Compression Wood as a Source of Reinforcing Filler for Thermoplastic Composites

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ABSTRACT: Compression wood (CW) is a reaction wood formed in gymnosperms in response to various growth stresses. Many of the anatomical, chemical, physical, and mechanical properties of CW differ distinctly from those of normal wood. Because of different properties, the CW is much less desirable than normal wood. This study was conducted to investigate the suitability of CW flour obtained from black pine (*Pinus nigra* Arnold) in the manufacture of wood plastic composite (WPC). Polypropylene (PP) and CW flour were compounded into pellets by twin-screw extrusion, and the test specimens were prepared by injection molding. WPCs were manufactured using various weight percentages of CW flour/PP and maleic anhydride-grafted PP (MAPP). Water absorption (WA), modulus of rupture (MOR), and modulus of elasticity (MOE) values were measured. The results showed that increasing of the CW percentage in the WPC increased WA, MOR, and MOE values. Using MAPP in the mixture improved water resistance and flexural properties. CW flour of black pine can be used for the manufacturing of WPC as a reinforcing filler.
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Key words: wood plastic composite; compression wood; polypropylene; reinforced thermoplastic composites

INTRODUCTION

Wood plastic composites (WPCs) have attracted considerable attention from industry in recent years. WPCs approximately have average annual growth rate of 18% in Northern America and 14% in Europe.[1,2] The use of wood flour or fiber as fillers and reinforcements in thermoplastics has been gaining acceptance in the applications of commodity plastics in the past few years.[3] The advantages of using a wood component in thermoplastic composites are that the biobased resource is nonabrasive, low in cost, widely available, sustainable, high filling levels possible, high specific properties, lower density per weight of raw material, flexible, and recyclable.[4] The physical form can vary from fine wood flour to wood fibers.[5] The cost and performance of the final composite products dictate the form of the wood to be used in the plastics. The typical plastics used in this technology are various types of polyethylene, PP, and polyvinyl chloride.

Reaction wood is an abnormal type of wood tissue formed in the living stems of both hardwoods and softwoods apparently as a result of abnormal growing conditions.[6] In softwoods, reaction wood is termed as compression wood (CW) and results in the production of wood cells rich in phenolic lignin and poor in carbohydrates. The wood present on the upper side of a branch or an inclined stem opposite to the CW is generally referred to as opposite wood.

The CW is characterized by relatively wide, eccentric growth rings that contain an abnormally large proportion of latewood. Most of the coniferous wood species can contain CW. Not only natural and plantation stands under adverse environmental conditions but also most improved and best-managed conifer forest can contain CW.[7] Both virgin spruce forests and plantations of southern pines and *Pinus radiata* have been found to contain on the average 15% CW by volume.[7] Many of the anatomical, chemical, physical, and mechanical properties of reaction wood differ distinctly from those of normal wood.[7–9] The cell wall thickness of CW traheids in the latewood is approximately twice that of the normal wood.[6] Density of the CW is commonly 30–40% greater than that of normal wood. The CW is usually somewhat darker than normal wood because of the greater proportion of latewood, and it frequently has a relatively lifeless appearance, especially in woods in which the transition from earlywood to latewood is abrupt.[10] S_2 layer of the CW has larger microfibrillar angle than that of normal wood tracheid. It is chemically different as well. The proportion of cellulose is about 10% lower than normal wood, and the proportion of lignin is correspondingly higher.[6]

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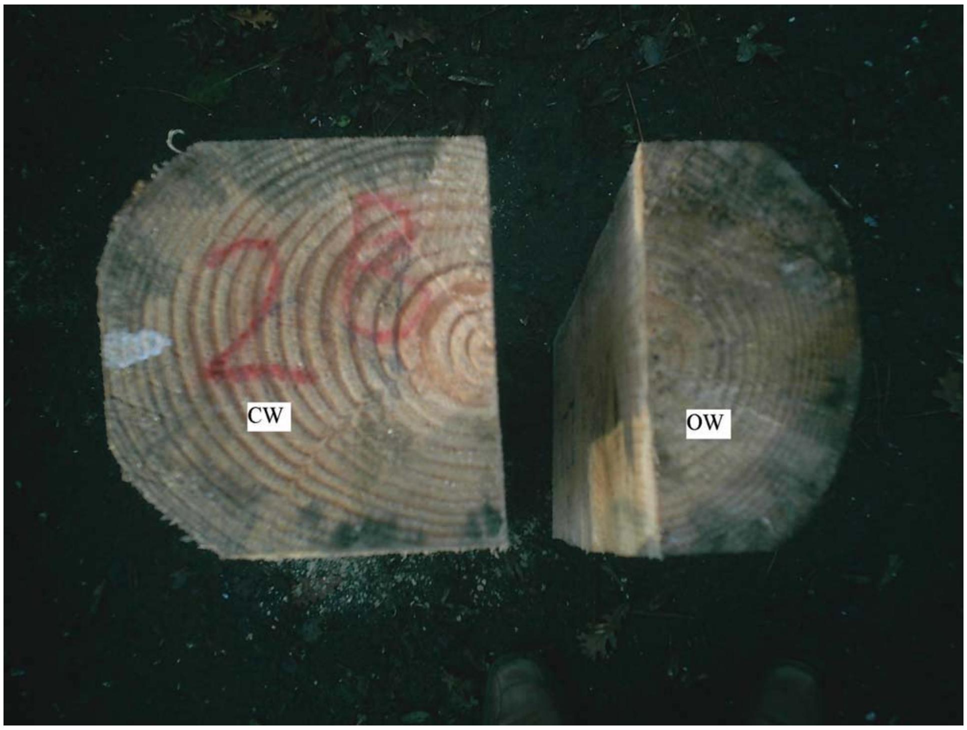

Figure 1 Compression wood (CW) and opposite wood (OW) sections. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

CW has a longitudinal shrinkage value of about 5–10%. CW expands and contracts longitudinally much more than normal wood as a result of changes in the humidity of the atmosphere.[7] The abnormal properties of CW make it an undesirable feature for commercial lumber,[7] wood-based panels,[11] and pulp and paper manufacture.[12] Previous studies reported that the water resistance and mechanical properties of wood-based panels such as particleboard and fiberboard made from furnishes containing CW were decreased compared with that of the panels made from normal wood.[11,13–15]

The physical and mechanical properties of the WPCs can be influenced by raw material characteristics.[2] Maldas et al.[16] investigated the effect of wood species on the mechanical properties of wood/thermoplastic composites. They reported that differences in morphology, density, and aspect ratios across wood species account for varying reinforcement properties in thermoplastic composites. Bouafif et al.[17] studied the effect of wood species, particle size, and fiber content on physical and mechanical properties of wood particle-reinforced high-density polyethylene. They concluded that the mechanical properties of WPCs varied significantly with fiber type and fiber loading. Wolcott[18] found that wood species has a significant influence on WPC structure and, therefore, its properties. It is known that CW has different wood characteristics, and these characteristics can affect physical and mechanical properties of WPCs. Also, the CW has undesirable properties to lumber, wood-based panels, and pulp paper manufacturing. To our knowledge, there is no information about the effect of CW on physical and mechanical properties of WPCs. The objective of this study was to determine some physical and mechanical properties of the PP composites reinforced with various mixtures of black pine CW and to evaluate the compatibilizer performance.

MATERIALS AND METHODS

Materials

Black pine (*Pinus nigra* Arnold) logs containing CW obtained from Bahcekoy Forest Enterprises in Istanbul, Turkey, were cut parallel to pith and separated CW section (Fig. 1). CW sections were processed by a rotary grinder and then classified using a horizontal screen shaker. CW flour passing through a U.S. 35-mesh screen and was retained by a U.S. 80-mesh screen. The CW flour was then dried in a laboratory oven at 100°C for 15 h to moisture content of 1–2%.

PP ($T_m = 160°C$, $\rho = 0.9$ g/cm^3, and MFI/230°C/2.16 kg = 6.5 g/10 min) was used as the polymeric material produced by Petkim Petrochemical, Turkey. Maleic anhydride-grafted PP [MAPP-OPTIM-425; reactive modifier maleic anhydride (MAH) content = 1 wt %] was obtained from Pluss Polymers, India.

Lignocellulose/plastic composite manufacture

The CW flour, PP, and MAPP were processed in a laboratory 30-mm-conical corotating twin-screw extruder (Aysa Instrument, Istanbul, Turkey) with a length-to-diameter (L/D) ratio of 30 : 1. The raw materials were fed into the main feed throat using a gravimetric feed system. The CW flour was compounded, separately, with virgin PP granulates in a corotating twin-screw extruder. The barrel temperatures of the extruder were controlled at 170, 180, 190, and 190°C for zones 1, 2, 3, and 4, respectively, while the temperature of the extruder die was held at 200°C. The screw speed was varied between 150 and 165 revolutions per minute and the pressure from 33 to 47 bars, depending on the materials being blended. The CW flour and PP were premixed before being fed into the first zone of the extruder. 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 being injection molded. Temperature used for injection-molded samples was 170–190°C from feed zone to die zone. The WPC samples were injected at injection pressure between 45–50 kg/m^2 with cooling time about 30 s. Finally, the composite panels were conditioned at a temperature of 23 ± 2°C and relative humidity of 50 ± 5% for at least 40 h according to ASTM D 618-08.[19] The formulations of WPCs are given in Table I.

Determination of water absorption

The water absorption (WA) test was carried out according to ASTM D570-05[20] specifications. The test samples were in the form of a disk 50.8 mm in diameter and 3.2 mm in thickness. Ten samples were taken from each group. The WA values of the sample were measured at different time intervals (2, 24, 48, and 72 h). Density values were measured on the WA samples.

Determination of flexural properties

The flexural properties, modulus of rupture (MOR) and modulus of elasticity (MOE), were measured in three-point bending test using a standard Material Testing System (Zwick /Z010 with 2.5 kN load cell) at a crosshead speed of 2.8 mm/min in accordance with ASTM D 790-03.[21] The bending measurements were performed at ambient conditions of 23 ± 2°C and 50 ± 5% relative humidity according to ASTM D 618-08. Five samples of each formulation were tested.

Statistical analysis

For the WA and flexural properties, all multiple comparisons were first subjected to an analysis of variance (ANOVA) at $P < 0.01$, and significant differences between the mean values of the samples were determined using Duncan's mean separation test.

TABLE I
The Formulations of WPCs

Composite Code	CW (wt %)	PP (wt %)	MAPP (wt %)
A	30	70	0
B	30	67	3
C	40	60	0
D	40	57	3
E	50	50	0
F	50	47	3
G	60	40	0
H	60	37	3

RESULTS AND DISCUSSION

Water absorption

The results of ANOVA and Duncan's mean separation tests for density and WA (2-, 24-, 48-, and 72-h water immersion times) values of WPCs are given in Table II. Statistical analysis found some significant differences ($P < 0.01$) between some WPC means for the density and WA values. Significant differences between WPC types were determined individually for these tests by Duncan's mean separation tests. The results of Duncan's mean separation test are shown by letters (Table II). Density values of the WPCs ranged from 1.06 to 1.11 g/cm^3 and increased with increasing the CW content. The WPCs containing MAPP have higher density with lower porosity compared with the WPCs without the coupling agent. Similar results were found by several researchers.[22,23]

Group B had the lowest WA value, whereas the highest WA value was found for the group G at all the immersion times. Figure 2 indicates the effect of the immersion time on the WA values of WPCs. The WA values of the WPCs increased with increasing water immersion times from 2 to 72 h. Also, the WA values of the WPC increased as CW content increased (Table II). For example, the average WA value for 2-h immersion time of the WPC containing 30% CW flour was 0.20% when compared with the WPC containing 60% CW flour, which was 0.66%. Similar results were also found by several researchers.[17,22,24] They found that WA values of WPC increased with increasing wood content. The moisture absorption in composites is 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.[25] With increase in the wood content, there are more water residence sites thus more water is absorbed. On the other

TABLE II
The Results of ANOVA and Duncan's Mean Separation Tests for Density and WA Values of WPCs

Composite code	Composite density (g/cm^3)	Water absorption (%)			
		2 h	24 h	48 h	72 h
A	1.055 (0.02) A	0.20 (0.04) AB	0.54 (0.16) AB	0.69 (0.23) B	0.79 (0.29) AB
B	1.059 (0.02) A	0.13 (0.03) A	0.33 (0.07) A	0.41 (0.07) A	0.51 (0.08) A
C	1.070 (0.03) AB	0.25 (0.09) B	0.57 (0.30) B	0.80 (0.32) B	0.92 (0.43) B
D	1.074 (0.02) AB	0.22 (0.08) B	0.48 (0.14) AB	0.65 (0.18) AB	0.76 (0.23) AB
E	1.087 (0.01) BC	0.52 (0.04) D	0.96 (0.13) C	1.26 (0.20) CD	1.44 (0.25) C
F	1.101 (0.01) CD	0.41 (0.09) C	0.81 (0.10) C	1.15 (0.10) C	1.38 (0.04) C
G	1.106 (0.01) CD	0.66 (0.04) E	1.22 (0.11) D	1.47 (0.13) D	1.59 (0.16) C
H	1.114 (0.01) E	0.55 (0.06) D	0.96 (0.13) C	1.30 (0.09) CD	1.44 (0.07) C

Numbers in parantheses are standart deviations. Groups with same letters in column indicate that there was no statistical difference ($P = 0.01$) between the samples according to the Duncan's multiply range test.

hand, the composites made from higher plastic content have less WA sites and thus lower WA.[22,26] The presence of hydroxyl and other polar groups in various constituents of the wood flour resulted in poor compatibility between the hydrophilic wood flour and the hydrophobic plastics, which increases the WA.[24]

Ayrilmis and Buyuksari[27] determined that WA values of WPC for 2-, 24-, 48- and 72-h immersion times containing 40% wood flour (50% Black pine and 50% Beech) and 60% PP were higher than CW and PP containing the same ratio. The differences in WA can be related to the chemical structures of the fillers. CW has lower cellulose and higher lignin compared with normal wood. The lower WA in the composites containing CW flour can be related to lower amounts of hygroscopic materials, cellulose, and hemicelluloses, in the cell walls of the CW.

Use of MAPP improved WA values of all the WPC groups. Similar findings were obtained by several researchers.[22,27] MAPP in the mixture improve adhesion between plastic and wood. The strong interfacial bonding between the filler and polymer matrix caused by the compatibilizing agents limits the WA of the composites. The addition of the coupling agent increases the ester linkages between the hydroxyl groups of wood flour and the anhydride part of MAPP.[28] Therefore, the amount of free OH in the wood cellulose is reduced, because some of them are interacting with succinic anhydride. Also, addition of MAPP decreases free volume of the composites. Because of these changes, the WA increment is rather less, compared with the composite formulation without MAPP.[24] Ayrilmis et al.[29] stated that WA values of WPC for 2-, 24-, 48-, and 72-h immersion times containing 40% pine cone flour and 3% MAPP were 0.67, 0.75, 0.91, and 0.98%, respectively. WPCs containing 40% CW flour and 3% MAPP have lower WA value compared with WPCs containing 40% pine cone flour and 3% MAPP.

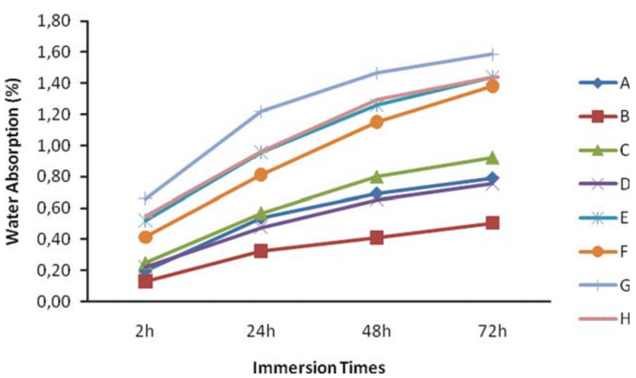

Figure 2 Effect of immersion times on the water absorption value of WPCs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Flexural properties

The MOR and MOE values of the WPCs are shown in Table III. Statistical analysis found some significant differences ($P < 0.01$) between some panel

TABLE III
The Results of ANOVA and Duncan's Mean Separation Tests for Flexural Properties of WPCs

Composite code	Flexural properties	
	MOR (N/mm^2)	MOE (N/mm^2)
A	45.67 (1.21) A	3403.9 (663.2) A
B	49.41 (3.88) B	3629.9 (430.2) A
C	49.53 (2.61) B	3738.9 (418.5) AB
D	51.81 (0.77) BC	3919.1 (144.3) ABC
E	51.28 (0.53) BC	4236.2 (35.8) BCD
F	53.97 (0.61) CD	4368.1 (66.1) CD
G	54.40 (2.84) CD	4514.3 (24.4) D
H	56.58 (0.44) D	5075.1 (7.1) E

Numbers in parantheses are standart deviations. Groups with same letters in column indicate that there was no statistical difference ($P = 0.01$) between the samples according to the Duncan's multiply range test.

means for the MOR and MOE values. Significant differences between panel types were determined individually for these tests by Duncan's multiple comparison tests (Table III). The highest MOR and MOE values were 56.58 and 5075.1 N/mm^2 for the group H, whereas the lowest values, 45.67 and 3403.9 N/mm^2, were found for the group A, respectively.

Ayrilmis and Buyuksari[27] found that MOR and MOE values of WPC containing 40% wood flour and 60% PP were 50.7 and 4170.1 N/mm^2, respectively. These values are slightly higher than our MOR and MOE values of WPC containing 40% CW. This difference can be attributed to anatomical properties and chemical composition of CW. Tracheids of CW have spiral checks or fissures and helical cavities in the cell wall. In addition, CW is harder and more brittle than normal wood because of its rounded and thick-walled tracheids and inflexible, because it has about 10% less cellulose and 8–9% more lignin and hemicellulose than normal wood.[8] Lower cellulose content in the CW can be another reason for this decrement, because reinforcing elements of the wood filler are cellulose filaments.

Ayrilmis and Buyuksari[27] reported that MOR and MOE values of WPC containing 40% olive mill sludge flour without MAPP were 40.40 and 3124.9 N/mm^2. WPCs containing the same ratio of CW have higher MOR and MOE values compared with WPCs containing olive mill sludge flour. MOR and MOE values of WPC containing the same ratio of CW are comparable with Berger and Stark[30] study results. They found that MOR and MOE values of WPCs containing 30, 40, 50, and 60% ponderosa pine wood flour were 43.1, 44.2, 41.8, and 38.8 N/mm^2 and 2580, 3220, 3660, and 4040 N/mm^2, respectively.

MOR value of the WPCs increased with increasing of wood content in the composite (Fig. 3). This result is in good agreement with the work of Nourbakhsh and Ashori.[26] They found that flexural strength of WPC increased with increasing wood content up to 85% due to the good interfacial bonding. Berger and Stark[30] found that MOR value of WPCs increased up to 40% and then decreased with increasing ponderosa pine wood flour content in the WPC. This difference could be attributed to the higher density of CW. Because of the higher density of CW, it has lower volume in 60% wood filler than those of lower density wood species. MOE value of the WPCs also increased with increasing of wood content in the composite (Fig. 4). This increase could be due to the higher moduli of natural fibers compared with PP.[31] These result is consistent with previous studies.[31,32]

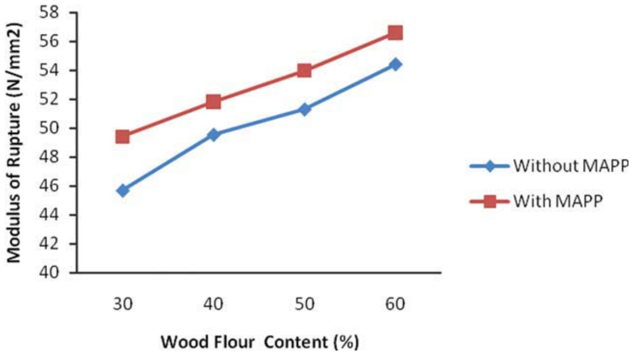

Figure 3 Effect of wood flour content on the MOR value of WPCs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

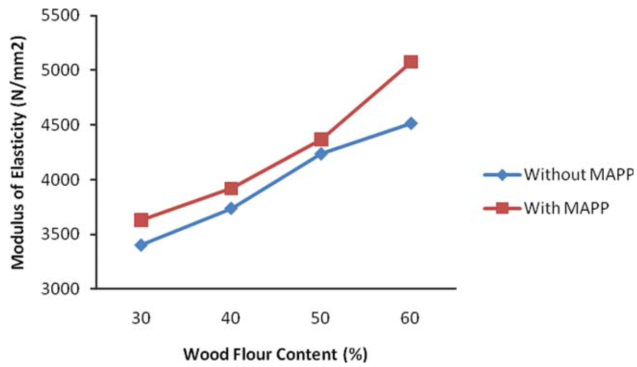

Figure 4 Effect of wood flour content on the MOE value of WPCs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The addition of the MAPP positively affected the flexural properties of the WPCs. The MOR and MOE values of the composites made by using 3% MAPP were higher than those of the composites at the same plastic to wood ratio. Addition of MAPP to the WPC including 30% CW flour improved MOR and MOE values for 8.2 and 6.6%, whereas MOR and MOE values of WPC including 60% CW flour increased 4.0 and 12.4%, respectively. The addition of the coupling agent improved the compatibility between the lignocellulosic material and PP through esterification and thus improved mechanical properties of WPC. Such improvements are due to the formation of ester bonds between the anhydride carbonyl groups of MAPP and hydroxyl groups of the wood fibers.[33] Ayrilmis and Buyuksari[27] found that MOR and MOE values of WPC containing 40% wood flour, 57% PP, and 3% MAPP were 55.8 and 4554.7 N/mm^2, respectively. The aforementioned values are higher than MOR and MOE values obtained in this study, in both investigations; WPCs contain the same ratio of wood flour and MAPP. This difference can be attributed to anatomical properties and chemical composition of CW. Ayrilmis and Buyuksari[27] determined that MOR and MOE values of WPC containing 40% olive mill sludge and 3% MAPP were 37.52 and 3244.3 N/mm^2, respectively. WPCs containing the same ratio of CW and MAPP have higher MOR and MOE values compared with WPCs containing olive mill sludge and MAPP.

CONCLUSIONS

The CW is an undesirable wood type for commercial lumber, wood-based panels, and pulp and paper manufacture due to lower water resistance and mechanical properties. WA, MOR, and MOE values of WPCs increased with increasing wood content. Use of MAPP improved the water resistance and flexural properties of composites. The water resistance and mechanical properties of WPCs containing CW are better than those of WPCs containing olive mill sludge and pine cone flour. CW flour of black pine can be utilized for WPC manufacturing as a reinforcing filler.

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