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Effect of boron and phosphate compounds on physical, mechanical, and fire properties of wood–polypropylene composites

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ABSTRACT

Physical, mechanical, and fire properties of the injection-molded wood flour/polypropylene composites incorporated with different contents of boron compounds; borax/boric acid and zinc borate, and phosphate compounds; mono and diammonium phosphates were investigated. The effect of the coupling agent content, maleic anhydride-grafted polypropylene, on the properties of the composites with fire-retardant was also investigated. The composites with the zinc borate had the highest dimensional stability and strength in the bending, tensile, and izod impact, followed by the monoammonium phosphate, borax/boric acid, and diammonium phosphate treatments. The treatments produced modest improvements in fire performance as indicated by reductions in the heat release rates. Best results were achieved with the phosphate treatments. The Scanning Electron Microscope–Energy Dispersive Spectroscopy elemental mapping of the samples revealed that the outer surface of the wood fibers was coated by some crystalline deposits of the fire-retardants.

1. Introduction

Wood–plastic composites (WPCs) represent an emerging class of materials that combines favorable performance and cost attributes of both wood and thermoplastics. Lignocellulosics are increasingly applied for reinforcement in thermoplastics such as polypropylene and polyethylene due to wood's low density, good thermal insulation and mechanical properties, reduced tool wear, unlimited availability, low price, and problem-free disposal [1]. Wood flour is the most common lignocellulosic used in WPCs. It is a commercially available material sourced from industrial residues such as planer shavings, sawdust, and wood chips and ground to a consistent mesh size. WPCs are stiffer, exhibit less creep, and are more dimensionally stable than unfilled plastic lumber.

Current growth rate of the WPC market is 22% for North America and 51% for Europe [2]. Decking for outdoor applications represent the largest market for WPCs both in North America and Europe and in both regions growth is most rapid in the decking segment [3]. WPC market share in the European decking sector is estimated to be around 6%. In Europe, total WPC production amounts to 120 thousand tons (excluding product destined for the auto industry). Around 68 thousand tons of this production is currently destined for the decking sector. The positive growth in WPC decking has led manufacturers to introduce residential construction applications include siding, roofing, windows, door frames, and outdoor furniture. Further expansion into the residential construction industry and development of applications for the furniture industry require an understanding of the fire performance of the WPCs. As organic materials, i.e. both polymers and wood, are sensitive to fire, improvement of fire retardancy of the composite materials has become important in order to comply with the safety requirements of the WPC products. Polymers employed in WPCs, burn and drip in case of fire leading to a very risky scenario. Thus, FR agents must be employed in order to improve fire behavior. The fire performance of WPCs is not well understood, and there is little information regarding the effectiveness of various FRs in the public domain.

Even though a lot of work has been reported on the fire properties of thermoplastics [4–7], effect of FRs on the technological and fire properties of the wood flour reinforced thermoplastic composites only now is being more extensively investigated. The primary objective of this study was to determine effects of the boron

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compounds and phosphate compounds on the physical, mechanical, and fire properties of the injection molded WPCs with and without a coupling agent. The physical properties of natural fiber/polyolefin composites can be greatly enhanced by a coupling agent [8]. There is no any study related to effects of coupling agent content on the physical, mechanical, and fire properties of the WPC with FRs. The secondary objective was to investigate effect of the coupling agent content on the properties of the WPCs with FRs.

2. Materials and methods

2.1. Materials

Wood particles were obtained from beech (*Fagus orientalis* Lipsky) lumbers by using laboratory type disk chipper with three knives. The moisture content of the wood particles, as determined by oven-dry weight, was found to be 40–50% prior to the treatment. The wood particles were ground in a laboratory *Wiley* grinder. The wood flour passing through a US 35-mesh screen was retained by a US 80-mesh. The wood flour was dried in a laboratory oven at 102 °C for 24-h to a moisture content of 0–1% based on the oven-dry weight of wood and then stored in a polyethylene bag.

The polypropylene (PP) (MFI/230 °C/2.16 kg = 5 g/10 min) produced by Petkim Petrochemical Co., Turkey, was used as the polymeric material. Maleic anhydride-grafted PP (MAPP-Optim-425, MFI/190 °C/2.16 kg = 120 g/10 min) was supplied by Pluss Polymers Pvt. Ltd. in India.

Four FR systems (powder) were investigated:

1. A mixture of boric acid (BA) (H_3BO_3) (ρ = 1.7 g/cm^3) and borax (BX) ($Na_2B_4O_7{\cdot}10H_2O$) (ρ = 1.4 g/cm^3) (BA/BX, 1:1 by weight).
2. Zinc borate (ZB) ($3ZnO{\cdot}2B_2O_3$) (ρ = 2.8 g/cm^3).
3. Monoammonium phosphate (MAP) $NH_4H_2PO_4$ (ρ = 1.8 g/cm^3).
4. Diammonium phosphate (DAP) $(NH_4)_2HPO_4$ (ρ = 1.6 g/cm^3).

2.2. Preparation of injection molded WPC specimens

The wood flour, PP and MAPP granulates, and the FR powder were processed in a 30-mm co-rotating twin-screw extruder with a length-to-diameter (L/D) ratio of 30:1. The barrel temperatures of the extruder were controlled at 170, 180, 185, 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 to the moisture content of 1–2% before the injection molding. The temperature used for injection molded specimens was 180–200 °C from feed zone to die zone. The WPC specimens were injected at injection pressure between 45 and 50 kg/m^2 with cooling time about 30 s. Finally, the specimens were conditioned at a temperature of 23 °C and relative humidity (RH) of 50% according to ASTM D 618 [9]. Air-dry density values of the specimens varied from 1010 to 1070 kg/m^3. The raw material formulations used for the WPCs are presented in Table 1.

Table 1
Compositions of the injection molded WPC formulations.

WPC formulation[a]	WPC compositon (wt.%)			
	FR content	MAPP content	Wood flour	Polypropylene
Control	–	–	40	60
BX/BA	4	–	38	58
ZB	4	–	38	58
MAP	4	–	38	58
DAP	4	–	38	58
BX/BA	8	–	36	56
ZB	8	–	36	56
MAP	8	–	36	56
DAP	8	–	36	56
BX/BA	12	–	34	54
ZB	12	–	34	54
MAP	12	–	34	54
DAP	12	–	34	54
BX/BA	4	2	37	57
ZB	4	2	37	57
MAP	4	2	37	57
DAP	4	2	37	57
BX/BA	8	4	34	54
ZB	8	4	34	54
MAP	8	4	34	54
DAP	8	4	34	54
BX/BA	12	6	31	51
ZB	12	6	31	51
MAP	12	6	31	51
DAP	12	6	31	51

[a] BX/BA (1:1): borax/boric acid. ZB: zinc borate. MAP: monoammonium phosphate. DAP: diammonium phosphate. FR: fire retardant. MAPP: maleic anhydride-grafted polypropylene.

2.3. Determination of physical properties

The thickness swelling (TS) and water absorption (WA) tests after 2-h of boiling in water were carried out according to ASTM D 570 [10] specifications. The test specimens were in the form of a disk 50.8 mm in diameter and 3.2 mm in thickness. The conditioned specimens were entirely immersed for 2-h in a container of boiling distilled water. At the end of the immersion time, the specimens were taken out from the water and all surface water was removed with a clean dry cloth. The specimens were weighed to the nearest 0.01 g and measured to the nearest 0.001 mm immediately. Ten replicate specimens were tested for each WPC formulation.

2.4. Determination of mechanical properties

The flexural properties of the specimens with dimensions of 127 mm × 12.7 mm × 3.2 (thickness) mm, modulus of rupture (MOR) and modulus of elasticity (MOE), were measured in three-point bending tests using a standard material testing system (Zwick Roel Z010) at a crosshead speed of 2.8 mm/min in accordance with ASTM D 790 [11]. Tensile strength of the specimens (dogbone shape (type III)) were tested with a crosshead speed of 5 mm/min in accordance with ASTM D 638 [12] using a Zwick Roel Z010. Five replicate specimens were tested for the tensile and flexural properties of each WPC formulation. The izod pendulum impact strength (notched) were performed according to ASTM D 256 [13] using a Zwick Roel HIT5.5P impact testing machine. Ten replicate specimens were tested for the izod pendulum impact strength of each WPC formulation.

2.5. Fire performance

Heat release measurements in the cone calorimeter were conducted in accordance with ASTM E 1354 [14]. The US Forest Products Laboratory cone calorimeter used for these tests was a Model No Cone 2A, Combustion Analysis System (Auto-Cal) manufactured by Atlas Electric Devices Company of Chicago, IL. Specimens were 100 mm × 100 mm and specimen thickness was 10 mm. Specimens were conditioned at 23 °C and 50% RH prior to the testing. The cone calorimeter tests were conducted in the horizontal orientation with the conical radiant electric heater set at a heat flux level of 50 kW/m^2. The specimens were tested in the optional retainer frame but without the wire grid over the test specimen. Ignitability was determined by using a 4 s criteria for sustained ignition for observing the time for sustained ignition of the specimen. Two replicate specimens were tested for each type of specimen.

2.6. Statistical analysis

An analysis of variance, ANOVA, was conducted ($p < 0.01$) to evaluate the effects of the FR and MAPP contents on the physical and mechanical properties of the WPCs. Significant differences among the average values of the WPC types were determined using Duncan's multiple range test. Regression analysis of the cone calorimeter results as function of the treatment levels was conducted to determine the statistical significance of the changes in results due to the FR treatments.

3. Results and discussion

3.1. Physical properties

The TS and WA values of the untreated and FR-treated WPC specimens without the coupling agent (MAPP) are presented in Table 2. As compared with the control specimens, the water resistance of the uncoupled specimens significantly decreased with increasing the FR content. However, the water resistance improved with the addition of the coupling agent and when the MAPP and the corresponding FR contents were increased from 2 to 4 wt.% and 4 to 8 wt.%, respectively (Table 3). The significant differences for the uncoupled and coupled specimens with the FR are shown by letters in Tables 2 and 3, respectively. Among the treatment