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Preparation and characterization of bagasse/HDPE composites using multi-walled carbon nanotubes

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ABSTRACT

This article presents the preparation and characterization of bagasse/high density polyethylene (HDPE) composites. The effects of multi-walled carbon nanotubes (MWCNTs), as reinforcing agent, on the mechanical and physical properties were also investigated. In order to increase the interphase adhesion, maleic anhydride grafted polyethylene (MAPE) was added as a coupling agent to all the composites studied. In the sample preparation, MWCNTs and MAPE contents were used as variable factors. The morphology of the specimens was characterized using scanning electron microscopy (SEM) technique. The results of strength measurement indicated that when 1.5 wt% MWCNTs were added, tensile and flexural properties reached their maximum values. At high level of MWCNTs loading (3 or 4 wt%), increased population of MWCNTs lead to agglomeration and stress transfer gets blocked. The addition of MWCNTs filler slightly decreased the impact strength of composites. Both mechanical and physical properties were improved when 4 wt% MAPE was applied. SEM micrographs also showed that the surface roughness improved with increasing MAPE loading from 0 to 4 wt%. The improvement of physicomechanical properties of composites confirmed that MWCNTs have good reinforcement and the optimum synergistic effect of MWCNTs and MAPE was achieved at the combination of 1.5 and 4 wt%, respectively.

1. Introduction

Wood plastic composites (WPCs) have been growing rapidly for the past few decades, due to the specific advantages they can provide in comparison with the classic mineral filler/plastic composites. The term WPC refers to any composite that contains woody materials in the form of fiber or flour and thermoplastics. WPCs are widely used in many industries such as the aerospace, aeronautics, automobile, electronics, medical, and construction (Kiani, Ashori, & Mozaffari, 2011). Such materials are favored as new generation of reinforcing materials in thermoplastics since they represent renewable, abundant, and biodegradable natural resources (Ziaei Tabari, Nourbakhsh, & Ashori, 2011). However, WPCs exhibit lower physical (higher water absorption and thickness swelling), mechanical (less flexural and tensile strength) as well as thermal properties compared with traditional synthetic composites (Kordkheili et al., 2013). Various approaches are used for the improvement of mechanical properties of WPCs. There are two major ways to improve mechanical properties through the use of fillers: by treating it with coupling agents, and by changing its particle size (Ashori, 2012). Chemical coupling agents are substances, typically polymers, which are used in small quantities to treat a surface so that bonding occurs between the treated surface and other surfaces, e.g. wood and thermoplastics. The coupling forms include covalent bonds, secondary bonding (such as hydrogen bonding and van der Waals' forces), polymer molecular entanglement and mechanical interblocking (Kong, Hu, Chen, & Fan, 2005).

The incorporation of nanoparticles as reinforcing fillers is another method for improving the overall properties of WPCs. The nanoparticles are certainly one of the most outstanding and promising reinforcements that are being studied by many scientists all over the world. This is mainly due to their high surface area, low density and high Young's modulus, among other properties that can be transferred to the polymeric matrix if a good dispersion of the filler is ensured in the polymer. A nano-scale filler offers larger effective surface area than a micron-scale filler. As a result, there is more interphase region in a nanocomposite than in a microcomposite. Therefore, the properties of the polymer in the inter-phase region dominate the overall properties of the bulk nanocomposite. In other words, nanofillers can alter the properties of a large volume fraction of the polymer resulting in a significant change in properties at low loading (Chen, Ozisik, & Schadler, 2010). Carbon nanotubes (CNTs) are among the most studied nano-scale materials, because of their extraordinary mechanical and unique

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Table 1
Comparison and contrast of advanced fiber reinforcements vs. carbon nanotubes.

Fiber	Diameter (μm)	Density (g/cm^3)	Tensile strength (GPa)	Young's modulus (GPa)
Carbon	7	1.6	2.4–3.1	120–170
S-glass	7	2.5	3.4–4.6	90
Aramid	12	1.4	2.8	70–170
Boron	100–140	2.5	3.5	400
Quartz	9	2.2	3.4	70
SiC fibers	10–20	2.3	2.8	190
SiC whiskers	0.002	2.3	6.9	–
Carbon nanotubes	0.001–0.1	~1.3	Up to ~50	Up to ~1000

electronic properties. Since their discovery in 1991, CNTs have generated huge activity in most areas of science and engineering due to their unprecedented physical and chemical properties (Coleman, Khan, & Gun'ko, 2006). No previous material has displayed the combination of superlative mechanical, thermal, and electronic properties attributed to CNTs. These properties make them ideal not only for a wide range of applications but as a test bed for fundamental science. In particular, this combination of properties makes them an ideal candidate as an advanced filler material in nanocomposites. CNTs tend to have impressive mechanical properties (Table 1) (Bakunin, Suslov, Kuzmina, & Parenago, 2004). The reported specific strengths of CNTs are 10–100 times higher than the strongest steel. Perfect CNTs are highly elastic, and they can sustain high strains in tension without showing any sign of brittle behavior, plastic deformation or bond rupture (Chen et al., 2010). As a result, it is expected that when a polymer is reinforced with CNT, the resulting polymer/CNT composites will exhibit better properties than the unfilled polymer. CNTs can be synthesized as singular tubes or multi-walled forms, called single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs), respectively. SWCNT has a diameter of 1–3 nm whereas MWCNT has a diameter ranging from 10 to 100 nm. The length of both types of CNTs ranges from 0.5 to 50 μm (Popov, 2004).

Due to the global demand for fibrous materials, worldwide shortage of forests in many areas, and environmental awareness, research on the development of composites prepared using various waste materials is being actively pursued (Ashori & Nourbakhsh, 2010; Yao, Wu, Lei, & Xu, 2008). Literature review shows that among the possible alternatives, the development of composites using agricultural byproducts or agro-waste materials is currently at the center of attention (Panthapulakkal & Sain, 2007; Wang, Wang, Zhang, Wang, & Ren, 2009; Yao et al., 2008). Among many agro-wastes, bagasse is one of the most promising and suitable raw materials for both developing and developed countries (Ashori & Nourbakhsh, 2010). Bagasse, an abundant agricultural lignocellulosic byproduct is a fibrous residue of sugarcane stalks left over after crushing and the process of juice extraction from sugarcane. About 54 million dry tons of bagasse is produced annually throughout the world (Mulinari, Voorwald, Cioffi, da Silva, & Luz, 2009). Asia is the primary production region of sugarcane (45%), while South America is the second largest production region (35%) in the world. According to a report from Food and Agricultural Organization (FAO), Iran produces 5.3 million tons of bagasse annually (Tabarsa, Ashori, & Golamzadeh, 2011), which is mainly centered in the southwestern province, namely Khuzestan. The utilization of this biomass for processing of novel wood-based composites has attracted growing interest because of ecological and renewable characteristic of bagasse.

The initial objective of this work was to study the potential of bagasse as an alternative raw material for WPC. In addition, the effects of MWCNTs and coupling agent on the physico-mechanical properties of bagasse/high density polyethylene nanocomposite were evaluated.

2. Materials and methods

2.1. Materials

Lignocellulosic material. Bagasse stalks were supplied by Khuzestan Cultivation and Industry Co., Iran. The bagasse stalks were depithed and cut to 2–3 cm in length by hand. They were then washed, air-dried and screened through a series of screens to remove dirt. In order to reduce extractives effects, woody materials were treated with water at 50 °C for 48 h. The depithed bagasse stalks were ground with a Thomas-Wiley miller to fine powder of 40-mesh size, and then oven-dried and stored in sealed plastic bags before processing.

Polymer matrix. High density polyethylene (HDPE), with trade name of HD5620EA, an injection molding grade was supplied by Arak Petrochemical Co. (Iran), in the form of pellets. Some important physical and mechanical properties of the used polymer are presented in Table 1.

Coupling agent. Maleic anhydride grafted polyethylene (MAPE), in the form of powder (grade PPG-101) with a density of 0.92 g/cm^3 and a melting flow index of 5 g/10 min, was obtained from Kimia Javid Sepahan Co., Iran.

Nanoparticle. MWCNTs were supplied by the Iran Research Institute of Petroleum Industry, Iran. The outer and inner diameters of the MWCNTs were about 10 and 3.5 nm, respectively, and the purity was 90%.

2.2. Sample preparation

Formulations of the treatments used for the respective mixes prepared are given in Table 2. Composites were produced in a two-stage process. In the first stage, bagasse powder (BP), HDPE and MWCNTs were compounded with and without MAPE (depending on formulations) using a co-rotating twin-screw extruder. The barrel had five heated zones, which were set at 165, 170, 175, 180 and 185 °C, respectively. Screw speed was 60 rpm and the pressure at the die was 1500 MPa. The product was recovered by guiding the molten extrudate into a cold water stranding bath. The cooled

Table 2
Physical and mechanical properties of used HDPE.

Properties	Test method	Unit	Value
MFI @ 190 °C, 2.16 kg	ASTM D1238	g/10 min	20
Density	ASTM D1505	g/cm^3	0.956
Vicat softening point	ASTM D1525	°C	124
Tensile strength	ASTM D638	MPa	22
Tensile modulus	ASTM D638	MPa	900
Elongation at break	ASTM D638	%	700
Flexural modulus	ASTM D790	MPa	1000
Hardness shore D	ASTM D2240	–	66
Notched impact strength	ASTM D256	kJ/m^2	4

strands were pelletized using a pilot scale grinder (Collin model), dried and stored in sealed plastic bags. In the second stage, test specimens were injection molded at 190 °C to produce standard ASTM specimens. Molding conditions were: press temperature 190 °C and pressure during heating 4 MPa. Five replications were prepared for each treatment.

2.3. Measurements

2.3.1. Mechanical properties

The Izod impact strength test according to ASTM D256 (A) was carried out on notched samples with dimensions 62.5 mm × 13 mm × 3 mm using Santam pendulum impact tester (model SIT-20D) at room temperature. The notch depth was fixed at 2.5 ± 0.02 mm with angle 45°. Tensile and flexural properties were conducted using an Instron machine model 8112 according to ASTM D368 and ASTM D 790 procedures, respectively. The specimens were tested at crosshead speed of 2 and 1 mm/min at room temperature for tensile and flexural strength, respectively. All the reported values for the tests were the average values of five specimens.

2.3.2. Dimensional stability tests

The thickness swelling (TS) and water absorption (WA) tests were conducted in accordance with ASTM D 570. Before testing, the weight, and dimensions, i.e. length, width and thickness of each specimen were measured. Conditioned samples of each composite type were either soaked in distilled water at room temperature for 24 h. Samples were removed from the water, patted dry and then measured again. Each value obtained represented the average of 6 samples.

2.4. Statistical analysis

The experimental design consisted of two variable factors (namely MWCNTs and MAPE) and their interaction. Data for each treatment was statistically studied by analysis of variance (ANOVA). When the ANOVA indicated a significant difference among factors and levels, a comparison of the means was done employing Duncan's multiple range test (DMRT) to identify the groups that were significantly different from others at 99% and 95% confidence levels.

2.5. Morphological study

Studies on the morphology of the composites were carried out using a scanning electron microscope (SEM). SEM micrographs of the surfaces of specimens were taken using SEM Model WEGA-II TESCAN. The specimen was coated with a thin film (25 nm) of gold to avoid electrical charge accumulation during the examination and then analyzed at an accelerating voltage of 25 kV.

3. Results and discussion

The results of the mechanical and physical tests, along with statistical analysis, are shown in Tables 3 and 4 for all the fabricated composites. For easier comparison, percentages of changes (reduction or increment) for the properties are presented in Fig. 1. In general, both physical and mechanical properties were significantly influenced by the addition of MWCNTs and MAPE.

3.1. Tensile properties

Statistical analysis showed that the mechanical properties in terms of tensile strength and modulus were significantly influenced by the addition of MWCNTs and MAPE. According to the DMRT (Table 3), the differences between the mean values of the studied properties within and among each of the groups compared were significant. Samples treated with 1.5 wt% MWCNTs showed the highest values among the other types of specimens. Fig. 1a depicts the tensile strength and modulus of composites made with various MWCNTs and MAPE contents. In order to improve the bonding strength between the lignocellulosic filler and the matrix polymer, coupling agent (MAPE) has been used. The tensile strength value was observed to be 26.4 MPa for composites made with 1.5 wt% MWCNTs and 0 wt% MAPE, while maximum tensile strength was approximately 27.7 MPa for composites made with 1.5% MWCNTs and 4 wt% MAPE. In both cases, tensile strength of pure HDPE was enhanced at least 3–5% when MAPE was added. In general, both properties of the samples were increased when the MAPE content were increased from 0 to 4% by weight (Fig. 1a). Sun, Li, Zhang, Du, and Burnell Gray (2005) reported that the tensile strength of composites is mainly influenced by filler fraction and the interfacial adhesion between particles and matrix. The possible reason proposed for this kind of behavior may be the better interfacial adhesion between the matrix and bagasse flour. This is supported by the SEM micrographs (Fig. 2). Better adhesion results into more restriction to deformation capacity of the matrix in the elastic zone and increased modulus. Similar observations were reported for other lignocellulosic fibers based HDPE composites (Ashori & Nourbakhsh, 2011).

Table 3
Composition of the studied treatments.

Treatment code	BP (wt%)	HDPE (wt%)	MAPE (wt%)	MWCNT (wt%)
A1	30.0	70.0	0.0	0.0
A2	30.0	69.5	0.0	0.5
A3	30.0	69.0	0.0	1.0
A4	30.0	68.5	0.0	1.5
A5	30.0	68.0	0.0	2.0
A6	30.0	67.0	0.0	3.0
A7	30.0	66.0	0.0	4.0
B1	30.0	66.0	4.0	0.0
B2	30.0	65.5	4.0	0.5
B3	30.0	65.0	4.0	1.0
B4	30.0	64.5	4.0	1.5
B5	30.0	64.0	4.0	2.0
B6	30.0	63.0	4.0	3.0
B7	30.0	62.0	4.0	4.0

As can be seen from Fig. 1a, tensile properties were improved with the addition of MWCNTs. This result is consistent with the general observation that the introduction of nano-sized particles into a polymer matrix increases its tensile properties (Hussain, Hojjati, Okamoto, & Gorga, 2006). The enhancement is easily understood because filler in MWCNTs form can carry more tensile load. As mentioned earlier, the MWCNT is much stiffer than polymer matrix and as a result it adds stiffness to the composites. The phenomenon was stronger when using 4 wt% MAPE. The differences in strength improvement with respect to MAPE content are very prominent at the highest MWCNT content. These results confirm the strong interaction between the MAPE matrix and MWCNT. Similar results have been reported by Kordkheili et al. (2013), who studied the properties of polymer/wood flour/CNT nanocomposites. Their data showed that the tensile modulus of a polymeric material is remarkably improved when nanocomposites are formed with CNTs. However, Fig. 1a clearly illustrates further addition (more than 1.5 wt%) of MWCNTs cannot improve tensile properties. This could be explained by the dispersion and/or agglomeration of nanoparticles. The importance of dispersion and their effect on mechanical properties of composites made with CNTs has been discussed in many research works (Breton et al., 2004; Chang et al.,

Table 4
DMRT and mean values of composites made with or without MWCNTs and MAPE.

Treatment code	Tensile strength (MPa)	Tensile modulus (MPa)	Flexural strength (MPa)	Flexural modulus (MPa)	Elongation at break (%)	Impact strength (kJ/m^2)	Water absorption (%)	Thickness swelling (%)
A1	23.6A	959B	27.3A	1066A	2.1B	4.6AB	16.2I	11.3F
	(1.6)	(26.2)	(0.8)	(124)	(0.5)	(0.4)	(1.6)	(1.0)
A2	23.9AB	983AB	27.7A	1092B	3.4BC	3.7A	13.1H	9.5E
	(0.9)	(45)	(0.7)	(102)	(0.9)	(0.7)	(2.1)	(0.6)
A3	25.9AB	907A	28.1B	1108AB	4.4BC	3.9AB	10.6G	4.9C
	(1.7)	(81)	(2.2)	(94)	(1.1)	(0.6)	(0.9)	(1.4)
A4	26.4BC	1008AB	28.7B	1120AB	−2A	3.8AB	7.5EF	3.2BC
	(1.5)	(112)	(2.1)	(176)	(0.6)	(1.1)	(1.2)	(0.8)
A5	24.7AB	905A	27.8A	1111AB	−2.8A	3.7A	3.6BC	4.6C
	(0.9)	(66.2)	(1.4)	(183)	(1.1)	(0.3)	(1.7)	(1.3)
A6	24.4ABC	964B	27A	1091BC	3.9BC	3.9A	4.6CD	5.1C
	(1.6)	(93)	(3.0)	(72)	(0.9)	(0.5)	(0.8)	(2.1)
A7	24.2AB	956B	26.7AC	1074BC	4.7C	3.7A	2.1FG	3.1D
	(2.1)	(43)	(1.5)	(202)	(1.2)	(0.6)	(0.6)	(0.9)
B1	24.0AB	1002AB	27.9A	1123ABC	5.3C	4.2AB	9.1AB	7.3BC
	(1.8)	(86)	(2.1)	(179)	(1.5)	(1.1)	(1.3)	(0.7)
B2	24.3AB	1011ABC	28.3AB	1133ABC	8.3D	4.1B	6.1DE	4.5C
	(0.7)	(102)	(1.2)	(138)	(1.0)	(0.8)	(0.8)	(0.9)
B3	26.1AB	1023ABC	29AB	1137ABC	9.1DE	4.2AB	2.6ABC	3.2ABC
	(1.1)	(79)	(3.1)	(203)	(2.1)	(0.6)	(0.9)	(1.0)
B4	27.7ABC	1040ABC	30.4ABC	1166BD	12.6E	4.3AB	1.2A	1.9AB
	(2.2)	(121)	(2.3)	(191)	(1.8)	(1.2)	(0.5)	(0.7)
B5	26.4ABC	1018ABC	30ABC	1141BD	10.8EF	4.2AB	4.2CD	3.3BC
	(0.14)	(97)	(1.9)	(82)	(2.1)	(2.0)	(1.4)	(1.3)
B6	24.8ABC	985B	28.7AB	1124ABC	−1.5A	4.2AB	3.3ABC	2.5AB
	(1.0)	(72)	(1.7)	(22)	(0.4)	(1.6)	(1.2)	(1.1)
B7	24.6ABC	971B	28.3AB	1110ABC	8.1D	3.9A	1.4A	1.3A
	(1.4)	(62)	(2.3)	(102)	(1.3)	(1.4)	(0.9)	(0.7)

Note. The numerical value in the parenthesis is standard deviation. Different letters indicate significantly different groups ($P \leq 0.01$).

2005; Coleman et al., 2006; Zhang, Shen, Phang, & Liu, 2004). Due to the high surface area of CNTs, Van-der-Waals forces which exist between the CNTs lead to the agglomeration of the nanotubes within the polymer matrix. As a result, during the mixing of the nanotubes with a resin system, only few molecules of the polymer can penetrate between the agglomerated nano-fillers and react with them. To achieve an effective reinforcement by adding carbon nanotubes, CNTs should be dispersed uniformly into the resin.

3.2. Flexural properties

The flexural strength and modulus of the composites are shown in Fig. 1b as functions of the coupling agent and nanoparticle contents. The flexural properties of the composites vary significantly with MWCNTs and MAPE contents (Table 4). Similar with the trend results of tensile properties, composites made with 1.5 wt% MWCNTs and 4 wt% MAPE showed the maximum strength and modulus of flexural, whereas composites without MWCNTs and MAPE exhibited the lowest properties. It was found that composites with 4 wt% MAPE provided significantly higher flexural strength and modulus, compared with uncoupled samples. The flexural modulus in composites is mainly a function of the modulus of individual component. Flexural modulus of MWCNTs is considerably higher than BP and HDPE, respectively. Increased flexural properties for 1.5 wt% MWCNTs loading are attributable to the high stiffness of MWCNT with high aspect ratio. In addition, the increase in flexural properties was expected due to the improved adhesion between components in the composites.

As it can clearly be seen from Fig. 1b, with increase in MWCNTs contents from 1.5 to 3 wt%, the flexural properties are considerably decreased. Tavasoli Farsheh, Talaeipour, Hemmasi, Khademieslam, and Ghasemi (2011) reported that the modulus of composites at higher CNT loading might not be increased because of the CNT agglomerates. One of the most important parameters in fabricating composites is MWCNTs dispersion in the matrix. Tube aggregation is harmful to physical and mechanical properties of the resultant nanocomposites. Use of a solvent such as acetone is the best method to prevent the nanotubes from aggregating together and improves good dispersion of CNTs in nanocomposites (Kordkheili et al., 2013).

3.3. Izod impact strength

Impact strength shows the strength of material against breakage and the start of cracking in the weakest point of the composite, which is the connecting point between lignocellulosic material and polymer matrix. Fig. 1c presents the gradual decrease of notched impact strength with the incorporation of MWCNTs from 0.5 to 4 wt%. Statistical analysis (Tables 3 and 4) also showed that the samples filled with MWCNTs had significant lower impact strengths in comparison with the neat HDPE and the control samples (without MWCNTs). The highest decrement in impact strength was observed with the addition of 3 wt% of MWCNTs, where the impact strength decreased by 6.6% than that of neat HDPE. This proves that the impact strength suffers drastically with the addition of MWCNTs filler. This can be attributed to the poor dispersion due to the tendency of MWCNTs to agglomerate among themselves probably induced cracks at the filler-matrix interface region (initiation site of crack) and led to the inability of MWCNTs to support stress transmitted from the matrix. This region increases with increasing MWCNTs loading which resulted in the increase of impact strength reduction (Eitan, Jiang, Dukes, Andrews, & Schadler, 2003). Tavasoli Farsheh et al. (2011) reported that CNTs play a major role in determining the crack initiation process by lowering the interaction between the lignocellulosic material and the coupling agent.

The reduction for MAPE-treated samples was less than specimens without it (0 wt% MAPE). For good impact strength, an optimum bonding level is necessary. Generally, the presence of BP and MWCNTs in the HDPE matrix provides points of stress concentration, thus providing sites for crack initiation.

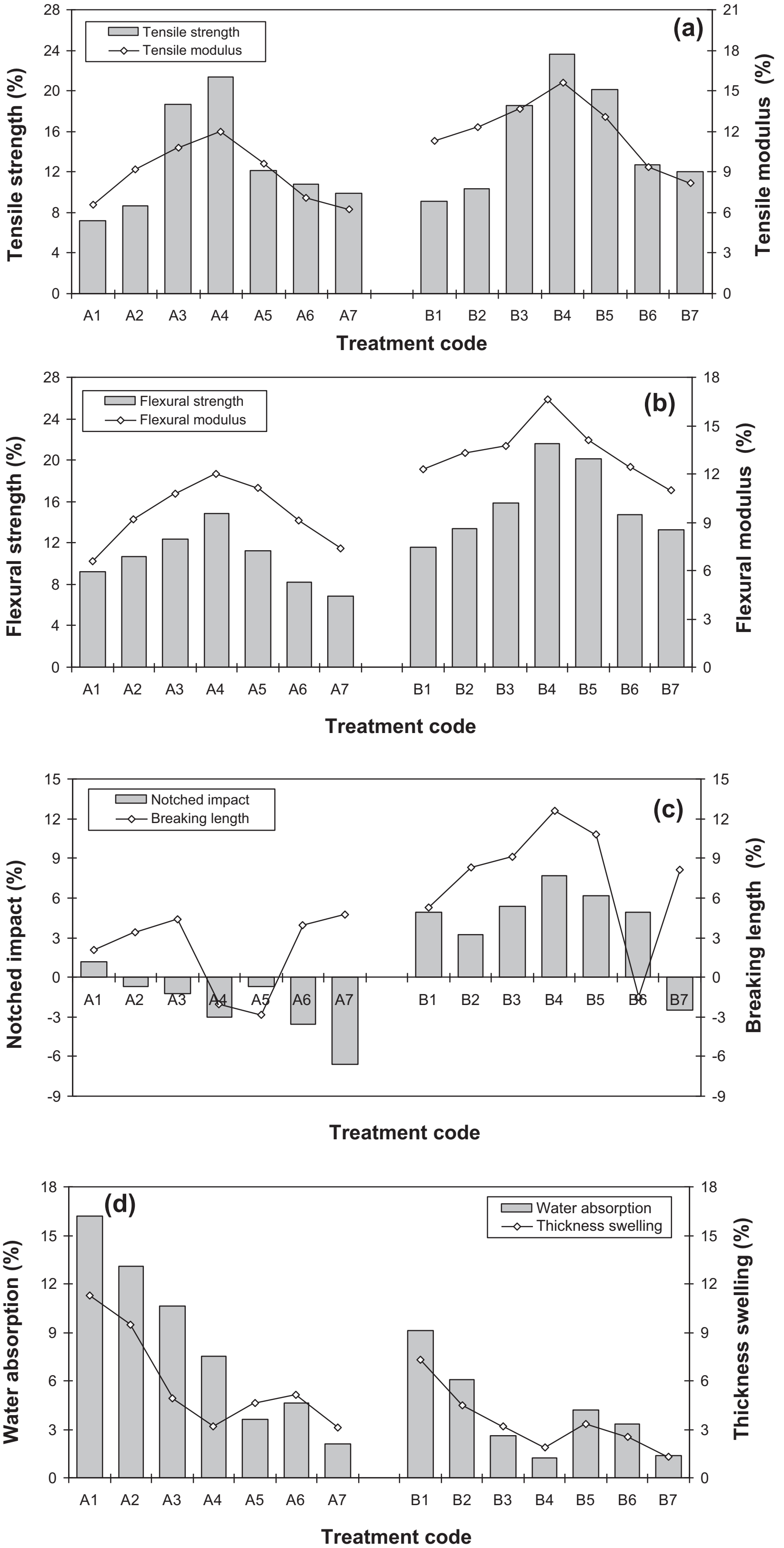

Fig. 1. Percentage of changes in the mechanical and physical properties of treated samples compared to the neat HDPE.

3.4. Water absorption and dimensional stability

The ANOVA and DMRT results of the 24-h water-soaking test for WA and TS of the composites are shown in Tables 3 and 4. It is to be noted that generally thermoplastic polymers such as HDPE do not absorb moisture due to their hydrophobic nature, indicating that moisture is absorbed by the hydrophilic woody component in the composite as well as voids and micro-gaps at the

Table 5
Analysis of variance on the effects of MWCNTs and MAPE contents and their interaction on some physical and mechanical properties.

Properties		Source of variations				
		A	B	A × B	Error	Total
Tensile strength	df	6	1	6	28	42
	SS	51.809	0.526	6.082	61.567	26766.470
	MS	8.635	0.526	1.014	2.199	
	F	3.927*	0.239	0.461		
Tensile modulus	df	6	1	6	28	42
	SS	12558.186	44603.326	15319.97	233709.2	4.185E7
	MS	2093.031	44603.326	2553.329	8346.757	
	F	0.251	5.344*	0.306		
Flexural strength	df	6	1	6	28	42
	SS	21.463	17.615	3.795	95.347	33775.6
	MS	3.577	17.615	0.632	3.405	
	F	1.051	5.173*	0.186		
Flexural modulus	df	6	1	6	28	42
	SS	19721.238	8888.595	14452.571	480668.0	5.241E7
	MS	3286.8	8888.595	2408.76	17166.71	
	F	0.518	0.191	0.990		
Elongation at break	df	6	1	6	28	42
	SS	135.85	325.929	411.868	45.727	1860.36
	MS	22.642	325.929	13.864	68.645	
	F	199.577*	13.864*	42.033*		
Impact strength	df	6	1	6	28	42
	SS	0.326	1.456	0.222	27.722	706.535
	MS	0.054	1.456	0.037	0.990	
	F	1.471	0.055	0.037		
Water absorption	df	6	1	6	28	42
	SS	524.16	192.857	114.61	36.193	2430.64
	MS	87.360	192.857	19.102	1.293	
	F	149.199*	67.584*	14.777*		
Thickness swelling	df	6	1	6	28	42
	SS	230.46	69.686	18.622	30.88	1274.61
	MS	38.410	69.686	3.104	1.103	
	F	63.187*	34.828*	2.814*		

Note. A = MWCNTs; B = MAPE; df, degree of freedom; MS, mean of squares; SS, sum of squares; *F*, *F* value.

* Significant difference at the 1% level ($P \leq 0.01\%$).

interface. In other words, as BP content was constant (30 wt%) in all blends, the different water absorptions among all the manufactured composites can be attributed to the role of MWCNTs and MAPE. Weight gain upon exposure to water decreased as the percentage of MAPE and MWCNTs increased for all composites tested. Those composites containing 4 wt% MAPE absorbed less water compared with the 0 wt% MAPE samples. As explained before, this could be possible due to a better adhesion between matrix and cellulosic materials, decrease in the velocity of the diffusional processes due to the existence of fewer gaps in the interfacial region and also more hydrophilic groups as hydroxyls are blocked by the coupling effect. This hypothesis is confirmed by SEM micrographs (Fig. 2). As clearly seen, the surface of composite without MAPE is rough while coupled sample shows a very uniform and smooth surface (Table 5).

It can be observed that the composites containing 3 wt% MWCNTs have exhibited much lower water absorption as compared with those made without MWCNTs. According to Das et al. (2000), initially, water saturates the cell wall (via porous tubular and lumens) of the fiber, and next, water occupies void spaces. Since composite voids and the lumens of BP were filled with MWCNTs, the penetration of water by the capillary action into the deeper parts of composite was prevented. Another reason for less water absorption could be the hydrophobic and water repelling nature of MWCNTs surface that tends to immobilize some of the moisture, which inhibits the water permeation in the polymer matrix as reported by Kordkheili et al. (2013). Both the mentioned mechanisms may suggest that the water absorption has occurred in the surface layer.

Fig. 1d shows thickness swelling of the composites after 24 h immersion in distilled water. It can be seen that the composite without MWCNTs and MAPE exhibited the highest thickness swelling values among other samples. In constant level of MWCNTs content, the composites with 4 wt% MAPE exhibited the least thickness swelling values. Fig. 1d also indicates that at constant level of MAPE, the composites containing MWCNTs exhibited the less thickness swelling percentage as compared with those made without it. Tavasoli Farsheh et al. (2011) reported that addition of MWCNTs to PVC/wood flour composite decreased thickness swelling and water absorption of samples.

3.5. Morphological characteristics

Fig. 2a illustrates composite with 4 wt% MAPE and without MWCNTs. As can be seen, there is no separation of the fibers from the matrix and a very good interaction between the components can be inferred from the image. The strong adhesion that is observed at the interface has been already discussed in mechanical properties of the composites and is related to the coupling agent, which encapsulated fibers in the matrix and caused strong bonding. Fig. 2b corresponds to WPC without MAPE and MWCNTs which shows some cavities in the surface that can absorb water and/or reduce mechanical properties. This indicates that the level of interfacial bonding between the BP and MAPE in the composites without coupling agent is weak.

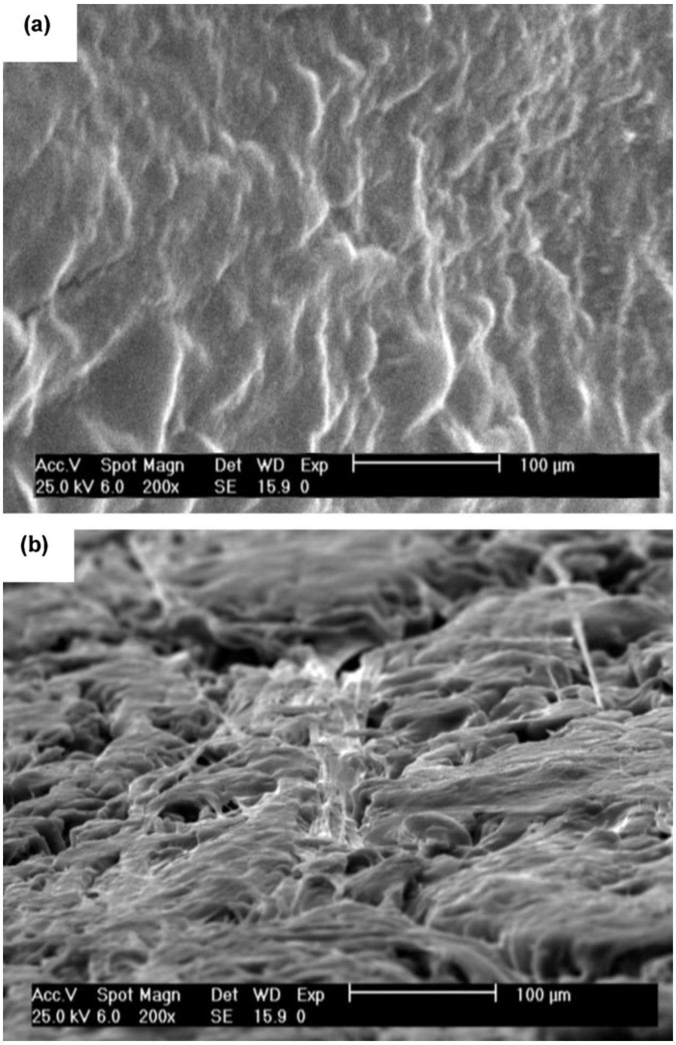

Fig. 2. SEM micrographs of (a) the surfaces of samples with 4 wt% MAPE (B1) and (b) without MAPE (A1).

4. Conclusions

This study investigated the effect of MWCNTs as well as MAPE on the physical and mechanical properties of WPCs. Some conclusions are as follows:

a) The physical and mechanical properties of the composites were improved with increase in coupling agent content, due to the better interfacial bonding between the BP and HDPE.
b) Addition of MWCNTs and MAPE improved (reduced) water absorption and thickness swelling of the composites considerably.
c) Only a small amount (0.5–1.5 wt%) of MWCNTs can improve tensile and flexural properties to a considerable level whereas further addition of MWCNTs content will no longer be effective.
d) The notched impact strength of the composites gradually decreased with increasing MWCNTs filler loading. This can be related to the increase of the probability for MWCNTs agglomeration that creates regions of stress concentrations that require less energy to elongate the crack propagation.
e) Among various treatments, composites containing 4 wt% MAPE and 1.5 wt% MWCNTs had the maximum improvements in both mechanical and physical properties.
f) The SEM micrographs provided evidence of the smoother surfaces in the composites made with MAPE. This was attributed to the better encapsulation of BP fibers by the HDPE matrix.

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