The Effect of Different Mineral Fillers on Starch/Rice Husk Composite Properties

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The objective of this research was to study the feasibility of producing biodegradable thermoplastic starch rice-husk composites. The effect of different types of mineral fillers on the various properties of thermoplastic starch composites filled with rice-husk flour, an agricultural waste residue, was studied. The mineral fillers aluminum trihydrate (ATH), magnesium dihydroxide (MDH), nanoparticulate MDH, and nanoclay were studied. It was found that the addition of the mineral fillers and especially nanofillers improved the dimensional stability and the mechanical properties of the composites, while decreasing their biodegradability. The thermogravimetric analysis (TGA) showed that substituting mineral fillers for some part of the lignocellulosic component increased the extents of weight-loss in the first and second steps, but decreased the weight-loss in the last step. This substitution also led to a slight decrease in the thermal decomposition temperatures at the curve peaks.

Keywords: Rice-husk; Mineral fillers; Aluminum three hydrates; Magnesium hydroxide; Thermoplastic starch; Nanofillers

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INTRODUCTION

In recent years, there has been a growing interest in the application of green chemistry, environmentally friendly materials, and industrial ecology. Applications in these fields can decrease the non-degradable contamination caused by petroleum-based plastic waste and achieve sustainable development of new products (Gonçalves *et al.* 2017; Suryanegara *et al.* 2017; Fekete *et al.* 2018). To ensure a sustainable environment, a large substitution of oil-based polymers by biodegradable materials in the manufacturing of commodity goods is required (Basu *et al.* 2016). These substitute materials, also known as biomaterials, are gradually replacing traditional oil-based plastics (Reddy *et al.* 2013; Rhim *et al.* 2013). In 2010, worldwide bio-plastic production was reported to be approximately 300,000 metric tons, which accounted for less than 1% of the 181 million metric tons of total plastic production (Nampoothiri *et al.* 2010).

Starch is currently regarded as one of the most promising biopolymers because it is readily available, inexpensive, environmental-friendly, and biodegradable (Fekete *et al.*2018). Starch, otherwise known as amylum, is a heterogeneous polymeric carbohydrate that consists of two types of polymers: amylose (linear and helical polysaccharide) and amylopectin (highly branched polysaccharide) (Brown and Poon 2005; Roy *et al.* 2012). Corn, potato, tapioca, and wheat starches are the most abundant and inexpensive commercially produced starches. Like cellulose, the starch hydrolysis process yields glucose molecules, so it can be a condensation polymer (Halley and Avérous 2014). The substitution of non-degradable oil-based polymers, such as polyethylene (PE), polypropylene (PP), and polyvinylchloride, by biodegradable biopolymers, such as starch, to produce biodegradable and environment friendly composites has been studied by many researchers (Nourbakhsh *et al.* 2014; Basu *et al.* 2016; Guzmán and Murillo 2018).

A wood-plastic composite (WPC) is a semi-biocomposite, which usually consists of a non-degradable oil-based polymer as the matrix and a biodegradable lignocellulosic material as the filler (Mirmehdi *et al.* 2014). The use of biopolymers as the matrix in a WPC converts it to a totally biodegradable biocomposite. Prevalently, wood is the main source of lignocellulosic filler in the manufacturing of WPCs, but it can be replaced by other lignocellulosic resources including recycled waste materials and agricultural residues (Lomelí-Ramírez *et al.* 2014; Mirmehdi *et al.* 2014; Nourbakhsh *et al.* 2014; Fekete *et al.* 2018).

Rice husk is an agricultural residue that is produced in large quantities as a byproduct from the grains during rice-processing. It is often regarded as a valueless byproduct of the rice milling process, with no significant application (Letcher 2012; Pacheco-Torgal *et al.* 2015; Siddique and Cachim 2018). The worldwide rice production is estimated to be approximately 700 million tons per year. Rice husk accounts for approximately 20% of the rice weight, considering its low bulk density, which are about 90 kg/m^3 to150 kg/m^3 (Siddique and Cachim 2018).

The addition of lignocellulosic fillers can improve the mechanical properties of thermoplastics, but it can also increase the burning rate of the resulting composite. Therefore, to reduce the flammability of WPCs, fire retardant agents such as ammonium polyphosphate (APP), melamine polyphosphate (MPP), aluminum trihydrate (ATH), and magnesium dihydroxide (MDH) can be employed during the compounding process (García *et al.* 2009; Suppakarn and Jarukumjorn 2009; Arao *et al.* 2014). Metallic hydroxides, such as MDH and ATH, are the more desirable kinds of flame retardants due to their good flame retardancy of WPCs and strong mechanical properties (Suppakarn and Jarukumjorn 2009; Arao *et al.* 2014).

Nanocomposites constitute a new development in the area of flame retardancy. The addition of nanomineral fillers can improve both the flame retardancy and the mechanical properties of composites. However, the high cost of nanomineral fillers restricts their use to highly value-added products and not in commodity products like construction materials (García *et al.* 2009; Arao *et al.* 2014).

In this study, the production feasibility and characterization of WPCs made of corn starch as the biopolymer matrix and rice husk as the lignocellulosic filler was investigated. The effects of adding some mineral fillers and nano filler on the properties of the produced samples were also studied.

EXPERIMENTAL

Materials

Corn starch was obtained from the Hamedan Alvand Converting Company (Hamadan, Iran). The analytical grade glycerol ($C_3H_8O_3$) that was used as a plasticizer was purchased from Merck Co. (Kenilworth, NJ). The rice husk that was used as lignocellulosic filler was obtained from the Gilan rice factories (Gilan, Iran). The rice husk was converted to flour using a laboratory mill and screened by 40-mesh and 80-mesh screens (Klyosov

2007). The MDH and ATH fillers were purchased from Iran Kimia Puyesh Bespar Co. (Isfahan, Iran). Both the fillers had a particle size of 2 µm. The magnesium hydroxide nano powder and nano clay were obtained from Saturn Co. (Abu Alanda, Jordan) and American Huston Co. (Abu Dhabi, UAE), respectively.

Starch Polymer Preparation

To produce the thermoplastic starch polymer, the starch and glycerol were mixed with a mixer at a ratio of 75:25 at 2000 rpm, for 30 min. The prepared mixture then was further mixed and heat-treated by a ZSK-25 co-rotating twin screw extruder (Coperion Werner & Pfleiderer, Stuttgart, Germany) to produce a usable starch polymer. Temperature of heating zones was set at 100, 105, 110, 115, 115 and 120ºC, respectively. This was performed at the Iran Polymer Petrochemical Research Institute.

Wood-Starch Granules Preparation

The constitutive materials were mixed according to treatment codes in Table 1. The resulting mixtures were extruded to produce wood-starch granules using a counter-rotating twin screw extruder (Dr. Collin Engelhardt GMBH D8510 Fürth, Germany). Temperature of heating zones was set at 120, 125, 130, 135, 135 and 140 °C, respectively.

Table 1. Constitutive Materials Percentages

Treatment Code	Polymer (wt%)	Rice-husk Filler (wt%)	Mineral Filler Type	Mineral Filler (wt%)	Nano Material Type	Nano Material (wt%)
1	70	30	-	0	-	0
2	70	25	ATH	5	-	0
3	70	20	ATH	10	-	0
4	70	25	MDH	5	-	0
5	70	20	MDH	10	-	0
6	70	25	ATH + MDH	5	-	0
7	70	20	ATH + MDH	10	-	0
8	70	20	MDH	8	N-MDH[a]	2
9	70	20	MDH	6	N-MDH	4
10	70	20	MDH	8	N-Clay[b]	2
11	70	20	MDH	6	N-Clay	4
12	70	20	ATH	8	N-Clay	2
13	70	20	ATH	6	N-Clay	4
PP	67[c]	30	-	-	-	0
HDPE	67[c]	30	-	-	-	0

[a] Nano-MDH; [b] Nano-Clay; [c] Plus 3% MAPP coupling agent

Wood-Starch Composite Panels Manufacturing

The prepared wood-starch granules were hot-pressed at 180 °C and 250 bar to produce 200 mm × 200 mm × 4 mm wood-starch composite panels (4 mm stencil thickness). Directly after opening the hot-presser, the panels were cool-pressed with cool water flow for 5 min under 30 bar pressure.

Properties Measurement

The water absorption and thickness swelling characteristics of the samples were determined after 2 h and 24 h of water immersion, based on the ASTM standard D7031-04 (2004). The tensile strength and the flexural properties were measured according to the

ASTM standards D638 (2014) and D790 (2017), respectively. To evaluate the thermo-influenced properties of the samples, the thermal gravimetry analysis (TGA) was performed, according to the ASTM standard E1131 (2008). The biodegradability of the samples was measured according to the ASTM standard D5988 (2018). The samples were analyzed *via* scanning electron microscopy (SEM, Model AIS2100; Seron Technology, Gyeonggi-do, Korea) in order to show the distribution and position of the particles and nanoparticles.

RESULTS AND DISCUSSION

Physical Properties

Table 2 lists the average physical properties (*i.e.*, density, water absorption, and thickness swelling after 2 h and 24 h of immersion) of the various board samples. The density of the boards increased as the mineral filler addition level increased, while the presence of the nanofillers did not affect the density values. The density of the composites is related to the density of their components. In the case of the observed samples, the higher density mineral fillers created composite samples that had higher densities.

Table 2. Physical Properties of the Composites

Treatment Code	Density (g/cm^3)		2h-Water Absorption (%)		2 h-Thickness Swelling (%)		24h-Water Absorption (%)		24h-Thickness Swelling (%)	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
1	1.24	0.04	24.55	2.51	42.25	2.14	57.54	3.31	92.50	4.86
2	1.32	0.03	20.40	1.42	33.00	1.95	42.74	2.18	71.75	3.24
3	1.39	0.02	11.07	2.78	30.50	1.01	20.64	1.45	51.50	2.95
4	1.29	0.07	19.36	2.03	40.75	1.96	41.25	2.05	81.25	3.12
5	1.41	0.04	12.69	1.08	38.50	1.54	25.07	1.41	61.75	3.04
6	1.30	0.06	20.13	1.86	40.25	1.36	45.27	2.14	80.75	2.87
7	1.37	0.04	18.06	1.56	41.25	2.03	36.49	1.66	71.00	2.76
8	1.34	0.03	12.56	1.02	28.25	1.84	20.96	1.17	50.25	2.08
9	1.30	0.04	10.74	0.97	22.60	1.23	19.86	1.62	41.00	2.41
10	1.31	0.01	12.41	1.40	27.55	1.12	23.93	1.08	52.00	2.35
11	1.33	0.04	10.40	0.74	15.58	0.98	20.14	1.52	38.50	2.60
12	1.36	0.03	11.37	0.89	25.93	1.02	21.17	1.21	49.50	2.19
13	1.36	0.02	7.80	0.75	10.10	1.18	18.30	1.06	30.50	2.07
PP	0.89	0.01	0.26	0.04	5.25	0.16	0.59	0.04	5.50	0.21
HDPE	0.93	0.02	0.39	0.03	6.75	0.24	1.06	0.07	7.00	0.14

The water absorption of the samples indicated that the starch-rice husk composite did not have suitable properties, as the water absorption values were relatively high in across all the treatments. The water absorption values of the composite samples were decreased by substituting some parts of the cellulosic filler with mineral fillers. The low solubility of the aluminum trihydrate and magnesium hydroxide in water (0.001 g/L and 0.0064 g/L, respectively) caused the water absorption values of the starch-rice husk composites to decrease. The lignocellulosic composite shrinkage is closely associated with the water absorbability of the composite components from the environmental moisture, so the composite dimensional stability depends mainly on the degree of wetting (Wilpiszewska and Spychai 2006). The high-level of water absorption of this composite was expected, so it is most practical in conditions where there is no water contact. Otherwise, a waterproof coating layer is needed. To further stabilize the composite, it is ideal to manufacture it at humidity conditions similar to those under which the product will be used (Wilpiszewska and Spychai 2006).

Water penetration into the composite texture can create distance between the structural components, which can result in swelling (Lomelí-Ramírez *et al.* 2014; Kenechi *et al.* 2016). The low water solubility of the applied mineral fillers and their non-water absorption led to a decrease in the thickness swelling amounts (Stepto 2003; Wilpiszewska and Spychai 2006). On the other hand, mineral fillers, particularly nanofillers, fill the pores of the composites and create more joints between the structural components, which decrease the water absorption and thickness swelling of the composites (Ren *et al.* 2018).

Mechanical Properties

The principal strength properties of the construction composites are influenced by based matrix polymers. However, the filler type plays an important role in the mechanical properties, especially in lignocellulosic-filled thermoplastic composites (Mirmehdi *et al.* 2014; Fekete *et al.* 2018; Ren *et al.* 2018). Figure 1 illustrates the tensile strength properties of the starch-rice husk composites. The results showed that the starch-rice husk composites had lower tensile strength values than the (PP)-rice husk and high-density polyethylene (HDPE)-rice husk composites. This was primarily due to the nature of the thermoplastic starch polymer and its comparatively weak polymer chain crosslinking. On the other hand, petroleum-based polymers such as PP and HDPE have strong polymer chain crosslinking (Mirmehdi *et al.* 2014).

Starch contains linear polymer chains of amylose and branched amylopectins. The ratio of these two components, their chains length, the branching degree, and the size and shape of the starch granules are the influential factors in the final thermoplastic starch properties (Ma and Yu 2004; Wilpiszewska and Spychai 2006). The destruction of the starch crystalline structure by breaking hydrogen bonds is conducted to produce the thermoplastic starch (Stepto 2003; Wilpiszewska and Spychai 2006).

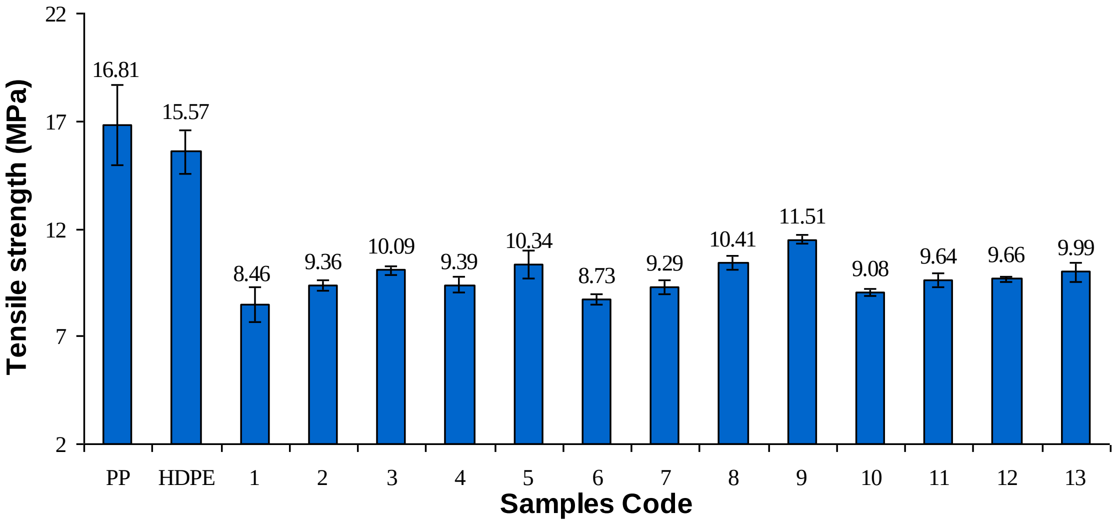

Fig. 1. Tensile strength values of the composites

Substituting the mineral fillers in place of the rice husk had a slightly positive effect on the tensile properties of the prepared composites in both ATH and MDH. The use of the nanofillers did not have any effect on this property (Fig. 1). It has been reported that the mechanical properties of the sisal/PP composites were enhanced by the addition of MDH (Suppakarn and Jarukumjorn 2009).

The tensile modulus of the different starch-rice husk composites is shown in Fig. 2. The HDPE-rice husk sample had the highest tensile modulus, followed by the PP-rice husk composite. The tensile modulus of the materials explains the relationship between stress (force per unit area) and strain (proportional deformation) in the linear elasticity regime of a uniaxial deformation. Thus, in approximately same strains, low tensile strength properties in the thermoplastic starch composites led to a lower tensile modulus. However, the mechanical properties of the prepared thermoplastic starch composites were comparable with those of other reports (Zhang *et al.* 2008; Avérous and Halley 2009; Fekete *et al.* 2018). The results indicated that the addition of mineral flame retardant fillers in some treatments caused the tensile modulus to increase slightly. Additionally, the use of nanomineral fillers, especially in the top 4% levels, made the composites stiffer, with greater tensile strength (Fig. 1) and lower strain. Therefore, the composites with nanomineral fillers had a larger tensile modulus than the composites with other treatments (Fig. 2).

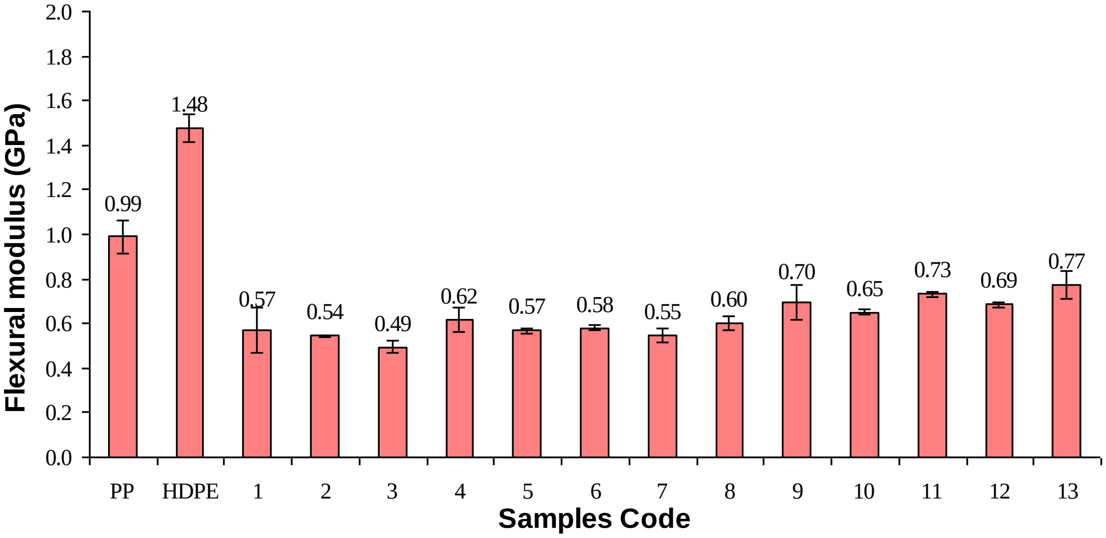

Fig. 2. Tensile modulus of the composites

The addition of glycerin plasticizer, in a moderate amount (15% w/w), resulted in a very stiff extruded plasticized potato and wheat starch composite. The prepared composite had a tensile modulus of 700 MPa to 900 MPa, which is comparable to the tensile modulus of HDPE composites (de Graaf *et al.* 2003).

The high amylopectin content in natural starch results in a lower degree of polymer-chains ordering because the branched character of the amylopectin, and therefore its thermoplastic starch has higher brittleness, lower strain, and thus lower tensile strength (de Graaf *et al.* 2003). The reduced interaction between the starch chains by the use of glycerin as a plasticizer provides greater chain mobility (Wilpiszewska and Spychai 2006). Therefore, the application of glycerin in higher levels causes a growth in the elongation at break. However, the tensile modulus and the tensile strength decrease at the same time (de

Graaf *et al.* 2003). Additionally, the impact strength of thermoplastic starch improves with the addition of glycerin plasticizer. Significant improvements have been observed with 20% w/w addition of this plasticizer (Wilpiszewska and Spychai 2006).

The flexure value as a function of load characterizes a material's bending ability. The flexural load value is the combination of the compression, shear, and tensile loads. The upper surface of the laminate undergoes compression, the middle portion experiences shear, and the lower face undergoes tension (Khalid *et al.* 2006). Figure 3 illustrates the bending strength of the starch-rice husk composite samples under flexural loading at the different mineral filler levels. Different filler types were compared with each other and with the control samples. There was a clear difference in the bending strength between the PP/HDPE based composites and the thermoplastic starch composites. The bending strength values of all the starch composites were approximately half the strength of the PP/HDPE based composites. This implies that the lower bending strength that resulted from the use of the thermoplastic starch polymer can be related to the higher brittleness value of the applied thermoplastic starch compared to the PP and HDPE petroleum-based polymers (Zhang *et al.* 2008; Avérous and Halley 2009; Fekete *et al.* 2018).

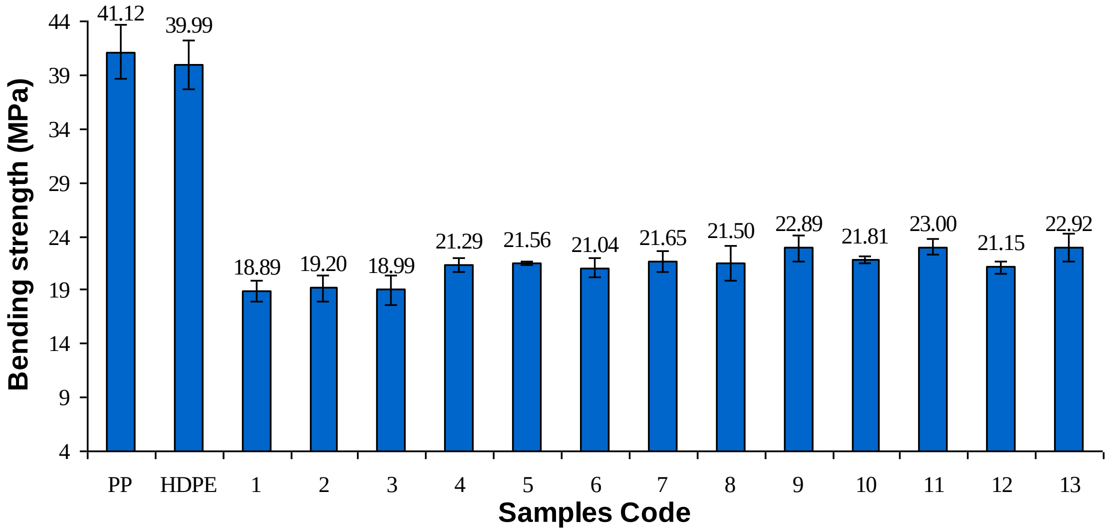

Fig. 3. Bending strength of the composites

The results showed that the partial rice-husk filler substitution with the mineral fillers had a slightly positive impact on the bending strength. Moreover, the use of nanofillers caused the bending strength of the starch composites to slightly increase (Fig. 3). The composite strength is partly determined by the quality of the bond at the interface, which allows stress to transfer from the polymeric matrix to the filler (Mirmehdi *et al.* 2014). The addition of the mineral fillers, particularly the nanofillers, to the components in the production of the starch-rice husk composites improved the bond quality between the polymeric matrix and the fillers.

Figure 4 indicates the flexural modulus values of the samples. The flexural modulus of the thermoplastic starch composites was lower than those of the PP- and HDPE-based composites. The starch polymer structure has a heterogeneous base made of both amylose and branched amylopectins with different portions based on the initial source of the starch, the ratio of amylose and amylopectin, their chains length, the branching degree, and the crystallinity degree. These characteristics affect the final properties of the produced thermoplastic starch and composites it is present in (Wilpiszewska and Spychai 2006). The branched character of the amylopectin and its high natural starch content causes a reduction in the degree of polymer-chains ordering, so its thermoplastic starch has a higher brittleness property and lower bending strength (de Graaf *et al.* 2003). Another important factor that influences the mechanical properties of thermoplastic starch composites is the process conditions of the thermoplastic starch production. These conditions include the temperature profile (in the extruder zones), the configuration and rotational speed of the screw/screws, and the type and quantity of added plasticizers. The reduction of interaction between the starch chains by the use of glycerin as a plasticizer provides a greater mobility in chains (Wilpiszewska and Spychai 2006; Avérous and Halley 2009). Therefore, using high amounts of glycerin creates increased strain (extension amounts) and decreases the flexural modulus and bending strength (de Graaf *et al.* 2003). There was no difference between the boards made with and without the mineral fillers, although the addition of the nanofillers slightly increased the flexural modulus of the composites (Fig. 4).

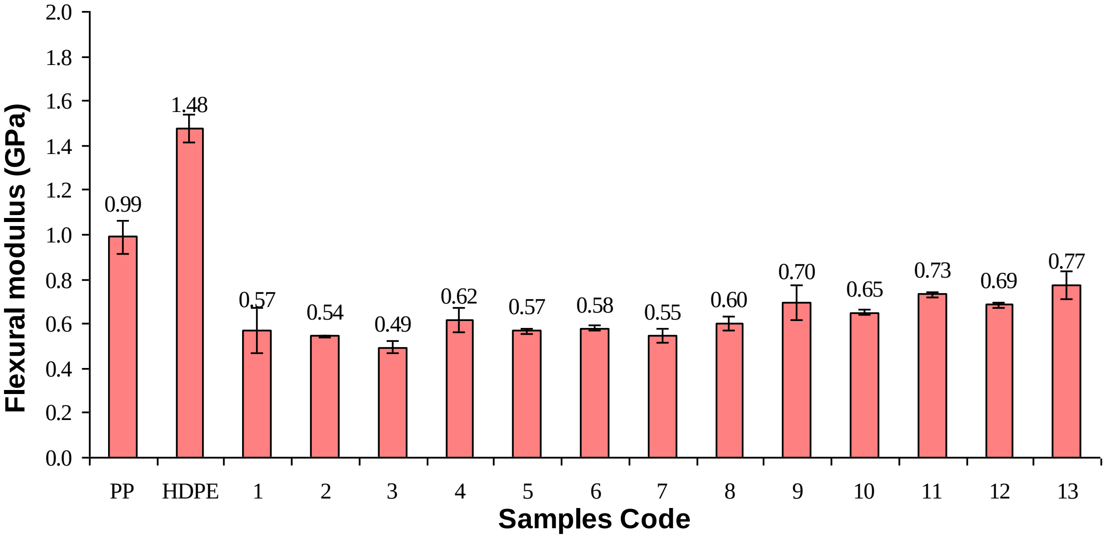

Fig. 4. Flexural modulus of the composites

Thermal Analysis

The TGA curves of the composites are shown in Figs. 5, 6, and 7. The mass loss below 100 °C can be ascribed to the water loss in the samples (Mohd Zain *et al.* 2016). All the treatment curves indicated that there were three different weight drop steps. The first step corresponds to the volatilization of the water and glycerol, the second step corresponds to the degradation of the amylose and amylopectin, and the last weight loss step corresponds to the pyrolysis of the lignocellulosic fillers (Olivato *et al.* 2015; Ren *et al.* 2018).

Substituting some parts of the lignocellulosic fillers with the ATH or MDH flame retardant mineral fillers increased the extent of weight-loss in the first and second steps due to water evaporation of the flame retardant materials. Both the ATH and MDH flame retardant fillers operate by decomposing upon heating to give off water, which is an endothermic process that takes heat from the fire (Kutz 2017). The thermal decomposition temperatures at the curve peaks slightly decreased because the water vapors are released from the flame retardant fillers. In addition, the weight-loss decreased in the last step due to the decreased amount of lignocellulosic filler in the composition (Figs. 6 and 7).

After incorporating the nanofillers (nano-MDH/nano-clay), the nanocomposites exhibited lower weight-loss rates in the first step and further degradation in the second step. Combined with a slightly higher maximum degradation temperature, this demonstrated an enhancement of the thermal stability. Similar findings were also reported for starch/nano-clay and starch/sepiolite nanocomposites (Chivrac *et al.* 2010; Ren *et al.* 2018).

The dispersion of the nanomineral fillers in the matrix increased the tortuosity of the ignition gas diffusion pathway and the char formation on the material surface. The strong interactions between the nanoparticles and the polymer matrix can also create a higher thermal stability. The barrier effect, which improves the thermal stability, is predominant when the nanomineral fillers are well dispersed in the matrix (Bordes *et al.* 2009; Chrissafis and Bikiaris 2011).

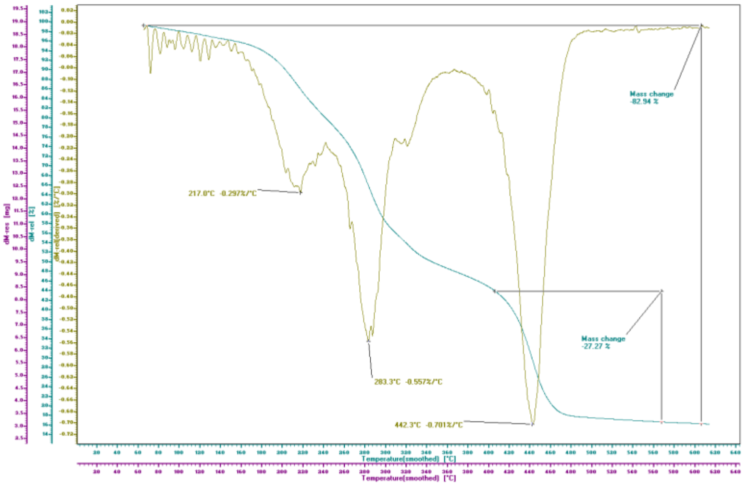

Fig. 5. The TGA of the control treatment (without the mineral fillers)

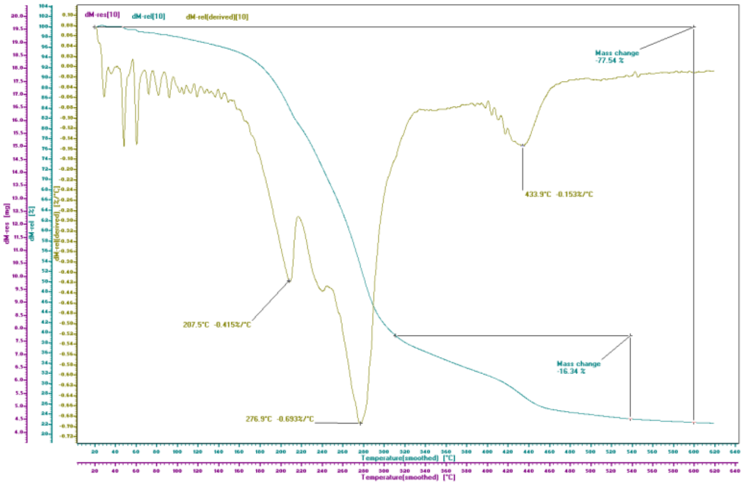

Fig. 6. The TGA of the treatment code 3 (10% ATH)

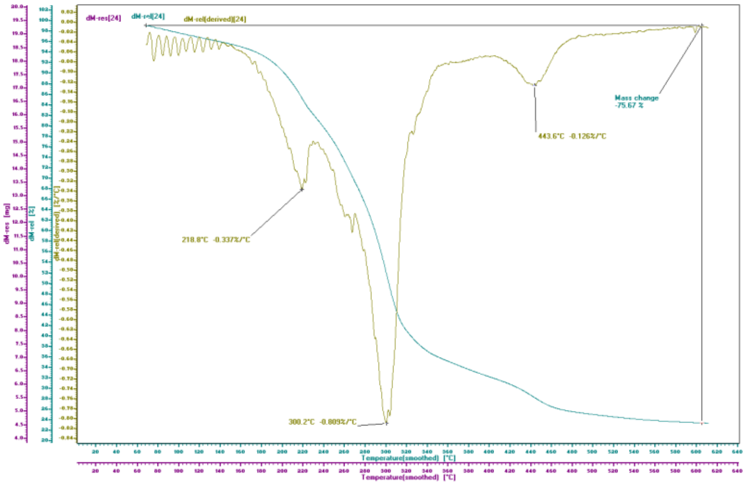

Fig. 7. The TGA of the treatment code 11 (6% MDH + 4% nanoclay)

Biodegradability

Table 3 shows the experimental data from the biodegradation tests that were performed on the thermoplastic starch-rice husk composites with various mineral fillers and nanofillers. As expected, there was no weight loss in the PP and HDPE-rice husk composite control samples during the 16-week inspections. The results showed that the degradation rate of the starch-rice husk samples increased over time. The dispersion and the decomposition of the specimens were observed after approximately 4 weeks and they continued to rise along with the burial time. The results showed that the addition of the mineral fillers and the nanofillers lowered the degradation rate of the samples.

Table 3. Biodegradability of the Composites

Treatment Code	2 Weeks-Biodegrad-ability (%)		4 Weeks-Biodegrad-ability (%)		8 Weeks-Biodegrad-ability (%)		12 Weeks-Biodegrad-ability (%)		16 Weeks-Biodegrad-ability (%)	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
1	10.2	0.52	22.0	1.78	48.2	3.12	72.8	4.15	97.9	6.02
2	8.1	0.47	17.8	1.42	38.5	2.64	60.0	3.26	83.0	4.88
3	7.0	0.23	15.6	1.03	34.9	2.08	55.9	3.51	77.3	4.26
4	8.2	0.41	18.7	1.68	40.1	3.20	62.5	3.24	87.3	4.34
5	7.4	0.32	16.3	1.22	36.4	2.63	57.9	3.74	78.5	3.26
6	8.5	0.40	18.9	1.53	40.7	2.87	64.1	3.21	89.0	4.15
7	7.6	0.28	17.0	1.03	38.2	2.64	59.1	3.96	80.1	5.01
8	7.0	0.26	14.7	0.38	32.6	2.06	52.0	3.45	74.5	3.99
9	6.4	0.27	14.0	1.02	31.4	1.80	49.8	3.04	70.1	3.84
10	7.1	0.34	15.6	0.91	34.0	2.36	54.0	3.70	76.5	4.79
11	6.4	0.20	14.2	0.78	31.4	1.95	50.2	3.22	70.8	4.02
12	6.7	0.43	14.1	1.04	31.1	2.03	49.6	2.87	70.0	3.58
13	4.2	0.20	10.9	0.74	24.6	1.58	38.2	2.46	54.1	3.61
PP	0.0	0.00	0.0	0.00	0.0	0.00	0.1	0.02	0.2	0.03
HDPE	0.2	0.09	0.5	0.17	0.8	0.05	1.1	0.12	1.1	0.11

The use of organic materials such as lignocellulosic components in the manufacturing of composite products has been shown to increase the composite biodegradability (Nourbakhsh *et al.* 2014). The addition of small amounts of cellulose (5% to 15%) did not improve the biodegradability of PE composites. However, cellulose addition levels upwards of 30% had an evident effect on the composite biodegradability properties of PE films (Kaczmarek and Ołdak 2006; Ołdak *et al.* 2006).

Other than the PP and HDPE control samples, the highest biodegradability was observed in the starch-rice husk composite with no mineral filler (treatment code 1) and the lowest biodegradability belonged to the starch-rice husk composite with 6% ATH + 4% nanoclay (treatment code 13). After 16 weeks, the sample with treatment code 1 had a degradation degree of approximately 98%, while the sample with treatment code 13 had a degradation degree of approximately 54%. Decreasing the water absorption of the starch-rice husk composites by substituting some parts of the cellulosic filler with mineral fillers, increasing the density, bonding and compressing the samples, and decreasing the composite internal pores by mineral and nanofillers reduced the weight loss in these composites during the biodegradation test.

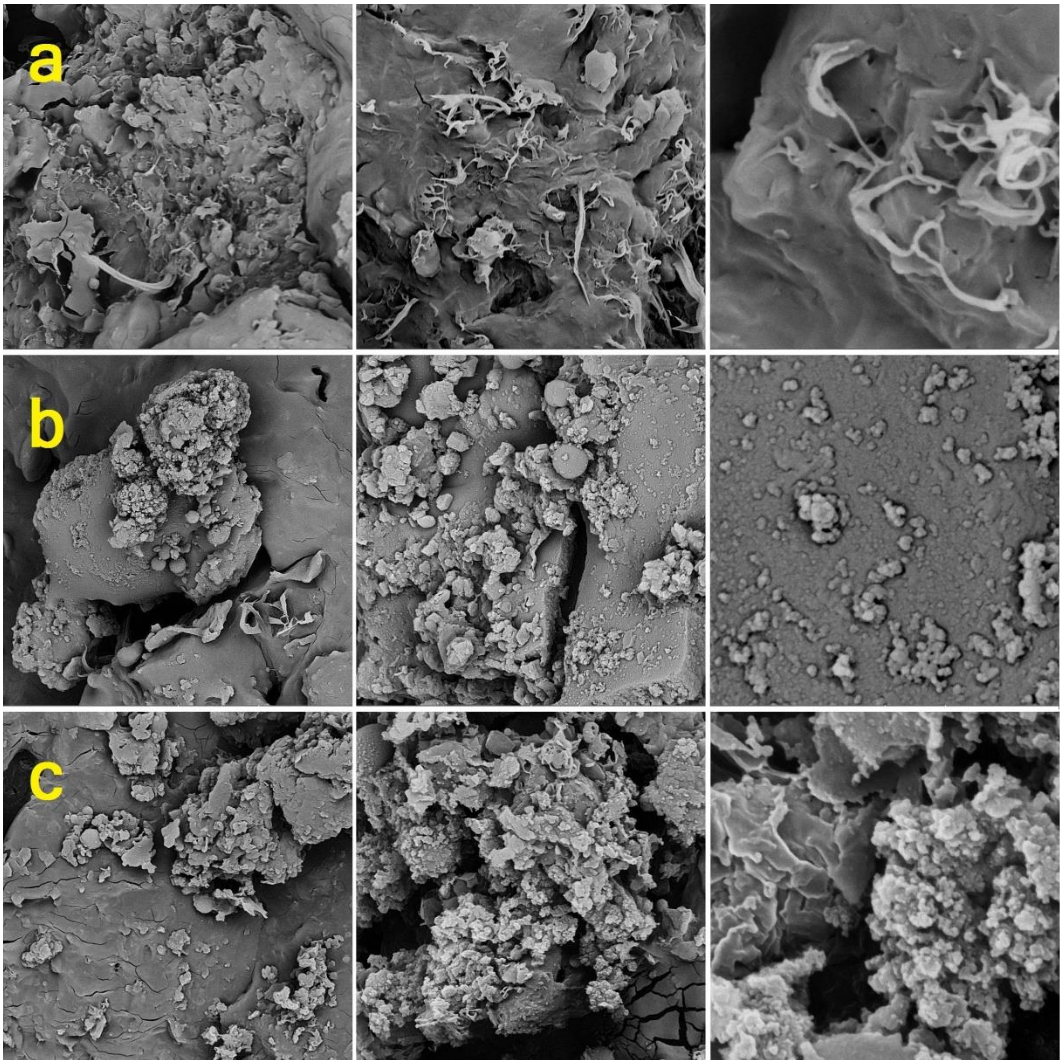

Fig. 8. SEM images of the a) treatment code 1, b) treatment code 3, and c) treatment code 11 composite samples at 5000×, 15000×, and 75000× magnification

Addition of mineral fillers and also the presence of nano mineral fillers had a positive effect on dimension stability of the samples. In fact, the low water solubility of applied mineral fillers and their no water absorption led to a decrease in the composite decomposition amounts (Stepto 2003; Wilpiszewska and Spychai 2006). On the other hand, mineral filers and especially nanofillers fill the pores of composites and also make more joints between structural components; therefore the bio-degradation rate is decreased.

Morphological Properties

To study the component sizes and their distribution in the composite matrix, SEM imaging was applied. Figure 8 shows the microscopic images of the cross section of the samples magnified by 5000×, 15000×, and 75000×. The mineral fillers are clearly seen in the composites structure, except for the control sample (Fig. 8a). The mineral fillers had a uniform distribution in the composite matrix. Figure 8c shows the thermoplastic starch composites filled with the nanomineral fillers (nano-clay). The nano particles were approximately 50 nm in size. As it has been shown in SEM images, the good combination of mineral fillers and also nano mineral fillers with thermoplastic starch polymer matrix caused to the increase in density, bonding and compression, and the decrease in composite internal pores, all of which make more joints between structural components.

CONCLUSIONS

1. The thermoplastic starch composites presented inferior properties compared to the polypropylene (PP) and high-density polyethylene (HDPE) rice-husk composites. Among starch-rice husk samples, treatment code 13 (6% aluminum trihydrate (ATH) + 4% nano-clay) had relatively better physical and mechanical properties.
2. The biodegradability of the thermoplastic starch composites was higher than that of the petroleum-based composites (PP and HDPE).
3. Substituting some of the lignocellulosic fillers with mineral fillers and nanofillers slightly increased the mechanical properties and the dimensional stability of the composites.
4. Thermogravimetric analysis (TGA) showed that the addition of the mineral fillers caused the weight-loss rate to increase in the first and second steps, and decrease in the last step. The addition of the mineral fillers also causes the thermal decomposition temperatures to decrease at the curve peaks.

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