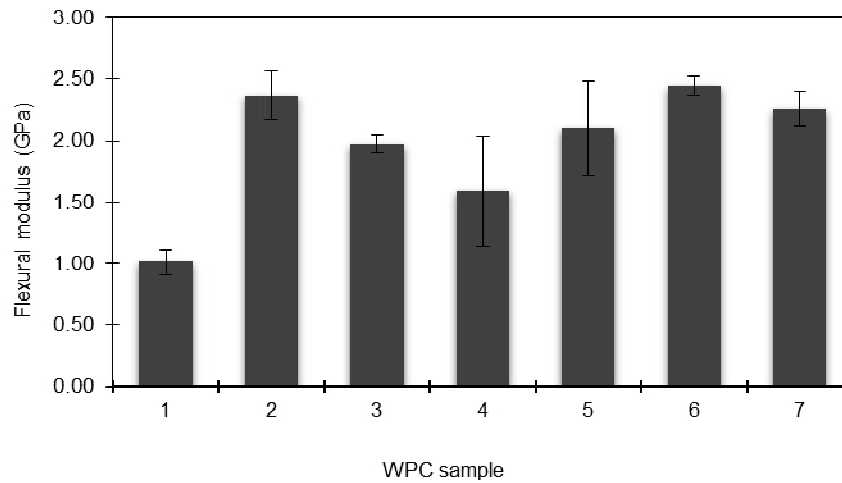


Figure 2. Flexural modulus of chemically and thermally modified and unmodified WF/PP composites.

Impact strength

Impact strength was measured by Charpy impact test of single notched specimens of unmodified and modified WPC samples. Single notched impact test was chosen because the pendulum impact tester machine did not provide sufficient energy to break un-notched PP – because PP matrix has high elasticity which is also shown by previous researches (Bledzki & Frauk, 2004; Bledzki et al., 2009).

The results of the impact test are shown in Fig. 3. From the results it can be seen that using fine WF in the PP matrix lowered the impact properties significantly (about three times) compared to pure PP (11 kJ m^{-2}) which is also shown in previous researches (Bledzki & Frauk, 2004; Bledzki et al., 2009). Using fine WF in the PP matrix reduces the impact strength because composite is more heterogenic than PP and it creates stress concentration regions in the WPC. These regions require less energy for breaking the composite under impact. Also, small WF particles are difficult to disperse due to their tendency to agglomerate which results in low impact energy therefore making the composite more brittle. The results show lower (50–100%) impact strength on chemically unmodified WF composites. The increased impact strength with chemically modified WF based composites can be explained by the fact that that alkaline treatment removes hemicelluloses, lignin and waxes which produces a rougher surface which in turn increases the length to diameter ratio or aspect ratio (L/D) thus enlarging the surface area of contact with the polymer matrix which increases the surface area of interaction at the interface (Ichazo et al., 2001). Higher impact strength on APTES modified WPC samples is also due to silanol groups in these composites that have strong bonds with hydroxyl groups of WF. These strong bonds increase interfacial adhesion between WF and the polymer matrix. It is supposed that the increased interfacial adhesion between WF and the polymer matrix is supported by the formation of siloxane by condensation reaction. (Kim et al., 2011). Therefore this impact test clearly shows the influence of chemical modification on the mechanical properties of WPC materials.

The results show (see Fig. 3) the highest impact values for WPC samples with APTES modified WF composites based on an addition of 2% glycerine (6 kJ m^{-2}). The addition of glycerine has increased impact strength by 70% due to a plasticization effect. This plasticization effect is caused by glycerine that plasticizes the amorphous components such as lignin and hemicellulose in wood by breaking some of the H-bonds present (Sanadi & Caulfield, 2008). However, there were no significant differences between thermally treated and untreated WF composite samples. Though, the impact values for thermally treated WF composites were slightly higher than those for untreated WF composites.

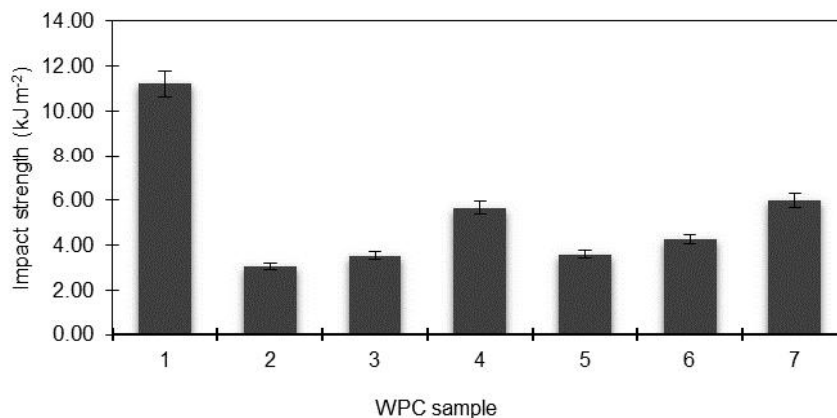


Figure 3. Impact strength of chemically and thermally modified and unmodified WF/PP composites.

Fourier transform infrared spectroscopy (FTIR)

FTIR spectra shows the changes of molecular interactions which lead to wave number shifts. The wavenumber values can be compared to multiple tables or specific software designed to give different chemical bond value range. Previous researches (Bodirlau et al., 2008; Emami et al., 2011) show that typical wood structure has peaks $3,300\text{--}4,000 \text{ cm}^{-1}$ indicating strong broad OH stretching and C-H stretching ($2,800\text{--}3,000 \text{ cm}^{-1}$) in methyl and methylene groups. Specific, fingerprint area absorption in the region from $600\text{--}1,800 \text{ cm}^{-1}$ are assigned to major cell wall components such as cellulose, hemicelluloses and lignin. (Rana et al., 2010).

In this study, FTIR spectra were collected by co-adding 32 scans at a resolution of 4 cm^{-1} in the range from $1,600\text{--}600 \text{ cm}^{-1}$ at room temperature. It is the range of typical PP FTIR spectra which was compared to WPC samples to see any differences. FTIR spectra changes in WPC samples are demonstrated on Figs 4 and 5. There is no difference in FTIR spectra peaks between thermally modified and unmodified WF based composites. WPC samples had similar peaks to pure PP. However, there were changes in peak intensity in the range of $1,164 \text{ cm}^{-1}$ to $1,025 \text{ cm}^{-1}$ which are only present in WPC samples. In this region ($1,164 \text{ cm}^{-1} - 1,025 \text{ cm}^{-1}$) chemical modification of WF leads to changes of characteristic peaks and peaks changes for APTES treated samples are shown in Fig. 5. Modification with APTES showed peak changes at $1,025 \text{ cm}^{-1}$ and $1,104 \text{ cm}^{-1}$ assigned to Si-O-C band indicating that the coupling reaction between WF and APTES

has occurred thanks to the NaOH treatment. The signal intensity of the composite mixtures in comparison to pure PP (blue) in the range of 600–800 cm^{-1} are mostly aromatic structures example lignin molecules (Figs 4 and 5). Bands specific to PP used as the polymer matrix in WPCs are also present as shown in Table 2 and Figs 4 and 5. Peaks at 1,456 cm^{-1} represent CH_2 deformation; 1,376 cm^{-1} represent symmetric CH_3 deformation; peaks at 1,164, 998 and 974 cm^{-1} represent isotactic polypropylene band (Jordi).

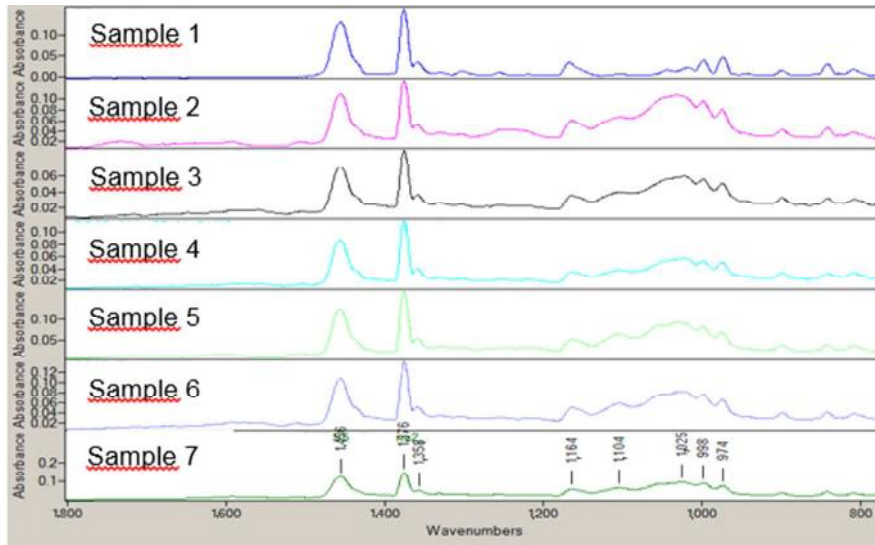


Figure 4. FTIR spectra of chemically and thermally modified and unmodified WF/PP composites.

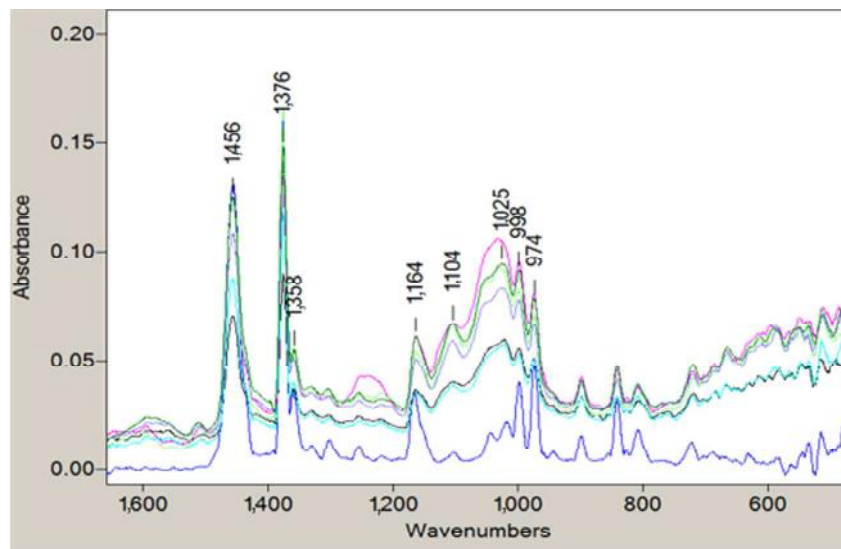


Figure 5. FTIR spectra peaks of chemically and thermally modified and unmodified WF/PP composites.

Table 2. FTIR peaks and identifications of WPC samples

| Wavenumber (cm ⁻¹) | Frequency (cm ⁻¹) | Bond | Functional group |
|--------------------------------|-------------------------------|-------------------------------------|------------------|
| 1,456 | 1,450–1,470 | CH ₂ and CH ₃ | Alkanes |
| 1,376 | 1,375–1,380 | CH ₃ | Alkanes |
| 1,358 | 1,350–1,370 | C–H | Alkanes |
| 1,164 | 1,000–1,320 | RCOOR | Ester |
| 1,104 | 1,000–1,100 | Si–OR | Silyl ether |
| 1,025 | 1,000–1,100 | Si–OR | Silyl ether |
| 998 | 900–1,050 | P–OR | Ester |
| 974 | 965–975 | cis RCH=HCR | Alkene |

CONCLUSIONS

This research focuses on exploring the use of thermally treated wood as a filler in thermoplastic composites. The objective was to investigate the different effects of chemically treated, thermally treated and untreated WF on the mechanical and physical properties of the obtained composites. It was found that thermally treated composite mixtures showed slightly higher MOE and flexural strength values than untreated wood mixtures thus suggesting that thermal treatment can increase the mechanical properties of the composite. However, there were no significant differences between chemically treated and thermally treated WF based composites. An addition of WF made the material more brittle as the impact strength results were lower than for pure PP. Thermally treated composite mixtures showed greater impact strength values than untreated composite mixtures. The addition of coupling agents helped to decrease the brittleness to some extent. FTIR showed that the coupling agent had reacted with the WF with the emergence of silyl ether groups (Si-OR). The addition of glycerine did not show any significant difference in the properties of the composites and may need further research. The use of thermally treated WF shows better mechanical properties than untreated WF composites. Waste materials from the timber industry can be easily used but perhaps the use of thermally treated wood may increase the price of the products.

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