ONLINE ISSN 2069-7430
ISSN-L 1841-4737

PRO LIGNO
www.proligno.ro

Vol. 13 N° 4 2017
pp. 269-275

COUPLING AGENT EFFECT ON THE PROPERTIES OF THERMOPLASTIC COMPOSITES FILLED SAND-DUST FROM MEDIUM DENSITY FIBERBOARD

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Abstract:
The study investigates coupling agent effect on some properties of thermoplastic composites filled with sand dust from medium density fiberboard (MDF). The physical, mechanical and morphological properties of the composites produced with the extrusion method were accomplished by using sand dusts of medium density fiberboard (SD_MDF) as lignocellulosic material, high density polyethylene (HDPE) and polypropylene (PP) as thermoplastic polymer and maleic anhydride grafted HDPE and maleic anhydride grafted PP as coupling agents. Coupling agents at different ratios were used to improve the adhesion between fiber and polymers in production, and their effects on the properties were evaluated. Thickness swelling and water absorption of the samples decreased when used coupling agent. Except for impact strength, flexural and tensile properties of the composites which increased with presence of a coupling agent. In the light of obtained results, it was specified that use of coupling agent improved physical, mechanical and morphological properties of SD_MDF filled thermoplastic composites. In addition, optimum coupling agent usage rate were determined as 3%.

Key words: *coupling agent; thermoplastic composite; sand dusts of Medium Density Fiberboard; mechanical properties; physical properties.*

INTRODUCTION

Natural fibers play an important role as filler or reinforcer for polymer composite industry due to having low cost with low density and high specific properties (Boran 2016, Cavdar and Boran 2016). Wood plastic composites are among the major natural fiber composites with a large production capacity.

The natural fiber filled thermoplastic composite production is not a simple and problem-free production. The most important problems in the production with the addition of natural fibers or flours into the plastic matrix can be summarized in two main categories. The first is moisture affinity and temperature sensitivity of natural fiber such as wood fiber/flour and the second is bonding problems due to the incompatibility between the natural fiber and the thermoplastic polymer. Coupling agents play a bridge between two materials by forming a chemical bonding with hydrophilic lignocellulosic material and increasing surface wettability of hydrophobic polymer chain (Oksman and Lindberg 1998, Zhang *et al.* 2002; Yang *et al.* 2007).

Much research has been done on the problem of incompatibility between wood flour and plastic and it has become necessary to transform wood flour surfaces into a hydrophobic structure through modification (Pritchard 1998, Cavdar *et al.* 2014). Various coupling agents have been used for this purpose. Among these agents, the most commonly used chemicals are synthetic polymers treated with maleic anhydride. In many studies on the use of compatibilizers, maleic anhydride grafted with synthetic polymers has proved to serve as a bridge between the lignocellulosic filler and the polymer matrix (Sanadi *et al.* 1997, Lu *et al.* 2000, San *et al.* 2008). The molecular weight and amount of the grafted maleic anhydride are important parameters for the effect of the compatibility. Maleic anhydride in maleic anhydride-grafted- polypropylene / polyethylene (MAPP / MAPE) provides a polar interaction such as acid-base interaction and can covalently linked to hydroxyl groups on lignocellulosic fillers (Felix *et al.*1993, Sanadi *et al.*1995, San *et al.* 2008).

In studies aiming to determine optimum usage ratio of compatibilizer, it has recommended 2-8% and 1-4% of the weight of the wood for WPCs produced at 50:50 and 70:30 wood / plastic ratio, respectively. In some studies, it has been concluded that the use of 1-3% compatibilizer in relation to the total weight of the WPCs is appropriate (Maldas *et al.* 1989, Krzysik *et al.* 1990, Myers *et al.* 1993, Lu *et al.* 2000).

The concentration of the coupling agent determines the compatibility between the materials in the composite. Some researchers have reported that coupling agent at low concentrations improves mechanical properties of the composites while the mechanical properties decreased with using higher concentration. Therefore, optimum usage ratio for coupling agent should be taken into consideration in production of natural fiber filled thermoplastic composites.

OBJECTIVE

The main objective of the present research investigates the effect of various coupling agent usage ratios on physical, mechanical and morphological properties of thermoplastic composites filled with sand dusts from MDF.

MATERIALS AND METHODS

In this study, sand dusts of MDF panels were provided by Kastamonu Integrated Forestry Industry and Trade Inc., Turkey. The dusts (≈200 mesh) were generated from the sanding of the panels produced from beech, pines and oaks fibers and urea formaldehyde resin based on 65 % solid content. High density polyethylene (HDPE)(MFI/190°C/2.16kg = 0.35g/10min) and polypropylene (PP) (MFI/230°C/2.16kg = 5g/10min) were purchased by Petkim Petrochemical Co., Turkey. Coupling agents, maleic anhydride grafted polyethylene (MAPE) (Licocene PE MA 4351, density: 0.99g/cm^3) and maleic anhydride grafted polypropylene (MAPP) (Licomont AR 504, density: 0.91g/cm^3) were supplied by Clariant International Ltd, in Germany.

Composite Manufacturing

SD_MDF, coupling agent and wax with HDPE or PP were mixed with high-speed mixer (Teknomatik, Turkey), speed range 5–1000rpm, for 5min. The compounding was accomplished using a laboratory scale single screw extruder (Teknomatik, Turkey). The set temperatures of the extruder were controlled at 170°C, 175°C, 180°C, 185°C, and 190°C for five heating zones and the extruder screw speed was set to 40 rpm. The cooled pellets in water were granulated and dried at 105°C for 24h. The granulated and oven-dried pellets were pressed under 100 kg/cm^2 pressure, at 200°C temperature for 20 min using a mould dimension of 20cm by 20cm by 0.5cm. After pressing, the composites were conditioned in a climatic room with the temperature of 20°C and the relative humidity of 65%. The raw material formulations used for the composites are presented Table 1.

Table 1

Parameters of manufacturing the thermoplastic composites

Composite panel type	Plastic type	Coupling agent	Composite formulations (%)			
			SD_MDF	Plastic	Coupling agent	Wax
Control_HDPE	HDPE	MAPE	40	54	-	3
Control-PP	PP	MAPP	40	54	-	3
A1	HDPE	MAPE	40	53	1	3
B1	HDPE	MAPE	40	51	3	3
C1	HDPE	MAPE	40	49	5	3
A2	PP	MAPP	40	53	1	3
B2	PP	MAPP	40	51	3	3
C2	PP	MAPP	40	49	5	3

Physical properties

Water absorption (WA) and thickness swelling (TS) of the thermoplastic composites were evaluated according to EN 317. Five samples for each group with dimensions of 50mm*50mm*5mm, were used to determine the WA and TS tests. The conditioned samples were weighed and their thicknesses were measured, then the samples were dipped into water for 6 months. The weight and thickness of the samples were measured periodically during six months. The samples were weighed, and their thicknesses were measured to calculate WA and TS rates.

Mechanical properties

Flexural and tensile properties and impact strength of the thermoplastic composites filled with SD_MDF were determined by ASTM D 638, ASTM D 790 and ASTM D 206, respectively. The flexural and tensile properties of all group samples were determined on Zwick Testing Unit with a capacity 10kN

(1000kg). Impact strength samples were notched with a Polytest notching cutter by RayRanTM and tested on a Zwick HIT5.5P impact-testing machine.

Scanning Electron Microscope

Morphological properties of the composites were accomplished using A JEOL JSM-5500 scanning electron microscope (JEOL Ltd., Japan). The impact samples were cryogenically fractured in liquid nitrogen, and then were gold coated by sputtering technique before the microscopic observations. Images were taken at 50 X SEM micrograph magnifications.

RESULTS AND DISCUSSION

Thickness Swelling and Water Absorption

The results of TS and WA of SD_MDF filled thermoplastic composites with coupling agent are shown in Figures 1 and 2. The TS and WA values of all samples increased with increment of water immersion time. For the HDPE based composites, TS values of HDPE based composites were ranged between 0.41% and 1.70% while those of PP composites were ranged between 1.50% and 1.82% after six months immersion time in water. Regarding WA values were found as 3.97% and 5.86% after six months immersion time for HDPE based composites. These values for PP based composites were found as 7.90% and 8.83% after the six months.

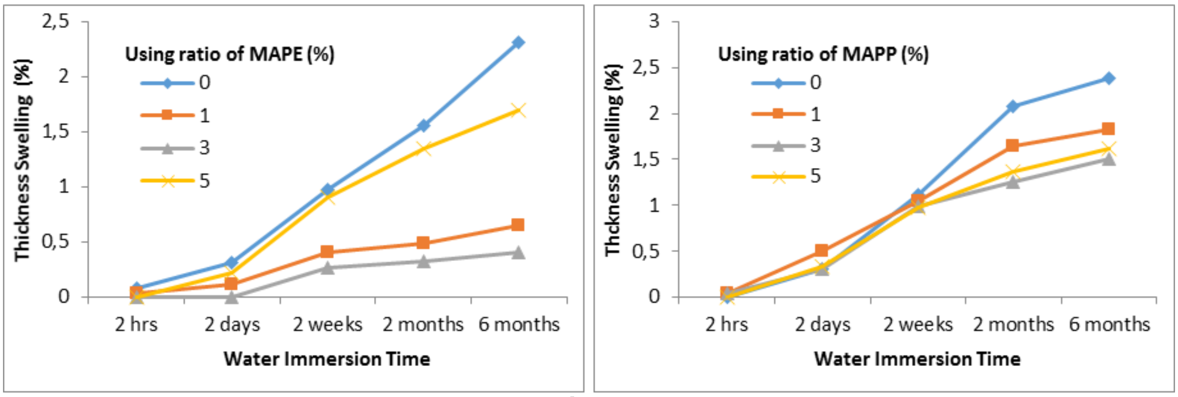


Fig. 1.
Coupling agent effect on thickness swelling of the thermoplastic composites.

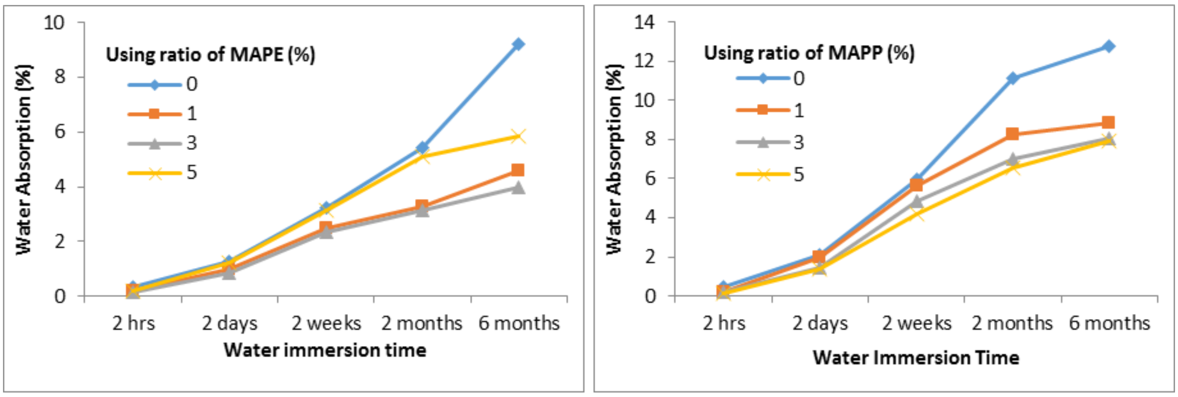


Fig. 2.
Coupling agent effect on water absorption of the thermoplastic composites.

The water absorption and thickness swelling of the composite samples were reduced with use of coupling agents. It has been supported by some reserachers that use of coupling agent decreased WA and TS of thermoplastic composites (Matuana *et al.* 2001, Panthapulakkal *et al.* 2005, Shakeri and Ghasemian 2010, Yang *et al.* 2005, Rozman *et al.* 2010, Hamzeh *et al.* 2011). This is probably due to the fact that the maleic anhydride in MAPE/MAPP reacts with the free -OH groups in the lignocellulosic materials, forming the ester bonds. Therefore, amount of free -OH groups are reduced and the samples with coupling agent are less water uptake than the control samples. Another possible reason is that coupling agent may increase the crystallinity of the composite. Some researchers have concluded that, the crystallinity of the composites produced using the coupling agent was higher than that of the blends without using the coupling agent. The rate of water absorption would be lower in composites with coupling agent, depending on the reduced permeability in crystalline regions (Ichazo *et al.* 2001, Shakeri and Ghasemian 2010).

However, HDPE based composites had higher dimensional stability (lower WA and TS) than PP based composites. This may happen due to the different characteristics between these plastics (Cavdar *et al.* 2011)

Mechanical properties

The results of mechanical properties of thermoplastic composites filled with SD_MDF and coupling agent are shown in Table 2.

Table 2

Mechanical properties of coupling agent and SD_MDF filled thermoplastic composites

ID	Flexural Properties		Tensile Properties			IS (J/m)
	FS (MPa)	FM (MPa)	TS (MPa)	TM (MPa)	EB (%)	
Control_HDPE	24.57[1]	1348.57	11.87	591.96	2.56	29.27
	0.88[2]	15.17	0.15	13.44	0.18	1.32
Control_PP	30.91	1427.49	13.63	710.43	2.81	19.17
	1.53	25.75	0.40	8.06	0.21	0.16
A1	24.75	1490.40	14.59	592.25	3.29	24.88
	6.78	261.55	0.98	48.54	0.31	2.31
B1	24.68	1692.57	12.82	598.38	2.71	21.68
	1.72	41.41	0.14	9.90	0.18	3.60
C1	24.87	1510.66	13.03	608.44	2.80	22.90
	1.48	25.44	0.34	8.07	0.23	2.51
A2	31.88	1649.10	14.48	729.15	2.93	15.78
	1.88	79.02	1.85	28.53	0.67	1.05
B2	32.01	1803.72	16.43	695	3.07	20.22
	0.50	80.61	0.95	22.60	0.09	0.56
C2	32.65	1791.18	16.16	605.43	3.39	17.76
	1.36	123.86	1.14	20.24	0.14	2.17

(1) Mean, (2) Standard deviation FS: Flexural Strength, FM: Flexural Modulus, TS: Tensile Strength, TM: Tensile Modulus, EB: Elongation at Break, IS: Impact Strength

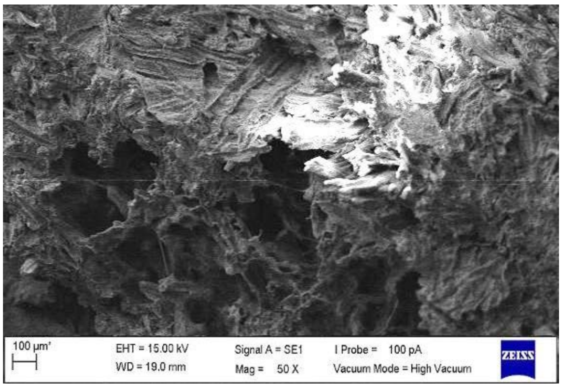
As shown in Table 2, the use of coupling agent improves the bonding between lignocellulosic material and plastics, thus increasing the bending strength values of all composite types. The use of MAPE and MAPP provided a small increase of 1% to 6% compared to control samples for HDPE and PP. In many studies, it has been proven that the coupling agent act as a bridge between the lignocellulosic filler and the polymer matrix (Sanadi *et al.* 1997, Lu *et al.* 2000, San *et al.* 2008). It is also stated that maleic anhydride in MAPP and MAPE provide a polar interaction such as acid-base interaction and covalent bonding to hydroxyl groups on lignocellulosic fillers (Felix *et al.* 1993, Sanadi *et al.* 1995, San *et al.* 2008). The use of coupling agent improved in the flexural modulus values of the the thermoplastic composites (Table 2). The best results were obtained with the use of 3% coupling agent. With using 3% MAPE, a 26% increase was achieved in the samples with HDPE. The use of 3% MAPP resulted in an increase of 26% for PP based samples.

The tensile properties of the samples were positively affected when coupling agent was used in the polymer matrix. As the use of coupling agent improves the bond between lignocellulosic material and plastics, tensile strength values of all composite types have increased (Table 2). An increase of 23% compared to the control samples was determined with 3% MAPE in HDPE samples. In PP-produced samples, an increase of 21% was achieved with 3% MAPP use. Many studies have been carried out on the investigation of the effects of the coupling agents on the mechanical properties of thermoplastic composites. Studies have shown that coupling agents increase the strength properties of composites (Felix *et al.* 1993, Sanadi *et al.* 1995, Sanadi *et al.* 1997, Lu *et al.* 2000, Li and Matuana 2003; Xu and Shuai 2007, Zhang *et al.* 2007, San *et al.* 2008, Mengeloglu and Karakus 2008). The use of MAPE and MAPP resulted in a 3% increase in tensile modulus values for two types of thermoplastics. Despite the fact that many studies have shown that there is a significant increase of 2-3 times in the properties of composites by increasing coupling agent use rates, there is no expected increase in the test results (Lu *et al.* 2000, Li and Matuana 2003, Xu and Shuai 2007, Zhang *et al.* 2007, San *et al.* 2008). However, in some studies, it has been reported that the significant improvement effect on the elasticity modulus properties was not observed when using coupling agent (Doan *et al.* 2006), and also indicated the values decrease in case of high usage of coupling agent (Santos *et al.* 2009). This situation is linked to two reasons. The first reason; the melt flow indexes of polyolefins grafted with maleic anhydrides are much higher than the melt flow indexes of polyolefins such as PP and PE. Therefore, it has a shorter polymer chain and lower molecular weight. Accordingly, use of coupling agent at high ratios may result in reduced modulus of elasticity. The second reason is that when MAPE and MAPP are used at high ratios, the thermoplastic polymer can be moved away from the lignocellulosic material and lead to weaker bonding and low resistance properties (Mohanty *et al.* 2006; Santos *et al.* 2009). The use of MAPE and MAPP also resulted in a small increase in the amount of elongation of the samples. Mengeloglu and Kabakci (2008) used 4% MAPE in eucalyptus wood flour filled thermoplastic composites and investigated the effects of coupling agent use on the properties of the composites. The results have indicated that MAPE use did not have a significant effect on the properties, causing a small increase in the amount of elongation at break.

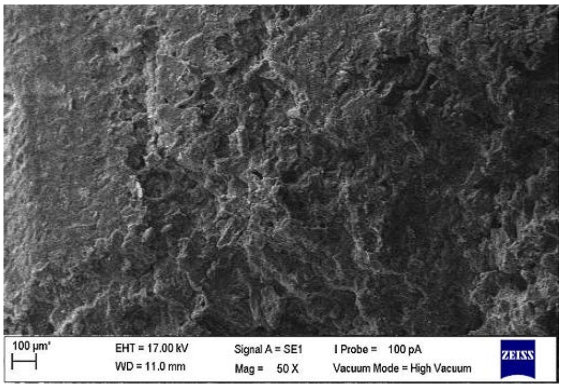
In contrast to other mechanical properties, impact strength of the samples decreased with MAPE and MAPP use. Myers *et al.* (1993) have studied the effect of use of MAPP on the properties of PP-wood flour composite. They found that MAPP use had a negative impact on notched impact strength of the composites.

Morphological Properties

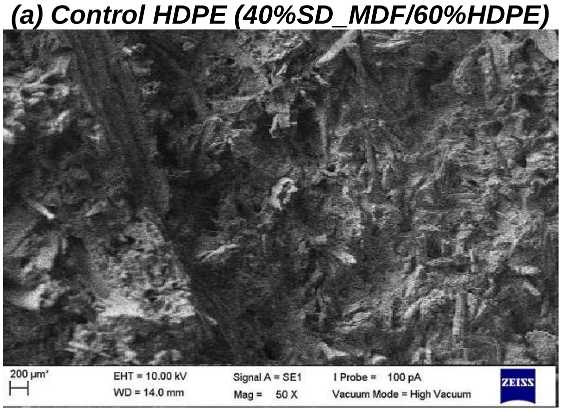
Fig. 3 shows SEM micrographs of SD_MDF and coupling agent filled thermoplastic composites at 50X magnifications. Some images show that the use of the coupling agent improves the bond between the lignocellulosic filler and the thermoplastic matrix. It was observed that the voids in the samples decreased and a more homogeneous distribution of the lignocellulosic material in the thermoplastic matrix was observed with using MAPE and MAPP by 3% compared to control samples.



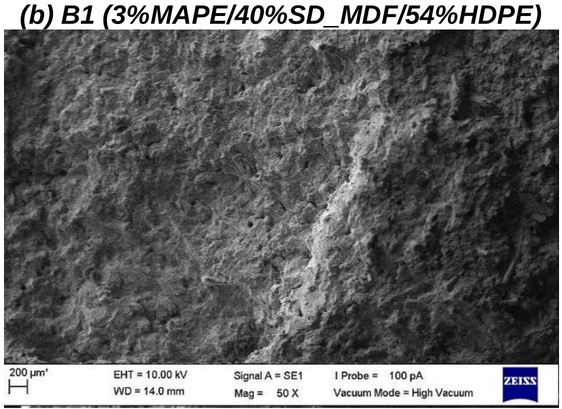
(a) Control HDPE (40%SD_MDF/60%HDPE)



(b) B1 (3%MAPE/40%SD_MDF/54%HDPE)



(c) Control PP (40%SD_MDF/60%PP)



(d) B2 (3%MAPP/40%SD_MDF/54%PP)

Fig. 3.
Coupling agent at 3% concentration effect on morphological properties of thermoplastic composites filled with SD_MDF.

CONCLUSIONS

1. TS and WA values of the composites increased with increment of the water immersion time. With the use of coupling agent, it was seen that TS and WA of the composites decreased in comparison with the control samples. The best results for TS and WA were obtained on composites produced using 3% coupling agent.

2. The use of coupling agent improves the bond between the lignocellulosic material and the thermoplastic, resulting in an increase in flexural strength and flexural modulus values for all composite types. The best results were seen with use of coupling agent by 3%.
3. With the use of MAPE and MAPP, tensile properties including of the tensile strength, tensile modulus and the elongation at break of the composites were increased.
4. In contrast to other mechanical properties of the composites, there is generally a slight decrement in impact strength with MAPE and MAPP use.

ACKNOWLEDGEMENT
This study was supported by a grant from the Ministry of Science, Industry & Technology, Turkey (00214.STZ.2007-2).

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