Morphology and Mechanical Properties of Zinc Borate-Pretreated Poplar Wood Flour/Plastic Composite

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The effect of zinc borate (ZB) treatment on the mechanical and morphological properties of wood flour/polypropylene composites was investigated. Wood flour was first treated with ZB solution (1% w/w in ethanol-distilled water), followed by 24 hours of soaking on an unheated magnetic stirrer hot plate until relatively complete saturation was reached. Then, composites based on ZB-pretreated, ZB-treated-during-manufacturing, and untreated wood flour, polypropylene and coupling agent were made by melt compounding and then injection molding. The ZB treatment had no significant influence on mechanical properties of the composite with the exception of tensile strength. The composite made with ZB-pretreated wood flour exhibited the same mechanical properties as the composites made with ZB-in-process-treated wood flour; however there were statistically significant differences between flexural modulus and tensile strength of ZB-pretreated composites and ZB-in-process treated ones. Specimens containing the ZB showed lower flexural, tensile, and impact strength compared with the untreated specimens. However, the zinc borate treatments produced modest improvements in hardness performance. The SEM micrographs revealed that the outer surface of the wood fibers was coated by some crystalline deposits of zinc borate.

Keywords: Zinc borate; Pretreatment; In-process; Mechanical properties; Wood-polypropylene composites

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INTRODUCTION

Wood-based composite materials are increasingly used for exteriors, where conditions are conducive to fungal, insect, and marine borer attack (Eaton and Hale 1993; Gardner *et al.* 2003). Wood-thermoplastic composites have traditionally been viewed as building materials that are not prone to biodegradation (Morris and Cooper 1998), and recently, the use of wood plastic composites (WPCs) as a substitute for wood decking has been increasing (Wolcott and Englund 1999). Although the presence of resin and preservative in the wood composites may be expected to slow fungal attack, several studies have shown that the wood component sorbs water and eventually decays, albeit more slowly initially than does solid wood of the same species (Simonsen *et al.* 2004).

Four preservative systems and treatment processes that have been used in the preservation of composites are: the use of pretreated wood, in-process and post-process preservative treatments, and the use of recycled treated wood elements in manufacturing

or the use of wood species with a high natural resistance against biodegradation (Gardner *et al.* 2003).

Of the four different preservative methods, the in-process preservative treatments, in which the preservative treatment is incorporated during the manufacturing process, are favored for composite made from flakes, particles, and fibers, whereas the use of pretreated wood is particularly common in some solid lumber laminates (Gardner *et al.* 2003). In recent years, borates (disodium octaborate tetrahydrate, zinc borate, and boric acid), as composite additives applied in powder form, have been used as preservatives for the in-process treatment of wood composites (Laks 1999; Gardner *et al.* 2003). Borates are excellent fungicides and insecticides, but the primary borate used for wood preservation, sodium octaborate tetrahydrate, is highly water soluble and tends to leach from wet wood (Murphy *et al.* 1995). Moreover, ZB is an excellent fungicide and insecticide, is far less soluble, and field testing of this material in Hawaii under harsh sub-tropical conditions is ongoing, with early inspections indicating promising results (Simonsen *et al.* 2004; Gardner *et al.* 2003).

Zinc borate is also commonly used as zinc flame retardant, a good substitute for antimony trioxide (EFRA 2006). Both polymers and wood are sensitive to fire. Thus, fire retardants must be employed in order to improve fire behavior of such composites.

Depending on the preservative treatment processes used, the preservative treatment will have either a negative impact within the manufacturing process or on the final product. For instance, one critical problem with the use of borates as preservatives for wood composite panels bonded with phenol-formaldehyde resins is the interaction between the borate and the resin during the manufacturing of the panel, which could significantly decrease the resin gel time (Gardner *et al.* 2003).

Lu *et al.* (2008) found that all ZB-treated wood-HDPE composites had lower mean tensile strengths than did the control (*i.e.*, the untreated wood-HDPE composites). However, in the concentration range between 0% and 9%, the tensile strengths of all ZB-treated wood-HDPE composites were not significantly different from that of the control.

It is well known that zinc borate (ZB), as an in-process inorganic biocidal additive with very low mammalian toxicity and cost, broad activity against fungi and insects, and high leaching resistance (Schultz and Nicholas 2003), is mostly used commercially in many wood composites, including plastic wood and particleboard (Laks 1999). However, there is no information currently available on the morphology and mechanical properties of ZB-pretreated poplar wood flour/plastic composite (ZB-PT-PWF/PC). This work investigates the feasibility of applying the ZB-treated wood flour to the WPCs in the pre-process (*i.e.*, whether the ZB treatment will have a negative impact on the mechanical properties of the WPCs).

The main objective of this study was to determine effects of zinc borate on the mechanical and morphological properties of composites based on wood flour and polypropylene.

EXPERIMENTAL

Materials

A polypropylene (PP) matrix with a melt flow index (MI) of 10 g/10 min and a density of 0.95 g/cm^3 was supplied by the Tabriz Petrochemical Company of Iran. The lignocellulosic material used as the reinforcing filler in the composite was fresh poplar

wood (*Populus deltoides*), which was obtained from the Amol farms of Iran. To obtain wood flour (WF), the wood was cut into small pieces and chopped using a laboratory electrical rotary mill. The WF size was between 40 and 60 mesh.

The maleic anhydride polypropylene (MAPP) was obtained from Eastman Chemical Products, Inc., as Epolene G-3003^{TM} polymer with 8% acid anhydride and a molecular weight of 103.500. It was used as the coupling agent.

Zinc borate (ZB) was provided by U.S. Borax Inc., 26877 Tourney Road, Valencia, California 91355, as their product Borogard B.

Wood Flour Treatment

Before the pretreatment, a ZB solution was prepared by the following procedure. A required amount of ZB (25 g) was placed into a container with 250 mL ethanol solvent and stirred for 30 min with a magnetic stirrer. Then a 250 mL suspension of ZB-ethanol solvent was placed into a container with 2250 mL distilled water and stirred for 30 min in a similar manner. The concentration level of the ZB was designed to be 1%, based on the weight of oven-dried wood flour. A certain amount of oven-dried poplar wood flour (PWF) was added into the treating solution and continuously stirred for 24 h. The ZB-pretreated poplar wood flour (ZB-PTPWF) was then filtered with a screen and stored at room temperature for 24 h, oven-dried at 80 ºC until it reached a constant weight, and then stored in sealed plastic bags to await blending with polypropylene. Before and after impregnation, the PWF was kept in a drying oven at 103 ± 2 ºC until a constant weight has been achieved. After the PWF and ZB-PTPWF were cooled in a desiccators, their oven-dry weights were measured (by 490 g and by 547 g, respectively). The retention ratio of the ZB (R %) was calculated as follows,

$$R\ (\%) = (M_b - M_a)/M_a \times 100 \quad (1)$$

where M_a and M_b (g) denote the oven-dry weights of the PWF prior to and after impregnation with ZB chemical treatment, respectively.

Composite Preparation

Table 1 shows the blend design for zinc borate-pretreated wood flour/ polypropylene composites. Before preparation of samples, poplar wood flour was dried in an oven at (65 ± 2) °C for 24 h. The mixing was carried out with a Hake internal mixer (HBI System 90, USA) at 180 °C and 60 RPM.

Table 1. Formulation of Composites

Code	ZB Concentration (wt %)	Wood flour (wt %)	Polypropylene (wt %)	MAPP (wt %)
UT-WPC	0	40	58	2
ZB-T-WPC	1 in powder	39	58	2
ZB-PT-WPC	1 in solution	40	58	2

UT-WPC: untreated wood flour/plastic composite; ZB-T-WPC: zinc borate treated wood flour in manufacturing process/plastic composite; ZB-PT-WPC: zinc borate pretreated wood flour/plastic composite

First the polypropylene was fed to a mixing chamber. After melting of the PP, coupling agent (MAPP) was added. At the fifth minute, the wood flour was fed, and the total mixing time was 11 min. The compounded materials were then ground using a pilot scale grinder (Wieser, WGLS 200/200 Model). The resulting granules were dried at 70 °C for 24 h. Test specimens were injection molded into ASTM standard by an

injection molder at 185 °C and injection pressure was 10 MPa (Eman machine, Iran). The nominal dimensions of specimens (Fig. 1) were 100×10×10 mm. The specimens were stored under controlled conditions (50% relative humidity and 23 °C) for at least 40 h prior to testing.

Fig. 1. Mechanical testing samples

Measurements

The flexural and tensile tests were conducted according to ASTM D790 and D 638, respectively, using an Instron machine (Model 1186, England); the tests were performed at crosshead speeds of 5 mm/min. A Zwick impact tester (Model SIT 20 D, Santam Co., Iran) was used for the Izod impact test. All the samples were notched on the center of one longitudinal side according to ASTM D 256. Hardness tests were carried out according to ASTM D 1037 specifications by an Instron hardness tester model 4486 and 10 KN load-cell. The cross-head speed was 5 mm/min (The amount of ball penetration in the specimen is 5.6 mm according to wood hardness standard, but because of the rupture of specimens at this rate, it was modified to 2 mm).

The morphology of composites was characterized using scanning electron microscopy (SEM, Model LEO 440i, Oxford) at 25 kV accelerating voltage. Samples were first frozen in liquid nitrogen and fractured to ensure that the microstructure remained clean and intact, and then coated with a gold layer to provide electrical conductivity.

The statistical analysis was conducted using SPSS programming (Version 16) method in conjunction with the analysis of variance (ANOVA) techniques. Duncan multiple range test was used to test the statistical significance at $\alpha = 0.05$ level. For each treatment level, four replicated samples were tested for each property.

RESULTS AND DISCUSSION

The results of Duncan's test indicated that the ZB treatment had no significant effect on the hardness of wood flour/polypropylene composites. In addition, there were no significant differences between hardness values of ZB-PT-WPC and ZB-T-WPC samples ($P<0.05$). As can be seen in Fig. 2, the slight increase found in the hardness values of ZB-pretreated samples may be due to the precipitation of ZB in the cell lumens and the cell wall of wood particles and the subsequent increase in density. Like the

preservative salts, fire retardant salts have also precipitated in the cell cavity and the cell wall (Winandy and Rowell 1984).

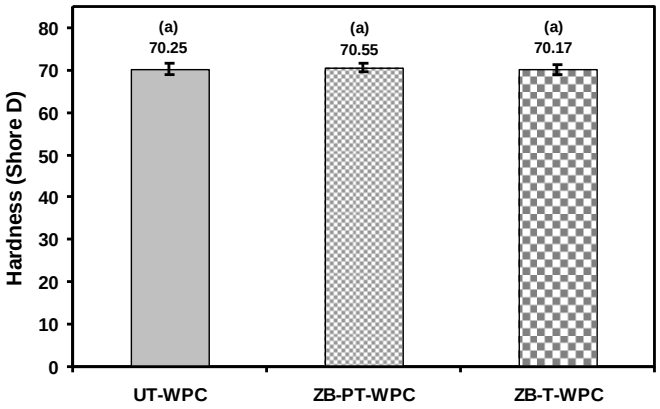

Fig. 2. Effect of zinc borate treatment on hardness of wood flour/polypropylene composites (Duncan's multiple range tests are given in the parentheses)

The results of Duncan's test indicated that the ZB treatment had no significant effect on the impact strength of the composites. There were no significant differences between ZB-PT-WPC and ZB-T-WPC samples ($P<0.05$). As can be seen in Fig. 3, the specimens containing the ZB showed lower notched impact strength compared with the untreated specimens. The impact resistance of the ZB-PT-WPC and ZB-T-WPC specimens decreased by 21% and 17.9%, respectively, compared to the UT-WPC specimens. This was mainly attributed to the poor compatibility between the wood and polymer matrix due to the crystalline deposits of zinc borate (Ayrilmis *et al.* 2012). Also, the ZB-T-WPC specimens had slightly higher average impact resistance than the ZB-PT-WPC ones. It seems that the ZB treatment is probably affected on dispersion and precipitation of ZB particles in the cavities of composites. So, we expected that the specimens containing the ZB-PT due to the formation of agglomeration cause the reduction of adhesion in the composite interface compared with the ZB-T specimens.

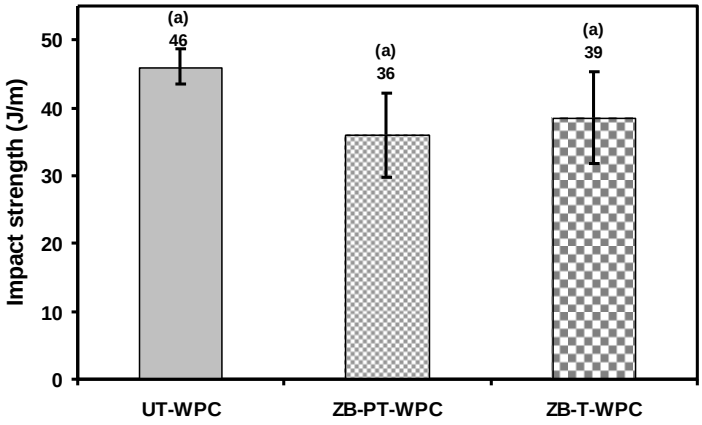

Fig. 3. Effect of zinc borate treatment on impact strength of wood flour/polypropylene composites (Duncan's multiple range tests are given in the parentheses)

The results of Duncan's test indicated that the ZB treatment had no significant effect on the flexural strength. However, there was a significant differences between the flexural modulus values of the ZB-PT-WPC and ZB-T-WPC ($P<0.05$). As can be seen in

Figs. 4 and 5, the flexural strength and modulus of ZB-PT-WPC and ZB-T-WPC specimens were less than the corresponding untreated specimens. This is probably due to the increase in stiffness caused by formation of ZB crystalline deposits in wood flour. This finding is consistent with those of previous studies (Ayrilmis *et al.* 2011a,b; Kurt and Mengeloglu 2011). Also, the ZB-T-WPC specimens had higher flexural strength and modulus than the ZB-PT-WPC ones. It seems that the specimens containing the ZB-PT due to the formation of agglomeration cause the reduction of adhesion in the composite interface compared with the ZB-T specimens.

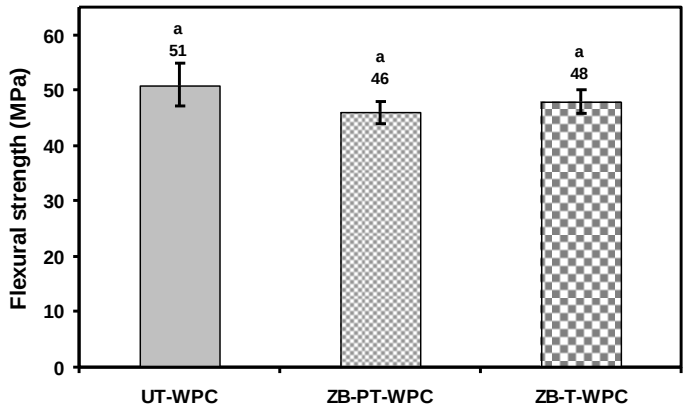

Fig. 4. Effect of zinc borate treatment on flexural strength of wood flour/polypropylene composites (Duncan's multiple range tests are given above each bar)

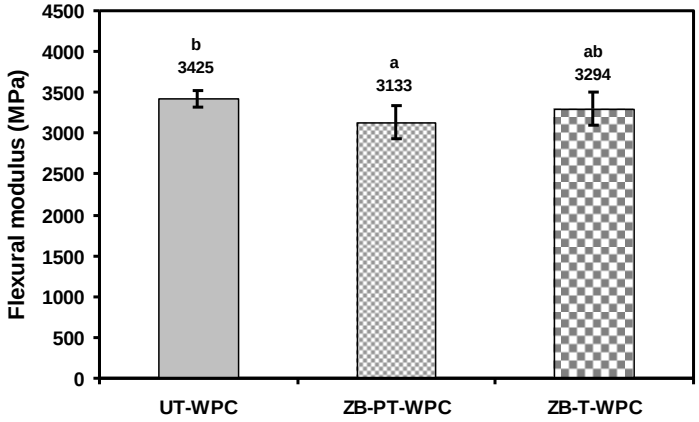

Fig. 5. Effect of zinc borate treatment on flexural modulus of wood flour/polypropylene composites (Duncan's multiple range tests are given above each bar)

The results of Duncan's test indicated that ZB treatment had a significant effect on the tensile strength of the ZB-T-WPC specimens ($P<0.05$). However there were no significant differences between tensile strength and modulus values of UT-WPC and ZB-PT-WPC. As can be seen in Figs. 6 and 7, the tensile strength and modulus of ZB-PT-WPC and ZB-T-WPC specimens were less than the untreated specimens. Also, the ZB-T-WPC specimens had higher flexural strength and modulus than the ZB-PT-WPC specimens. The reduction of tensile strength and modulus in the zinc-borated composites can be attributed to the same reasons as discussed concerning flexural strength and modulus.

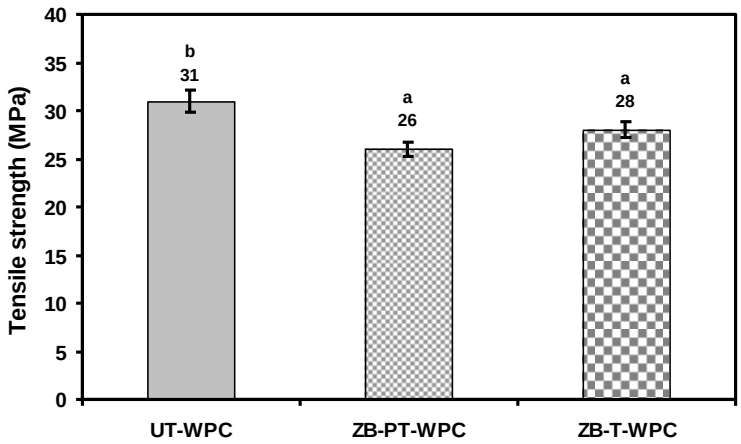

Fig. 6. Effect of zinc borate treatment on tensile strength of wood flour/polypropylene composites (Duncan's multiple range tests are given above each bar)

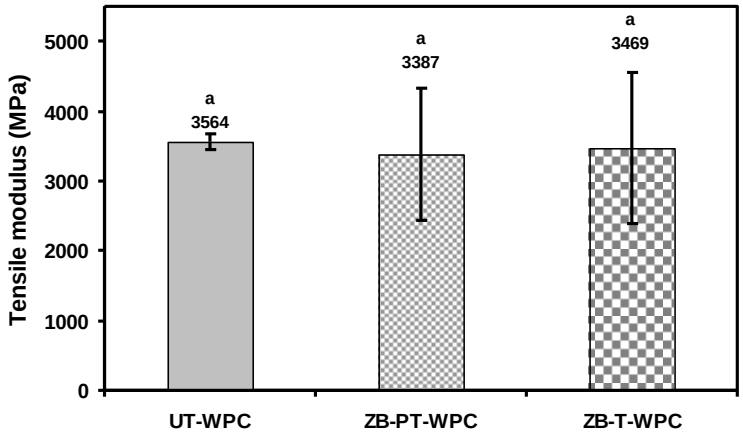

Fig. 7. Effect of zinc borate treatment on tensile modulus of wood flour/polypropylene composites (Duncan's multiple range tests are given above each bar)

SEM micrographs in Fig. 8 shows that the outer surface of the wood fibers was surrounded by some crystalline deposits of ZB, which increased the surface area of the solids within the WPC and reduced the bonding efficiency of the polymer. However, the interaction between the PP and WF treated with ZB can be improved, to some extent, by incorporation of the MAPP.

In ZB-treated specimens, several holes can be seen. These appear to result from the fiber pull out from the matrix, indicating poor bonding between wood flour and polymer matrix (Fig. 8). The number of such holes in ZB-PT-WPC (Figs. 8c and 8d) was larger than ZB-T-WPC (Figs. 8a and 8b); the compatibility between polymer and wood flour was probably affected.

It is also evident from Figs. 8e and 8f that there were considerably fewer such holes and many broken fiber ends embedded in the polymer matrix indicating better compatibility between wood flour and matrix.

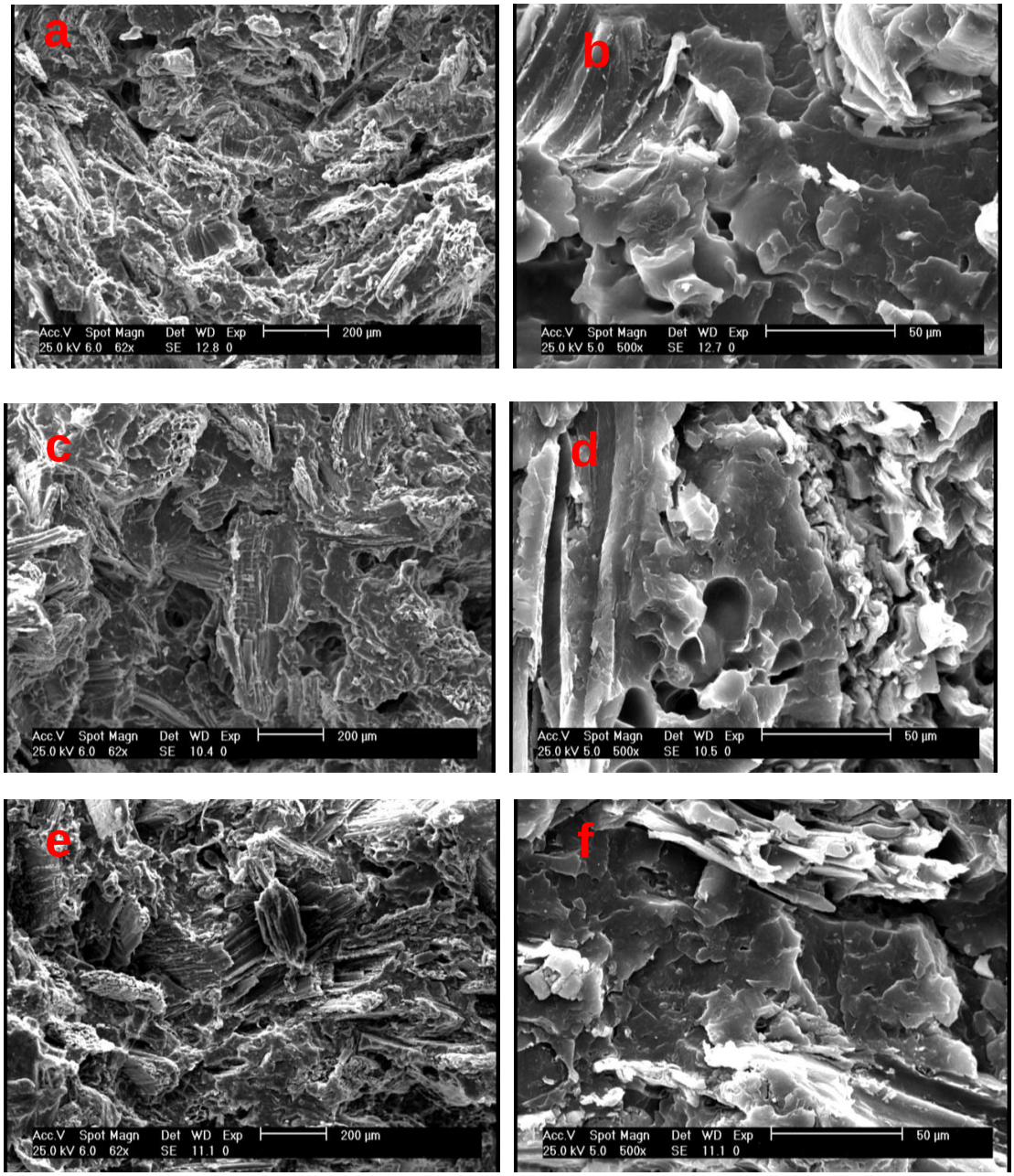

Fig. 8. SEM micrographs of the fracture surfaces in the composites under different treatments: ZB-T-WPC (a - b); ZB-PT-WPC: (c - d); and UT-WPC: (e - f)

CONCLUSIONS

From the research work herein, the following conclusions can be drawn:

1. Zinc borate treatment had no significant influence on mechanical properties of wood flour/polypropylene composites with the exception of tensile strength.
2. The specimens containing the ZB showed lower flexural, tensile, and impact strength compared with the untreated specimens. However, the zinc borate treatments produced modest improvements in hardness performance.

3. The SEM micrographs revealed that the outer surface of the wood fibers was coated by some crystalline deposits of zinc borate, which increased the surface area of the solids within the WPC and reduced the bonding efficiency of the polymer.

ACKNOWLEDGMENTS

The authors are grateful for the support of the Department of Wood Science and Paper Technology, Karaj Branch, Islamic Azad University. This article is extracted from Alireza Badritala's M.S. dissertation.

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Article submitted: July 31, 2012; Peer review completed: September 12, 2012; Revised version received: December 8, 2012; Accepted: January 3, 2013; Published: January 7, 2013.