Physical and Mechanical Properties of Walnut Shell Flour-Filled Thermoplastic Starch Composites

Narjes Abdolhosseini Sarsari, Shademan Pourmousa,* and Ajang Tajdini

The goal of this work was to evaluate the technical feasibility of walnut shell flour (WSF) as substitute for wood in walnut shell flour/thermoplastic starch (WSF/TPS) composites. The effects of walnut shell flour (WSF), thermoplastic starch (TPS), and nanoclay on the physical and mechanical properties of WSF/TPS composites were investigated. The composite samples were formed in a Colin extruder with four-chamber heat with temperatures. Then, test samples were made using injection molding. The addition of up to 40% WSF greatly improved the tensile strength, flexural strength, and elasticity modulus of the composite. Also, the composites made with higher WSF contents had increased thickness swelling and water absorption. The incorporation of nanoclay (0% to 5%), greatly improved the tensile properties. Soil burial degradation experiments showed that biodegradation was accelerated by the increase of starch in the composite mixtures. The study showed that WSF can be successfully utilized for the manufacture of composites with useful physical and mechanical properties.

Keywords: Nanocomposites; Walnut shell flour; Thermoplastic corn starch; Nanoclay; Physical properties; Mechanical properties

Contact information: Department of Wood and Paper Science and Technology, Agricultural and Natural Resources Faculty, Azad Islamic University, Karaj Branch, P. O. Box 31485-313, Karaj, Iran;
** Corresponding author: sh.pourmousa@gmail.com*

INTRODUCTION

Recently, the demand for biodegradable materials made from renewable resources has been increasing due to the increase in the prices of raw materials, especially those obtained from the oil and natural gas sector, and environmental concerns related to non-renewable resources. Many synthetic polymers are estimated to require 50 decades to fully decompose, and polymeric wastes pose a great threat to the environment because of their non-degradability and microbial resistance (Obasi 2015).

Starch is a natural biopolymer that is frequently used as a substitute for the petrochemical-base non-biodegradable plastic materials in environmentally friendly packaging materials. Native starch is not a true thermoplastic, but it can be converted into a plastic-like material called thermoplastic starch (TPS). Biodegradable composites produced with pure TPS have poor mechanical properties, and they are more hygroscopic than composites made with synthetic polymers due to the hydrophilic nature of the components (Müller *et al*. 2012). These problems, along with the necessity of reinforcing and substitutions, has prompted the use of agricultural residues in biodegradable composites with varying properties (Ashori and Nourbakhsh 2010; Ahankari *et al.* 2011). Agro-waste composites offer excellent engineering potential because they are light-weight, environmentally friendly, economical, renewable, and abundant and have high strength and rigidity, and they provide a plausible environmental solution to municipal waste disposal

(Pirayesh *et al*. 2012; Zahedi *et al*. 2015). Some combinations of agricultural wastes such as palm kernel shell, coconut shell, walnut shell flour, cocoa pod husk, oil palm agro wastes, peanut shell, rubber seed shell flour, almond shell flour, and thermoplastic materials have been successfully developed (Malkapuram *et al.* 2009; Pirayesh *et al.* 2012; Pirayesh *et al*. 2013; Chun *et al.* 2013; Salmah and Ismail 2013; Obasi *et al.* 2014; Zaaba *et al.* 2014; Mohd Suhaimi and Ismail 2014; Zahedi *et al.* 2015).

Walnut (*Juglans regia* (L.)) is an important crop that is cultivated for its edible nuts in temperate regions. After China, Iran ranks 2nd in walnut production, producing about 454,000 metric tons of walnut from 2013 to 2014 (FAO 2015). Consequently, walnut shells, as agricultural by-products, are abundant in Iran. To date, walnut shells have had no economic value or industrial usage in Iran. Normally they are incinerated or dumped without control due to logistic problems such as seasonal production in small-scale factories, transport costs, and lack of bioenergy plants (Pirayesh *et al.* 2012).

Compared with cellulosic materials, walnut shells contain lower amounts of the hygroscopic materials (cellulose and hemicellulose) and higher amounts of the hydrophobic materials (lignin). The chemical composition of walnut shell fibers includes cellulose (23.9%), hemicellulose (22.4%), lignin (50.3%), and ash (3.4%) (Zahedi *et al.* 2015). Because of the lower amounts of hygroscopic materials and higher amounts of hydrophobic materials in walnut shell compared with wood, polymer-based composites containing walnut shell filler have notable competitive advantages in outdoor applications that demand a high dimensional stability, such as decking or siding (Pirayesh *et al.* 2013).

Much attention has also been devoted to agrowaste-reinforced biodegradable matrices, such as poly (lactic-acid) (Anuar *et al.* 2012), thermoplastic starch copolymers (Moriana *et al.* 2011), poly(butylene succinate) (Thirmizir *et al.* 2011), and starch-grafted-polypropylene/kenaf fibers composites (Hamma *et al.* 2014).

The physical and mechanical properties of thermoplastic bio-composites depend on the interaction between the natural filler and the thermoplastic material, and the incompatibility between the hydrophilic natural filler and hydrophobic thermoplastic matrix is often an issue (Obasi *et al.* 2014). Polar hydroxyl groups in the natural filler hinder wetting by the nonpolar polymer matrix, which often leads to poor mechanical properties after blending (Tserki *et al.* 2005).

The addition of small amounts of nanoclays can enhance water resistance as well as mechanical properties of both thermoplastic and thermoset-based wood composites (Chan *et al.* 2011; Valente *et al.* 2011; Ferreira *et al.* 2011). The incorporation of nanoclay in starch-based materials improves the barrier and mechanical properties of the composites (Dean *et al.* 2007; Kampeerapappum *et al.* 2007; Ardakani *et al.* 2010). However, these improvements are strongly linked to the hydrophilic or hydrophobic nature of clay, due to the hydrophilic characteristic of starch (Müller *et al.* 2012). To improve the properties without interfering with the biodegradability of the composites, the reinforcement of starch with nanoscale minerals has been considered. Natural montmorillonite (MMT) with TPS is an interesting alternative to the production of nanocomposites with starch because, due to their hydrophilic nature, these materials exhibit good mutual dispersion. Yu *et al.* (2006) reported on the preparation and properties of starch/MMT nanocomposites prepared with thermoplastic corn starch and activated MMT by the melt intercalation method. Transmission electron microscopy (TEM) results indicate that the MMT layers become exfoliated and uniformly dispersed in the starch matrix at the nanometer level. Tensile strength and Young's modulus increased proportionally with increased filler content up to 8%. Water resistance of the nanocomposites also improved. The improvement in exfoliated

nanocomposite starch has been attributed to the high aspect ratio and homogeneous dispersion of MMT in the polymer matrix.

In this study, walnut shell flour and nanoclay fillers were added to thermoplastic starch (TPS) to enhance the mechanical and biodegradable properties of polymeric bio-composites. The objective was to investigate the effect of walnut shell flour and nanoclay filler content on physical and mechanical properties and environmental biodegradability of the walnut shell flour/thermoplastic starch (WSF/TPS) composites.

EXPERIMENTAL

Materials

Thermoplastic corn starch (TPS)

Thermoplastic corn starch flour (28% amylose, with 11% moisture) with a melt flow rate (MFR) of 3 g/10 min and a density of 1.3 g/cm^3 was supplied by Kimya Chimi Zangan Co. (Tehran, Iran).

Lignocellulosic material

The walnut shells were supplied from dry fruit walnut manufacturer (Cellulose Aria Co (Tehran, Iran). Prior to their use, the shells were cleaned of dirt and impurities and ground into flour using a Thomas-Wiley mill (Model 3383L10, Swedesboro, NJ, USA). Particles that passed through a 40-mesh screen but were retained on the 60-mesh screen were used. The particles were dried in a laboratory oven at 103 ± 2 °C for 24 h to reach 1% to 3% moisture content.

Nanoclay

Powdered organophilic montmorillonite (MMT; Cloisite® 15A, was purchased from Southern Clay Products Inc. (Texas, USA) and used as the nanoparticle. The MMT was modified with the quaternary ammonium salt dimethyl, dehydrogenated tallow, 2-ethylhexyl quaternary ammonium (CEC = 125 meq/100 g clay, d_{001} = 31.5 Å) (HT = hydrogenated tallow), with an approximate composition (by mass) of 65% C18, 30% C16, and 5% C14 (Zahedi *et al*. 2015).

Coupling agent

Powdered maleated anhydride grafted polypropylene (MAPP) (grade PP-G 101 with a density of 0.91 g/cm^3 and a melt flow index of 64 g/10 min) was obtained from Kimia Javid Sepahan Co., (Esfahan, Iran). This non-biodegradable copolymer was used to improve the possible interfacial adhesion interfacial adhesion between the WSF filler and the TPS matrix.

Methods

Sample preparation

The formulations of the composites and their weight fractions used for the respective blends are given in Table 1. Prior to compounding, the walnut shell flour (WSF) was oven-dried at 100 °C for 24 h to remove any additional moisture. The thermoplastic starch (TPS) was prepared with corn starch and glycerol (Kimya Baspar Asia Co., Tehran, Iran) using 0.25 g of glycerol per gram of starch. The starch, glycerol, and nanoclay (NC) were mixed in a domestic mixer for 15 min before being extruded.

Compounding was performed in a Haake internal mixer (HIB, sys 90, NJ, USA). The walnut shell filler (WSF) and thermoplastic starch (TPS) were melt-blended in a co-rotating twin-screw extruder (Model T20, 1990, Dr. Collin GmbH, Germany) at temperatures of 160 °C, 170 °C, and 180 °C with a screw speed of 60 rpm. Maleated polypropylene (MAPP) was used as the compatibilizer at 3 wt. %. After melt blending in the Haake mixer, the mixed materials were cooled for about an hour at room temperature and then ground using a pilot scale grinder (Wieser Company, WGLS 200/200 Model, MA., USA).

The granulated samples were dried for 12 h at 100 °C in an oven prior to injection molding. Finally, the composite samples were produced using an injection molding machine (Imen Machine Aslanian Company, Tehran, Iran) at a melting temperature of 160 °C, a molding temperature of 40 °C, an injection pressure of 10 MPa, and cooling time of 20 s.

The sheets were oven-dried over night at 70 °C to reduce moisture content and then stored in air-tight containers for at least 40 h according to ASTM D618-13 (2013).

Table 1. Formulation of the Composites

WSF (wt.%)	TPS (wt.%)	NC (wt.%)	MAPP (wt.%)
0	100	0	0
0	97	0	3
	94	3	
	92	5	
30	67	0	
	64	3	
	62	5	
40	57	0	
	54	3	
	52	5	
50	47	0	
	44	3	
	42	5	

Characterizations

Tensile and flexural test

Tensile and flexural tests were carried out using a universal Instron testing machine (Model 1186, Instron Corp, Canton, Mass, USA), according to ASTM D638-10 (2010), and ASTM D790-10 (2010) respectively, with the samples obtained as described. Tensile properties were measured at room temperature at 5 mm/min crosshead speed to obtain the tensile strength and elasticity modulus. The flexural strength and modulus was evaluated in accordance with ASTM D790-10 (2010) with a three-point bending geometry at a crosshead speed of 2 mm/min and a load cell of 1 kN.

Impact test

The impact test was conducted on notched rectangular samples according to ASTM D256-10 (2010) using a Zwick impact tester (Model 5102, Germany) with a 4.0 J hammer.

Water absorption test

The water absorption study of the composites was determined according to ASTM D7031-11(2010). Cut samples of dimensions 20 × 20 × 20 mm^3 were dried in a vacuum at 45 °C for 24 h, weighed to get the initial dry weight to the nearest 0.001 g, and then immersed in distilled water for a period of 63 days. The weight of each sample was measured every seven days to obtain the change in weight. The percent water absorption (%WA) was calculated as in Eq. 1:

$$\text{Water Absorption (\%WA)} = \left[100\left(\frac{\text{Final dry wt. after immersion}}{\text{Initial dry wt. before immersion}}\right) - 1\right] \quad (1)$$

Thickness swelling test

The initial thickness of each sample was measured using a digital veneer caliper. After a 7-day immersion in distilled water at room temperature, the sample was dried before its new thickness was measured. The percent thickness swelling (%TS) was determined as follows:

$$\text{Thickness Swelling (\%TS)} = \left[100\left(\frac{\text{Final thickness}}{\text{Initial thickness}}\right) - 1\right] \quad (2)$$

Soil burial degradation experiments

Soil burial is a traditional and standard method for degradation because of its similarity to actual conditions of waste disposal (Laxmeshwar *et al.* 2012). Sample biodegradability was studied by weight loss over time in a soil environment. Specimens of each composite were placed in a series of perforated boxes containing moisturized soil. The specimens (20 × 20 × 100 mm^3) were buried 150 mm beneath the surface of soil, which was regularly moistened with distilled water. The samples were removed at predetermined time points, washed with water several times to stop the degradation, dried at room temperature to a constant weight, and then stored in darkness until testing. The buried samples were removed at 8, 12, 16, and 20 weeks, washed with water, and dried in a vacuum oven at 50 ± 1 °C for 24 h before evaluation. The samples were then weighed to determine the average weight loss as follows:

$$\text{Weight Loss (\%WL)} = \left[100\left(\frac{\text{Final weight}}{\text{Initial weight}}\right) - 1\right] \quad (3)$$

Statistical analysis

The experimental design consisted of two variable factors (namely WSF and NC) and their interaction. Data for each treatment were statistically studied through analysis of variance (ANOVA), and the comparison of the means was done employing Duncan's multiple range test (DMRT) to identify the groups that were significantly different from others at 95% confidence levels. Average values were obtained from five runs for each sample test.

RESULTS AND DISCUSSION

The experiments and statistical analysis showed that both physical and mechanical properties were significantly influenced by the increased WSF loading and nanoclay

content (Table 2). According to the Duncan's multiple range tests, the differences between the mean values of the studied properties, the effects of WSF loading and nanoclays content, and their interaction on some physical and mechanical properties were significant (Table 3).

Table 2. ANOVA of WSF/TPS Composite Physical and Mechanical Properties

		MS									
Sources of Variations	df	MORb	MOEb	MORt	MOEt	Impact	WA (2 h)	WA (24 h)	TS (2 h)	TS (24 h)	WL
WSF	2	10.06**	0.59*	9.68**	0.52*	4.01**	0.54*	1.18*	1.26*	0.73*	0.45*
NC	2	25.16*	0.72*	7.06*	0.61*	2.15*	0.48*	0.56*	0.62*	0.29*	0.22*
WSF× NC	4	3.28*	0.53*	2.94*	0.48*	0.54*	0.21*	0.19*	0.28*	0.21*	0.17*
Error	18	1.06	0.10	0.84	0.10	0.33	0.13	0.29	0.39	0.22	0.17
	27										

WSF, walnut shell flour; df, degree of freedom; MS, mean of squares; MOR, modulus of rupture; MOE, modulus of elasticity; WA, water absorption; TS, thickness swelling; WL, weight loss. *Significant difference at the 5% level (P < 0.05%); ** Significant difference at the 1% level (P < 0.01%)

Table 3. DMRT and Mean Values of Physical and Mechanical Properties of WSF/TPS Composites

Types of Composites	MORb (MPa)	MOEb (MPa)	MORt (MPa)	MOEt (MPa)	Impact Strength (J/m)	WA 2h (%)	WA 24h (%)	TS 2h (%)	TS 24h (%)
WSF0 TPS 100 NC 0 MAPP 0	12.45 ^{c}	1028 ^{c}	3.78 ^{c}	1121 ^{c}	3.25 ^{c}	7.14 ^{b}	8.28 ^{b}	7.62 ^{b}	9.75 ^{c}
WSF 0 TPS 97 NC 0 MAPP 3	13.44 ^{c}	1131 ^{c}	4.46 ^{c}	1239 ^{c}	3.96 ^{c}	7.31 ^{b}	8.00 ^{b}	7.79 ^{b}	9.36 ^{c}
WSF 0 TPS 94 NC 3 MAPP 3	13.21 ^{c}	1167 ^{c}	4.51 ^{c}	1457 ^{c}	3.01 ^{c}	6.23 ^{c}	6.89 ^{c}	7.55 ^{b}	7.92 ^{c}
WSF 0 TPS 92 NC 5 MAPP 3	14.11 ^{c}	1200 ^{c}	4.78 ^{c}	1439 ^{c}	4.31 ^{c}	5.79 ^{c}	6.96 ^{c}	7.88 ^{b}	7.85 ^{c}
WSF30 TPS 67 NC 0 MAPP 3	19.66 ^{b}	2456 ^{b}	5.66 ^{b}	1678 ^{b}	4.92 ^{c}	8.44 ^{b}	10.21 ^{a}	8.03 ^{b}	13.93 ^{b}
WSF30 TPS 64 NC 3 MAPP 3	20.38 ^{b}	2523 ^{b}	5.89 ^{b}	1859 ^{b}	7.13 ^{b}	6.20 ^{c}	8.67 ^{b}	5.99 ^{c}	9.44 ^{c}
WSF30 TPS 62 NC 5 MAPP 3	21.45 ^{ab}	2730 ^{b}	5.92 ^{b}	1930 ^{b}	7.53 ^{b}	5.93 ^{c}	7.90 ^{b}	5.36 ^{c}	6.97 ^{d}
WSF40 TPS 57 NC 0 MAPP 3	23.77 ^{a}	3166 ^{ab}	6.23 ^{ab}	2689 ^{a}	5.27 ^{c}	9.62 ^{a}	11.28 ^{a}	8.51 ^{b}	15.79 ^{a}
WSF40 TPS 54 NC 3 MAPP 3	23.44 ^{a}	3376 ^{ab}	6.42 ^{ab}	2984 ^{a}	8.56 ^{a}	6.95 ^{c}	7.69 ^{b}	7.78 ^{b}	13.40 ^{a}
WSF40 TPS 52 NC 5 MAPP 3	24.46 ^{a}	3561 ^{ab}	6.78 ^{ab}	3128 ^{a}	9.14 ^{a}	6.23 ^{c}	7.51 ^{b}	7.40 ^{b}	12.37 ^{b}
WSF50 TPS 47 NC 0 MAPP 3	22.13 ^{a}	3144 ^{ab}	7.45 ^{a}	3087 ^{a}	6.29 ^{b}	10.78 ^{a}	11.15 ^{a}	10.87 ^{a}	16.57 ^{a}
WSF50 TPS 44 NC 3 MAPP 3	25.49 ^{a}	4209 ^{a}	7.70 ^{a}	3491 ^{a}	6.54 ^{b}	10.67 ^{a}	11.94 ^{a}	7.99 ^{b}	14.50 ^{a}
WSF50 TPS 42 NC 5 MAPP 3	26.09 ^{a}	4651 ^{a}	8.23 ^{a}	3511 ^{a}	6.28 ^{b}	9.63 ^{a}	11.48 ^{a}	6.68 ^{c}	12.44 ^{b}

Flexural and Tensile Strength

As shown in Table 3, the effect of WSF and NC contents and their interactions on both of the flexural strengths and tensile strengths were determined to be significantly different. The highest modulus of rupture in flexural and tensile tests, MORb (26.09 MPa and 25.49 MPa) and MORt (8.23 MPa and 7.70 MPa), were obtained for WSF/TPS composites produced using 50% WSF and 3 wt% to 5 wt% NC contents, respectively. Figure 1 shows that walnut shell flour increased the flexural strength and tensile strength of thermoplastic starch composites. Composites made with 3% and 5% NC and 50% WSF showed the highest strength in both of the flexural and tensile tests, whereas the lowest modulus of rupture in the flexural and tensile tests, MORb (12.45 MPa and 13.44 MPa) and MORt (3.78 MPa and 4.46 MPa), were measured for composites containing 100% thermoplastic starch. Thus, increasing the WSF contents in the thermoplastic starch mixture significantly increased the MORb and MORt values of WSF/TPS composites compared with the neat TPS composites.

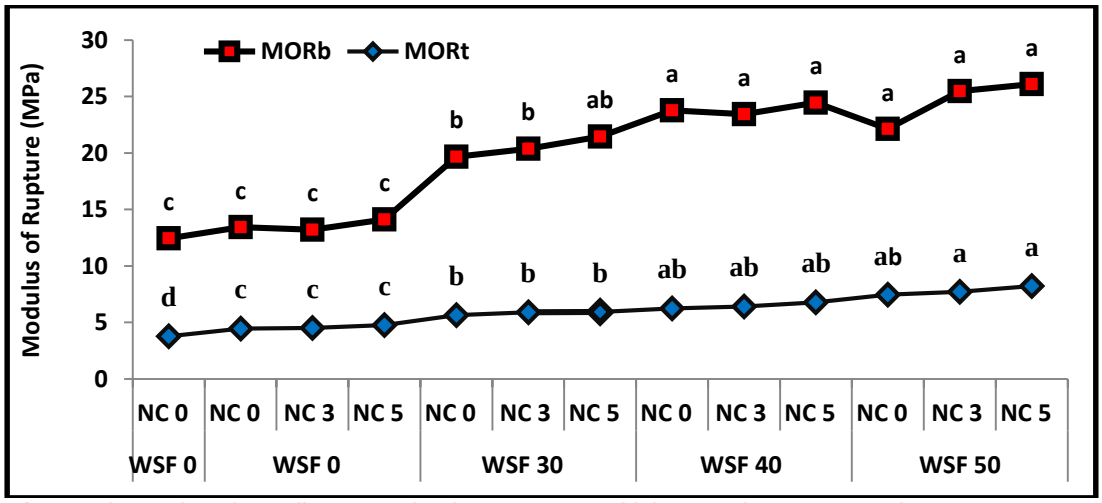

Fig. 1. Flexural and tensile strengths (MORt & MORb) in WSF/TPS composites

Flexural and Tensile Elasticity modulus

Comparing the mean flexural and tensile elasticity modulus results in Table 2 showed that both values were significantly influenced by the WSF loading, NC content, and their interactions. All WSF/TPS composites types showed statistically meaningful differences ($P < 0.05$) from each other in their MOEb and MOEt mean values. The MOE mean values showed similar trends to the results of the MOR mean values. The MOEb mean values of WSF/TPS composites ranged from 1028 MPa to 4651 MPa, and the MOEt mean values ranged from 1121 MPa to 3511 MPa. Depending on the amount of WSF in the thermoplastic starch matrix, the mean values of MOEb and MOEt increased compared with the mean values of those obtained from composites fabricated of the neat TPS, without WSF and NC fillers (Fig. 2). The MOEb of WSF/TPS the composites made with 30%, 40%, and 50% WSF had 2.17 to 2.41, 2.80 to 3.50, and 2.78 to 4.11 times higher, respectively, than the MOEb of the WSF/TPS composites made with neat TPS composites. The same trend, albeit with a slower slope, can be seen in the MOEt mean values. In comparison, the MOEt mean values of WSF/TPS composites made with 30%, 40%, and 50% WSF were 1.28 to 1.47, 2.05 to 2.38, and 2.35 to 2.67 times higher respectively, than those obtained from neat TPS composites.

The interaction effects of WSF and NC content on both of the flexural and tensile modulus (MOEb and MOEt) in WSF/NC composites, made with 3% and 5% NC and 50% WSF, showed the maximum mean values for flexural modulus (3.64 GPa and 3.36 GPa) and tensile modulus (2.85 GPa and 2.77 GPa), whereas composites without NC and containing 30% WSF exhibited the lower modulus (2.92 GPa and 2.48 GPa, respectively, for MOEb and MOEt).

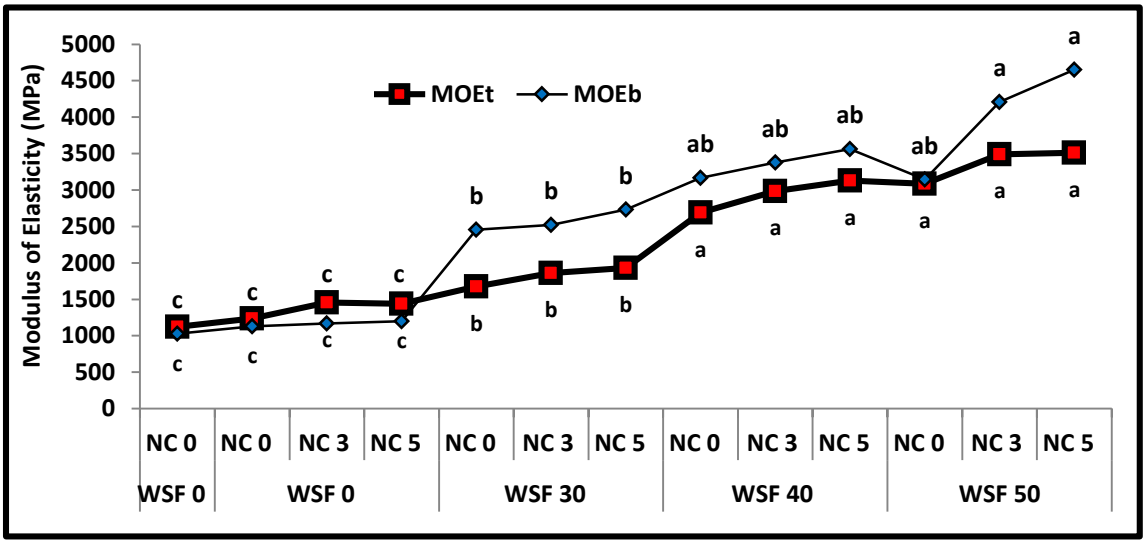

Fig. 2. Flexural and tensile flexural modulus (MOEt & MOEb) in WSF/TPS composites

This result showed that the addition of walnut shell flours in the mixture of TPS composites had an appropriate effect on the mean values of MOE and MOR. Fiber loading was an influential factor in WSF/TPS composite properties. In general, both properties of the composite specimens were increased when the WSF content increased from 30% to 50% by weight, and this increase was associated with the addition of 3% and 5% nanoclays. This result agrees with previous studies using natural fillers blended with synthetic polymers. Tawakkal *et al.* (2012) observed an appreciable increase in the flexural strength of the composite from 10 wt% to 60 wt% kenaf-derived cellulose (KDC) compared with neat polylactic acid (PLA), but they noticed that above 50 wt% KDC, the flexural strength decreased with increasing KDC content. A similar trend was also observed by Rahman *et al.* (2010) where the flexural strength increased with rice husk (RH) filler addition up to 35 wt%; beyond that, the flexural strength decreased.

As shown in Figs. 1 and 2, tensile and flexural properties were improved with the addition of nanoclays. The flexural modulus in composites was mainly a function of the modulus of individual components. When NC loading increased up to 5 wt%, flexural strength and modulus improved. Improved mechanical properties of the samples containing up to 5 wt% NC loading may be attributed to the high stiffness of clay platelets and the lower percolation points created by the high aspect ratio organo-clays. As mentioned in other studies, the beneficial effects could be attributed to two factors. Firstly, the high surface area of the silicate layers in the polymer matrix resulted in a higher extent of interaction with the polymer chains. Secondly, good interfacial adhesion between the nanoscale clay particles and the TPS matrix caused the mobility of polymer chains to be restricted under loading (Khanjanzadeh *et al.* 2012). Khanjanzadeh *et al.* (2012) indicated that the nanoclay was dispersed more uniformly through the polymer matrix at low

concentrations (3 wt%) to increase the surface attraction between the clay and the polymer matrix. The cited authors suggested that this behavior is the agglomeration/clogging of the nanofillers or the filler-filler interaction, resulting in induced local stress concentration in the nanocomposites. Agglomeration might also reduce the clay aspect ratio and reduce the contact surface area between the organoclay and the polymer matrix. Agglomeration of the nanoparticles within the polymer matrix happens due to the high surface area of the nano-particles and van der Waals forces between them (Ashori *et al.* 2013). Park *et al.* (2003) also tested the effect of the filler concentration of the TPS/clay hybrid with Cloisite Na^+ and Cloisite 30B. The results indicated that both the tensile and water vapor barrier properties were generally increased with increasing clay content. McGlashan and Halley (2003) tested the use of nanoscale MMT in thermoplastic starch/polyester blends, finding excellent improvements in film blow-ability and tensile properties. *Yixiang et al.* (2005) showed that the addition of organo-clays into a starch acetate matrix influenced the mechanical properties of the hybrid. Huang *et al*. (2004) reported on the preparation and properties of starch/MMT nano composites prepared with thermoplastic corn starch and activated MMT by the melt intercalation method. Their results indicated that the MMT layers were exfoliated and uniformly dispersed in the starch matrix at the nanometer level. Tensile strength and Young's modulus increased proportionally with the increase in filler content up to 8%. In the present study, the flexural and tensile strength of WSF/TPS composites was improved by 40% by the incorporation of 3 wt% and 5 wt% NC, which was attributed to a well-formed interface allowing better stress transfer from the matrix to the filler.

Impact Strengths

Analyses of impact strengths are shown in Tables 2 and 3. The highest mean values of impact strengths (9.14 J/m) were obtained for the WSF/TPS composite samples produced using 30% and 40% WSF and 3 wt% up to 5 wt% NC contents, respectively. There was a reduction in impact strength in composites made of 50% WSF. There was an increase in impact strength for composites that contained 3 wt% and 5 wt% nanoclays compared with the samples without nanoclay. Figure 3 shows that the addition of WSF contents increased the impact strengths of composites.

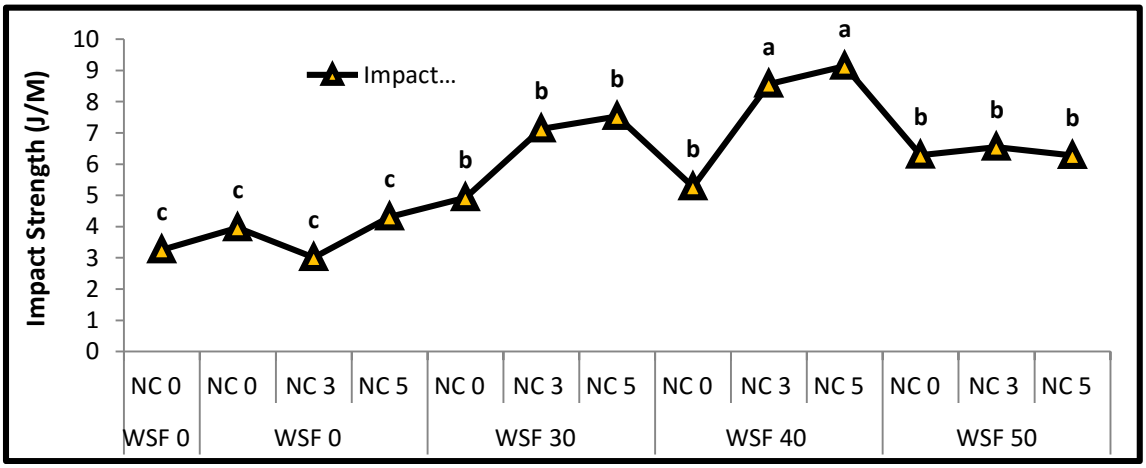

Fig. 3. Means of impact strengths in WSF/TPS composites

Similar results were also obtained for different polymer composites containing 3 wt% to 5 wt% natural filler content; higher contents caused the impact strength to drop (Lou *et al.* 2007; Rahman *et al.* 2010; Tawakkal *et al.* 2012; Obasi 2015). The decrease in impact strength indicated that the amount of matrix was probably not sufficient to transfer the stress effectively during a sudden impact in combination with the lower absorption characteristic of the filler (Tawakkal *et al.* 2012). In another study by Obasi (2015), high filler content increased the chances of fiber agglomeration, which resulted in regions of stress concentration requiring less energy for crack propagation (Sreekumar *et al.* 2007).

Water Absorption

The results of the ANOVA test and Duncan's mean separation test for thickness swelling (TS) and water absorption (WA) of WSF/TPS composites made using the mixture of TPS and WSF for 2 h and 24 h water immersion times are given in Table 2. The WA mean values of all composites types showed significant differences ($P < 0.05$) from each other. The WA values of the WSF/TPS composites containing WSF, after 2 h water immersion time, shifted up 5.79% to 11.14% compared with composites made from 100% TPS. Likewise, for 24 h water immersion time, these figures were 6.96% and 12.28%, respectively (Table 3).

The water absorption values observed in the WSF/TPS composites after 2 h and 24 h water immersion times are shown in Fig. 4. As expected, incorporation of WSF improved the water repellency of the composites. The composites produced using 50% WSF exhibited the highest amount of water absorption. This result was expected due to the hydrophilic nature of cellulose fibers; hydrogen bonds formed between water molecules and the free hydroxyl groups present in the cellulose and hemicelluloses of WSF. These results were simillar to the results of Khanjanzadeh *et al.* (2012), which showed that increasing almond shell flour (ASF) content in the mixture of polypropylene-based hybrid composites caused the formation of more water residence sites (OH groups), resulting in more absorbed water. As mentioned in Zahedi *et al.* (2015), the mechanisms of water uptake in a composite include diffusion through the matrix, capillarity through natural fibers, or movement *via* porosities in the matrix or at the fiber-matrix interface. Consequently, water absorption depends not only on the relative hydrophilic character of the fiber and the matrix, but also on the fiber-matrix interphase and the morphology of the composites.

The composites filled with nanoclays generally absorbed less water at 2 h and 24 h, respectively, than the untreated ones. Similarly, organically modified montmorillonite (OMMT) in the almond shell flour-polypropylene (ASF/PP) composites acts as a barrier medium that hinders water flow into the composite from all directions, thus resulting in decreased equilibrium water content (Zahedi *et al.* 2015). It seems that because of decreasing the available space for water absorption due to the occupation of void spaces in the textures, nanoclays acted according to the known mechanism for the lower water uptake of nanocomposites. Simillar results have been reported by Khanjanzadeh *et al.* (2013) and Zahedi *et al.* (2015). As mentioned by others, NC most likely acted as barrier, providing prolonged pathways for the water molecules and reducing the hydrophilicity (Alexandre *et al.* 2006). Alternatively, nanoparticles could obstruct the capillaries in WSF so that water cannot flow (Shi *et al.* 2007).

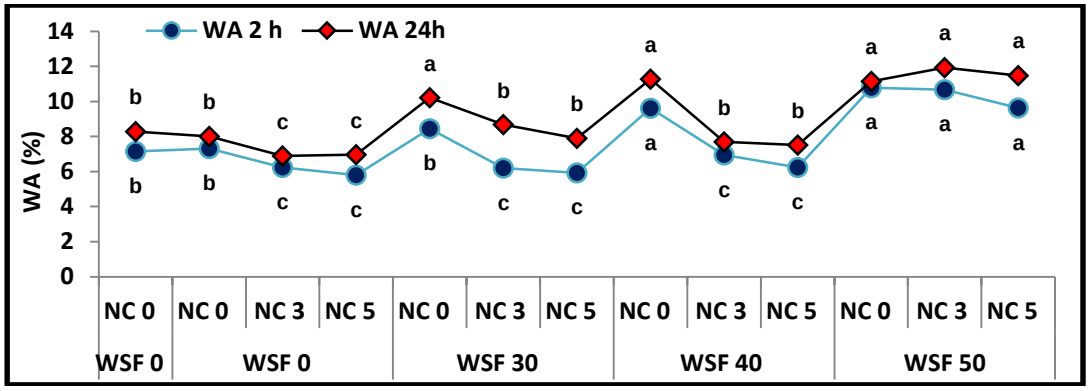

Fig. 4. Means of water adsorption after 2 h and 24 h (WA 2 h & WA 24 h) in WSF/TPS composites

Thickness Swelling

Thickness swelling (TS) of WSF/TPS composites ranged from 5.36% to 10. 87% and 6.97 to 16.57% after 2 h and 24 h water immersion, respectively. The TS results were similar to those of WA (Fig. 5). Statistical analysis showed that the TS was significantly different ($P < 0.05$) for WSF/TPS composites at various contents of WSF and NC fillers (Table 2). Furthermore, composites with higher percentages of WSF were more susceptible to the thickness swelling. This effect might be due to the increase of WSF content in the composite formulation. Ayrilmis *et al.* (2013) reported that wood fibers were primarily responsible for thickness swelling and water absorption in WPCs.

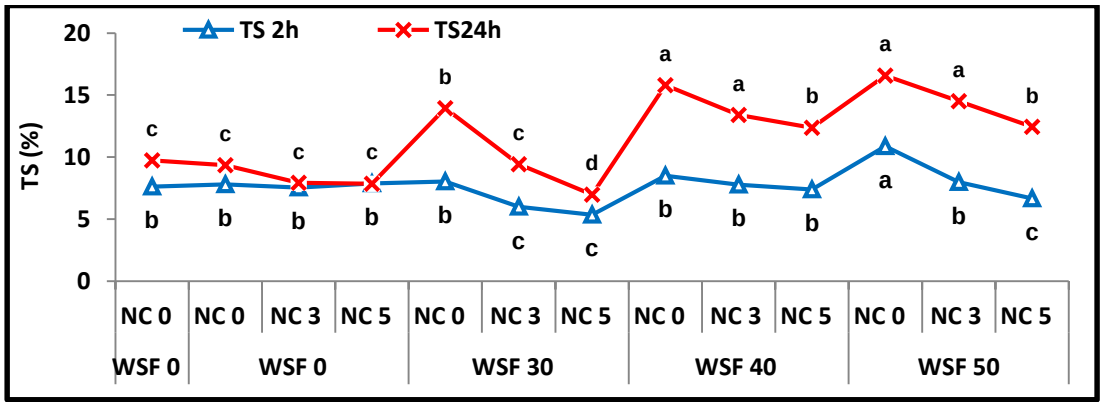

Fig. 5. Means of thickness swelling after 2 h and 24 h (TS 2 h & TS 24 h) in WSF/TPS composites

The thickness swelling of the composites increased with the water absorption, and thus, had a trend similar to that of the water absorption. The composite without NC and 50% WSF exhibited the highest TS values (10.87% and 16.57% after 2 h and 24 h water immersion, respectively). At 5% NC, the composites with 30 wt% WSF exhibited the lowest TS values. Figure 5 also indicated that at constant level of WSF, the composites containing NC exhibited less TS than those without NC. These results are consistent with other reports (Kord *et al.* 2010; Ashori and Nourbakhsh 2011; Valente *et al.* 2011; Khanjanzadeh *et al.* 2012).

Weight Loss

As shown in Fig. 6, the weight loss in all samples increased as the amount of starch increased in the composite. The highest amount of weight loss occurred in composites made with neat starch. The presence of walnut shell flour caused a significant increase in their natural durability. It seems that the presence of large amounts of lignin in combination walnut shell flour helped to decrease the weight loss of WSF/TPS composites in soil burial degradation test. The possible reason for the lower weight loss of WSF/TPS specimens could be the broken down nature of the starch structures, such that they no longer were effective against to damaging fungus in the soil.

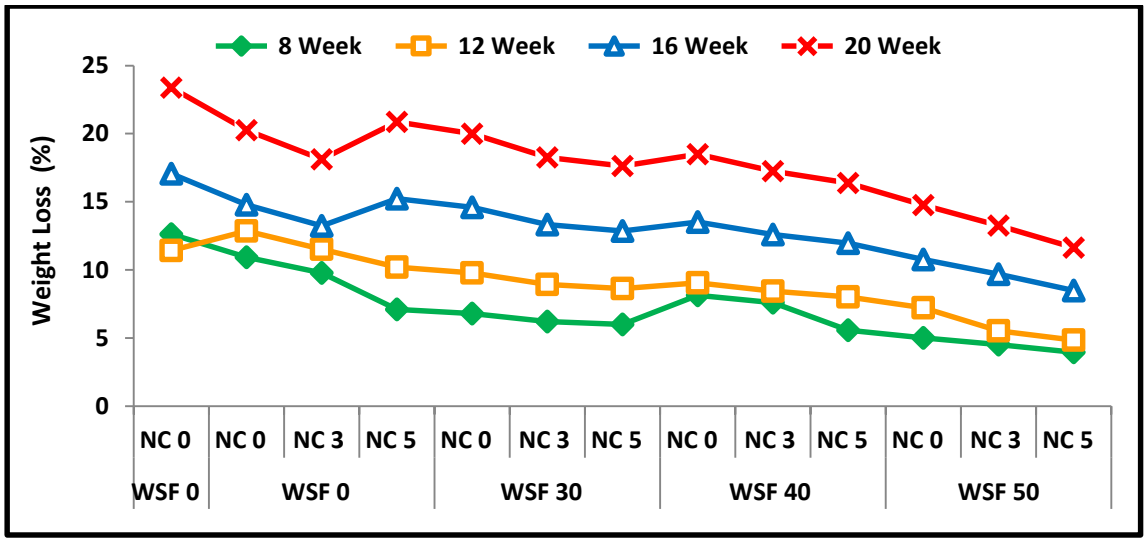

Fig. 6. Weight loss of samples buried in soil for 8, 12, 16, and 20 weeks

The results showed that use of walnut shell flour in mixtures of WSF/TPS composites not only improved the mechanical and physical properties, but also increased their biodegradability. These effective advantages are not as easily achieved when composites are formulated from oil derivatives. Due to these positive and beneficial effects, it is concluded that the utilization of walnut shell as a natural filler in starch biopolymer composites will foster a new application route in the conversion of agro wastes to useful resources for the use of these materials to form new classes of green composites. This promotes the universal call for improved environmental sustainability through the reduction of municipal solid wastes and "waste to wealth" generation.

CONCLUSIONS

1. The study showed that walnut shell flour (WSF) can be successfully utilized together with thermoplastic starch (TPS) in WSF/TPS composites with useful physical and mechanical properties.
2. The incorporation of 40% and 50% WSF improved the mechanical properties of the composites better than neat TPS. Tensile strength, flexural strength, modulus strength, and impact strength increased with increasing WSF and the addition of NC.

3. Flexural properties and tensile properties of WSF/TPS composites improved with the addition of 5 wt% NC. The water absorption and thickness swelling of composites were lowered with increased NC content.
4. Although WSF is a biodegradable material, the composite's biodegradation was accelerated by increasing the starch in their mixtures. With the increase in time period, the percentage of biodegradation increased.

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