Waste Pine Cones as a Source of Reinforcing Fillers for Thermoplastic Composites

Nadir Ayrilmis, Umit Buyuksari, Turker Dundar

Department of Wood Mechanics and Technology, Istanbul University, Bahcekoy, Sariyer 34473, Istanbul, Turkey

ABSTRACT: In this study, we evaluated some physical and mechanical properties of polypropylene (PP) composites reinforced with pine-cone flour and wood flour. Five types of wood–plastic composites (WPCs) were prepared from mixtures of cone flour, wood flour, PP, and a coupling agent. The water resistance and flexural properties of the composites were negatively affected by an increase in cone-flour content. Extractives in the cone flour had a significant effect on the flexural properties of the WPCs. However, the flexural properties and water resistance of the WPC samples were not significantly affected by the addition of 10 wt % of the cone flour when compared to the WPC samples made from wood flour. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 2324–2330, 2010

Key words: composites; polypropylene; recycling; renewable resources

INTRODUCTION

The use of plant-based fiber as an additive to plastics has accelerated rapidly over the past decade, primarily because of improvements in process technology and economic factors. Further development of these applications of biorenewable fibers for use by the plastics industry could provide attractive new value-added markets for agricultural products while simultaneously displacing petrochemical-based plastic resins. The primary advantages of using lignocellulosic fibers as additives in plastics are their low densities, low cost, nonabrasive natures, the possibility of high filling levels, high specific properties, biodegradability, availability of a wide variety of fibers throughout the world, and the generation of an agricultural economy.[1]

The pine tree is one of the most common species in both Europe and North America, but it is mainly in the Mediterranean area where it obtains its highest importance in production and consumption. *Pinus pinea* L. is often called *stone pine* and sometimes *umbrella nut*. These names apparently come from the idea that this tree grows well in stony ground and also because, at times, it has a shape rather like an umbrella. *P. pinea* cones are of the most significant value among the *Pinus* species because the pine nut (pinyon), which is the edible seed of the pine, is a widely used and highly appreciated food source. The stone pine forests of Turkey cover 54,000 ha,[2] and the total cone production of the stone pine was approximately 3500 tons in 2006 according to forestry statistics of the Turkish General Directorate of Forestry.[3] Large quantities of cones are produced annually throughout the world, especially in pine plantations grown for the pulp and paper industry.

Coupling agents play a very important role in the improvement of compatibility and bonding strength between polar wood fibers and nonpolar thermoplastics in wood-fiber/polymer composites. Maleated polypropylene (MAPP) has been extensively used in wood-fiber/polymer composites. The maleic anhydride (MAH) present in MAPP provides polar interactions, such as acid–base interactions, and can also covalently link to the hydroxyl groups on the lignocellulosic fiber.[4]

A growing demand for wood–plastic composites (WPCs) has led to continuous efforts to find new resources as alternatives to wood. With the increasing population of the world, the sustainable utilization of forest resources has been adversely influenced. One of these residuals is waste pine cones, which are produced in high quantities in the pine nut industry. Pine cones are collected, dried to facilitate seed release, and generally discarded or burned in the stove in winter. They do not require any additional cost for collecting and drying. For this reason, the waste pine cone could play an important role in the manufacture of value-added lignocellulosic/plastic composites and may be the most efficient use of the pine cone in Mediterranean countries having stone pine forests. An extensive literature search did not reveal any information about the utilization of

the stone pine cone as an alternative to wood in the manufacture of WPCs. From the literature, we know that the physical and mechanical properties of the lignocellulosic/plastic composites can be influenced by the raw material characteristics.[5–11] The objective of this study was to determine some physical and mechanical properties of polypropylene (PP) composites reinforced with various mixtures of wood flour and cone flour.

EXPERIMENTAL

Materials

Fresh cones were collected from the stone pine (*P. pinea* L.) in the Fatih Forest District Sample in Belgrade Forest in Istanbul, Turkey. The cones were spread on plastic films and exposed to sunlight for 1 week. After drying, the cones opened up, and their nuts fell out. The pine cones without nuts were soaked in a hot water for 4 h at 90°C. This treatment was believed to partially remove the gum on the surface of the cones and to improve the grinding process and bonding properties of the cone flour. After the treatment, the wet cones were dried in an oven at 60°C for 10 h to a moisture content of 20–30% on the basis of the oven-dried cone weight. After drying, the cones were then processed by a rotary grinder without additional water. Finally, the cone flour was passed through a U.S. 35-mesh screen and was retained by a U.S. 80-mesh screen (Fig. 1). The cone flour was then dried in a laboratory oven at 100°C, for 15 h, and a moisture content of 1–2% was reached.

Wood particles (a 50 : 50 blend) consisting of pine (*Pinus nigra Arnold var. pallasiana*) and beech (*Fagus orientalis* Lipsky) species were obtained from a commercial particleboard plant in Turkey. The moisture content of the particles, as determined by their oven-dried weight, was found to be 4–5% before the treatment. The wood particles were processed by a rotary grinder without additional water. The wood flour was passed through a U.S. 35-mesh screen and was
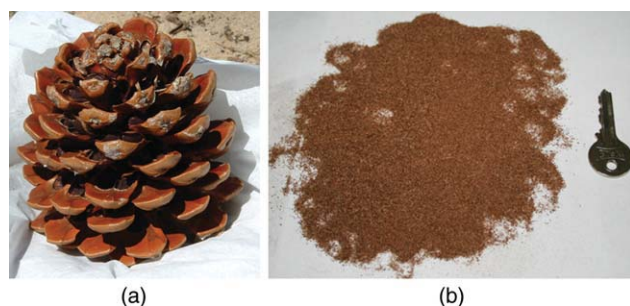

Figure 1 (a) Cone of the stone pine (*P. pinea*) and (b) cone flour of the stone pine passed through a U.S. 35-mesh screen and retained by a U.S. 80-mesh screen. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE I
Compositions of the Evaluated Formulations

WPC formulation code	Wood flour (wt %)	Cone flour (wt %)	PP (wt %)	MAH-grafted PP (wt %)
WPC1	40	–	57	3
WPC2	30	10	57	3
WPC3	20	20	57	3
WPC4	10	30	57	3
WPC5	–	40	57	3

retained by a U.S. 80-mesh screen and was then dried in a laboratory oven at 100°C for 15 h to a moisture content of 1–2%.

Polypropylene (PP) (melting temperature = 160°C, density = 0.9 g/cm^3, melt flow index at 230°C and 2.16 kg = 6.5 g/10 min) produced by Petkim Petrochemical Co. (Izmir, Turkey) was used as the polymeric material. MAH-grafted PP [MAPP-OPTIM-415 with the reactive modifier MAH (MAH content = 1 wt %)] was supplied by Pluss Polymers Pvt., Ltd. (New Delhi, India).

Composite preparation

The wood flour and the waste cone flour were dried to a 1–2% moisture content with in an air dryer oven at 100°C for 24 h and then stored in a polyethylene bag in an environmental controller. The cone and wood flours, PP, and MAPP granulates were preblended in a mixer and then processed in a 30-mm conical, corotating, twin-screw extruder (Aysa Instrument Com., Istanbul, Turkey) with a length-to-diameter ratio of 30 : 1. The raw materials were fed into the main feed throat with a gravimetric feed system. The barrel temperatures of the extruder were controlled at 170, 180, 190, and 190°C for zones 1, 2, 3, and 4, respectively. The temperature of the extruder die was held at 200°C. The extruded strand passed through a water bath and was subsequently pelletized. These pellets were stored in a sealed container and then dried for about 3–4 h before they were injection-molded. The temperature used for the injection-molded samples was 170–190°C from the feed zone to the die zone. The WPC samples were injected at an injection pressure between 45 and 50 kg/m^2 with a cooling time of about 30 s. Finally, the samples were conditioned at a temperature of 23 ± 2°C and a relative humidity of 50 ± 5% according to ASTM D 618-08.[12] The formulations of the composites are given in Table I. The density values of the samples varied from 0.99 to 1.03 g/cm^3.

Determination of the water resistance

Thickness swelling (TS) and water absorption (WA) tests were carried out according to ASTM D 570-05

TABLE II
Results for the Water Resistance of the Composites

Composite code	Composite density (g/cm^3)	Water resistance							
		TS (%)				WA (%)			
		2 h	24 h	48 h	72 h	2 h	24 h	48 h	72 h
WPC1	0.99 (0.03)	0.30 (0.08)^A	0.41 (0.12)^A	0.50 (0.15)^A	0.62 (0.18)^A	0.44 (0.16)^A	0.52 (0.08)^A	0.63 (0.15)^A	0.72 (0.14)^A
WPC2	1.03 (0.01)	0.34 (0.11)^A	0.46 (0.16)^{AB}	0.53 (0.22)^A	0.66 (0.16)^{AB}	0.48 (0.12)^A	0.56 (0.15)^A	0.66 (0.24)^A	0.76 (0.20)^A
WPC3	1.01 (0.02)	0.43 (0.13)^B	0.50 (0.14)^B	0.61 (0.18)^B	0.70 (0.20)^B	0.56 (0.15)^B	0.65 (0.18)^B	0.75 (0.16)^B	0.86 (0.33)^B
WPC4	1.03 (0.04)	0.50 (0.16)^C	0.60 (0.19)^C	0.69 (0.09)^C	0.79 (0.13)^C	0.63 (0.20)^C	0.71 (0.23)^C	0.82 (0.32)^C	0.94 (0.27)^C
WPC5	1.02 (0.01)	0.53 (0.14)^C	0.68 (0.16)^D	0.73 (1.16)^C	0.83 (0.22)^C	0.67 (0.11)^C	0.75 (0.16)^C	0.91 (0.21)^D	0.98 (0.19)^C

The same letters in a column indicate that there was no statistical difference ($p < 0.01$) between the samples according to Duncan's multiple-range test. The values in parentheses are standard deviations.

specifications.[13] The test samples were in the form of disks 50.8 mm in diameter and 3.2 mm in thickness. Ten replicate samples were tested for each WPC formulation. The conditioned samples were placed in a container of distilled water maintained at a temperature of 23 $\pm1°$C. The weights and thicknesses of the samples were measured at different time intervals during the long period of immersion. At the end of 2, 24, 48, and 72 h of submersion, the samples were removed from the water one at a time, all surface water was wiped off with a dry cloth, and the samples were weighed to the nearest 0.001 g and measured to the nearest 0.001 mm immediately. The value of WA as a percentage was calculated as follows:

$$WA(t) = \frac{W(t) - W_0}{W_0} \times 100 \tag{1}$$

The value of the TS as a percentage was calculated as follows:

$$TS(t) = \frac{T(t) - T_0}{T_0} \times 100 \tag{2}$$

where TS(t) is the thickness swelling at time t (%), T_0 is the initial thickness of the sample, and $T(t)$ is the thickness at time t. The density of the sample was measured on the TS sample.

Determination of the flexural properties

The flexural properties, modulus of rupture (MOR), and modulus of elasticity (MOE) were measured in three-point bending tests with a standard material testing system (Zwick Z010 with a 2.5-kN load cell) at a crosshead speed of 2.8 mm/min in accordance with ASTM D 790-03.[14] The MOR and MOE values of the samples with dimensions of 127 × 12.7 × 3.2 (thickness) mm^3 were determined at ambient conditions of 23 ± 2°C and 50 ± 5% relative humidity

according to ASTM D 618-08. Five replicate samples were tested for each WPC formulation.

RESULTS AND DISCUSSION

Water resistance

Table II displays the TS and WA values of the WPC samples. There were no significant differences in the densities of the samples. The TS and WA values significantly decreased with increasing cone-flour content. Significant differences were determined individually for these tests by Duncan's multiple-comparison tests. The results of the Duncan's multiple-range tests are shown by letters in Table II. The lowest TS value was 0.30% for the samples containing 40% wood flour (WPC1), whereas the highest TS value was found as 0.53% for the samples containing 40% cone flour (WPC5) after 2 h of submersion in water. Similar trends were also observed after 24, 48, and 72 h of submersion (Table II). Statistical analysis found some significant differences between the WPC types. Hardboard (density $\geq$ 800 kg/m^3) standard ANSI/AHA A135.4[15] was used here for comparison of the TS and WA values because there was no established minimum property for WPC. The TS and WA values of all of the composite types did not exceed the hardboard (3.2 mm thickness) minimum property requirements of 20% (TS) and 25% (WA) according to ANSI/AHA standard A135.4. The TS and WA values of the samples were also much lower than those of conventional wood-based panels, such as particleboard, oriented strandboard, and medium-density fiberboard, because the matrix polymers were hydrophobic.[4] With increasing pinecone content in the composite, more water was absorbed. On the other hand, plastics are water repellent and have much lower water sorption capabilities than wood. The TS and WA curves for all of the formulations are presented in Figure 2.
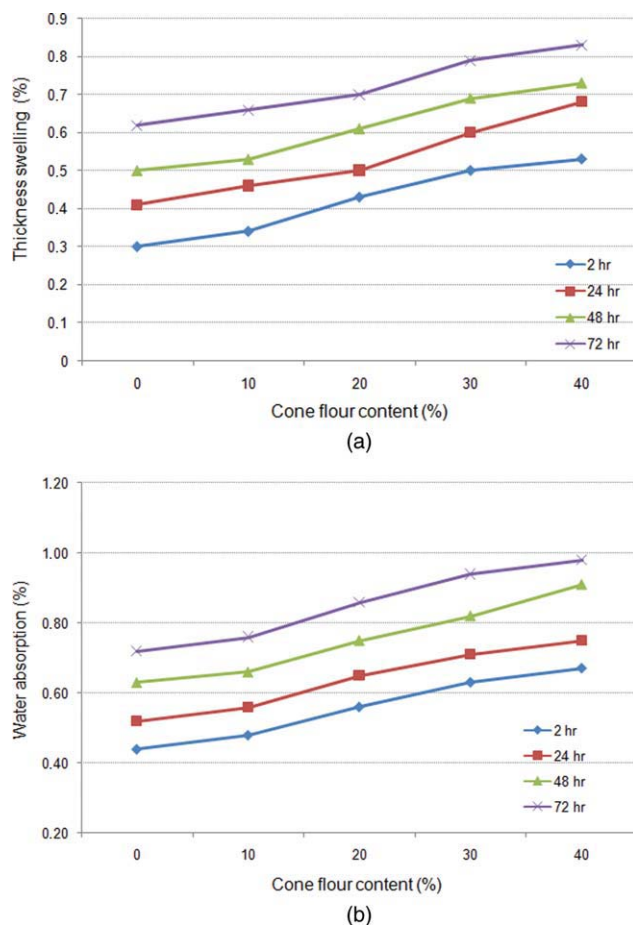
Figure 2 Influence of the cone-flour content on (a) TS and (b) WA of the WPC samples. [Color figure can be viewed in the online issue, which is available at www. interscience.wiley.com.]

The moisture absorption in composites was mainly due to the presence of lumens, fine pores, and hydrogen-bonding sites in the wood flour; the gaps and flaws at the interfaces; and the microcracks in the matrix formed during the compounding process.[16] Cellulose is a hygroscopic polar molecule and easily undergoes hydrogen bonding, which accounts for the tendency of wood to absorb moisture from the environment. The hydroxyl groups on cellulose are largely responsible for its reactive nature. A high proportion of cellulose is crystalline. The absorption of water by cellulose depends on the number of free hydroxyl groups, not those linked with each other. Therefore, water cannot enter crystallites. Only amorphous regions are accessible by water.[17] Polar hydroxyl groups on the lignocellulosic material are contributed predominantly by holocellulose (cellulose and hemicellulose) and lignin.[18] As expected, the water resistance of the WPCs decreased with increasing lignocellulosic content (Table II).

Although the amount of holocellulose, which has a large of polar hydroxyl groups, in the cone flour

was lower than in wood flour,[19] the WPC formulations containing higher cone-flour and lower wood-flour contents showed higher TS and WA values. This was attributed to a higher extractive content of the cone flour. The pine cone contains significant amounts of ethanol/toluene extractives (29.2%) compared to wood (5.1% for sapwood and 22.6% for heartwood).[19] They also contain a high amount of phenolic extractives, such as phenol and condensed tannins. The total phenol and condensed tannin contents of the stone pine cones were found to be 28.6 and 14.5 mg/g, respectively, whereas there were no hydrolyzable tannins, such as gallo and ellagtannin, determined in the cones.[19] In previous studies, it was reported that the contents of extraction substances in pine cones had a big role, as they determined the bond quality of fiberboard and particleboard.[20,21] A similar effect was observed in this study. The results of TS and WA revealed that surface inactivation of the filler, a surface phenomenon resulting in a loss of bonding ability, increased with increasing ratio of the cone flour in the mixture of wood fiber and cone flour because of a high extractive content in the pine cone. Large amounts of the extractives in the cone flour caused a decrease in the polarity on the surface of the filler and a decrease in the wettability, so they limited MAPP performance. A similar result was found in a previous study.[22] Large amounts of extractives in bark flour caused a decrease in the polarity on the surface of the filler and a decrease in the wettability. Thus, we concluded that a larger amount of the pine cone influences the MAPP performance in such a way that it could not cause good bonding between PP and the filler.

It is known that essential oils have a disadvantageous effect on the gluability of the cone flour of the stone pine because they repel water and result in a lower wettability.[20] The essential oil of the stone pine (*P. pinea*) cone is readily distinguished from other cone oils, such as those of *Pinus nigra*, *Pinus halepensis*, and *Pinus pinaster* because of its high limonene content (61.6 vs 0.7–1.6%).[23] Among other compounds, myrcene and β-caryophyllene, the α-pinene percentage was three times higher in the cones (19.4%) than in the needles and branches.[23] Albritton and Short[24] and Slay et al.[25] reported that both ethanol-soluble and water-soluble extractives played major roles in determining adhesive bond quality. There was evidence about the positive relationship between wood wettability and adhesion.[26] Saputra et al.[27] stated that extractives formed a weak boundary layer in pine wood flour and that the removal of this layer by extraction improved the shear strength between the PP matrix and the extracted wood filler.

Generally, it is necessary to use compatibilizers or coupling agents to improve the filler/fiber bonding

TABLE III
Results for the Flexural Properties of the Composites

Composite code	Flexural properties	
	MOR (N/mm^2)	MOE (N/mm^2)
WPC1	48.1 (2.17)^A	5005.2 (109.4)^A
WPC2	46.8 (1.57)^{AB}	4967.7 (91.2)^A
WPC3	45.3 (1.35)^B	4660.1 (59.6)^B
WPC4	43.1 (1.61)^C	4415.0 (82.8)^C
WPC5	41.9 (1.32)^C	4355.3 (68.5)^C

The same letters in a column indicate that there was no statistical difference ($p < 0.01$) between the samples according to Duncan's multiple-range test. The values in parentheses are standard deviations.

and, in turn, enhance the water resistance. Compatibilizing agents have a positive effect on WA. The strong interfacial bonding between the filler and polymer matrix caused by the compatibilizing agent (the MAPP chemically bonds with the OH groups in the lignocellulosic filler) limited the WA of the composites. The cone flour had less cellulose, more lignin, and more extractives than wood flour.[18] The compatibility between the lignocellulosic and PP improved with the addition of MAPP (3%) because the anhydride moieties in MAPP entered into an esterification reaction with the surface hydroxyl groups of the wood flour.[28]

Mechanical properties

Significant differences ($p < 0.01$) were found in the values of the MOR and MOE. Significant differences between the composite groups are displayed in Table III. The MOR and MOE values of the WPC samples decreased with increasing cone-flour contents from 10 to 40% in the composite. For example, the average MOR and MOE values of the composites containing 40% wood flour (composite code WPC1) were 48.1 and 5005.2 N/mm^2 as compared to composites containing 40% cone flour (composite code WPC5), which were about 41.9 and 4355.3 N/mm^2, respectively (Fig. 3). In a previous study, the MOR and MOE values were found to be 72.4 and 3220 N/mm^2 for WPCs made from 57% PP and 40% hardwood fiber, and 3% coupling agent, respectively.[4]

Wood is a lignocellulosic material made up of three major constituents (42–44% cellulose, 27–28% hemicelluloses, and 24–28% lignin) with some minor constituents (3–4% extractives).[29] The major portion of wood is crystalline cellulose. The aligned fibril structure of the cellulose, along with strong hydrogen bonds, has a high stiffness; thus, the addition of wood flour can increase the stiffness of thermoplastic-based composites. MOE is a measure of how well a material resists tension. A smaller MOE illus-

trates that less stress causes more strain and vice versa. Its value is a measure of the stiffness of the material. As shown in Table III, the MOE values of the composites containing wood flour were significantly higher than those in the composites containing cone flour. This could be explained by a strong interfacial adhesion between PP and the wood flour because of their higher cellulose content because cellulose was the main component providing the wood's strength and structural stability. Lignin, as an amorphous polymer, did not greatly contribute to the mechanical properties of the wood flour but played an important role in binding the cellulose fibrils, which allowed efficient stress transfer to the cellulose molecules. According to Bledzki and Gassan,[30] an increase in the composite's strength could be ascribed to higher cellulose and lignin contents and to better dispersion and adhesion to the matrix.

The better interfacial adhesion between wood flour and PP, due to the high cellulose content, increases the toughness or ductility.[31] Moreover, the
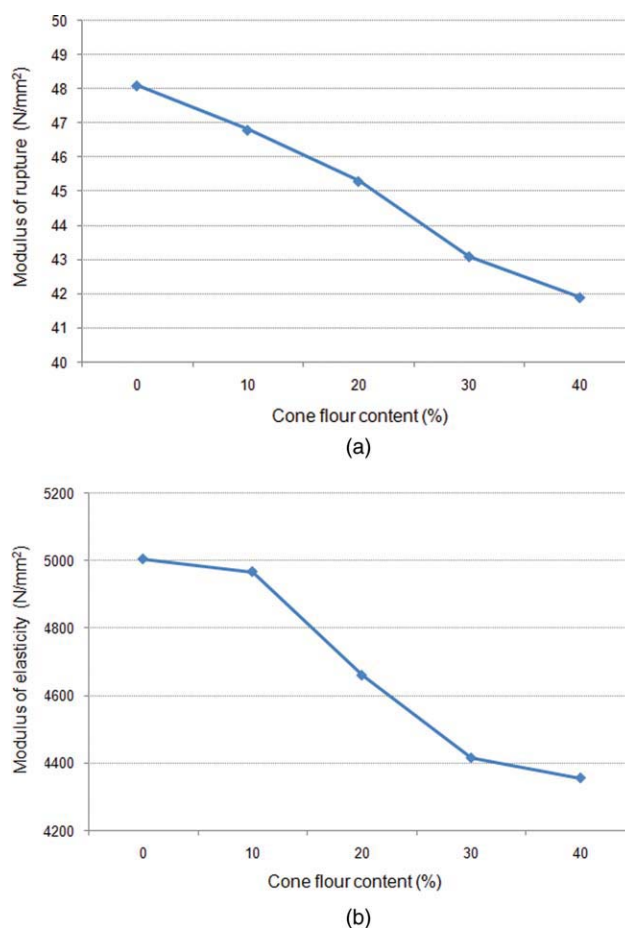

Figure 3 Influence of the cone-flour content on (a) MOR and (b) MOE of the WPC samples. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

ratio of lignin and cellulose can also play a role: the higher it is, the better the interfacial adhesion that can be achieved because lignin acts as a natural adhesive within the cellulose.[32] Hence, wood filler increases the stiffness of the polymer without excessively increasing the density.[33] Pine cones contain less cellulose and lignin than wood. The amounts of holocellulose (hemicelluloses and cellulose) and lignin in the stone pine cone were found to be 67.6 and 37.2%, respectively, on the basis of the weight of extracted wood.[19] Lower MOR and MOE values of the samples containing high cone-flour contents were attributed to lower cellulose and lignin contents in the pine cones. However, the flexural properties and water resistance of the WPC samples were not significantly affected by the addition of 10 wt % pine cone when compared to the WPC samples made from wood flour. The addition of the coupling agent improved the compatibility between the lignocellulosic material and the PP through esterification and, thus, reduced WA and improved the dimensional stability and mechanical properties.[28]

Extractives have a significant effect on the bonding performance of wood–PP composites and wood-based composites.[20,21,27] In a previous study, it was found that extractives in wood flour had a negative effect on the flexural properties of the PP composites reinforced with wood flour.[27] In the same study, significant differences were also observed in the stiffness between extracted Douglas fir wood–PP and unextracted wood–PP composites. On the basis of the results of the MOR and MOE values, it can be stated that the extractives in the pine cone had a similar effect on the bond strength between the cone flour and PP. However, the surface of the cone flour may be improved by several means. Treatment with chemicals, such as sodium hydroxide, calcium hydroxide, nitric acid, hydrogen peroxide,[34] and borax,[35] can partially improve the surface activation of the cone flour.

CONCLUSIONS

The pine cone was found capable of serving as a new reinforcing filler in the manufacturing of thermoplastic polymer composites. The flexural properties and water resistance of the composites were negatively affected by increasing cone-flour content. However, the flexural properties and water resistance of the WPC samples were not significantly affected by the addition of 10 wt % pine cone when compared to the WPC samples made from wood flour. Reductions in the flexural properties and water resistance of the WPC composites containing a high content of cone flour were attributed to higher contents of the extractives in the stone pine cone

versus those of stone pine wood. On the basis of the findings obtained from this study, WPCs containing 10% cone flour appear to be a practical choice for applications, such as roof siding and outdoor decking, where a high water resistance is needed.

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