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EFFECT OF NANOCLAY CONTENTS ON PROPERTIES, OF BAGASSE FLOUR/ REPROCESSED HIGH DENSITY POLYETHYLENE/ NANOCLAY COMPOSITES

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ABSTRACT

The effect of nanoclay contents on the physical and mechanical properties of bagasse flour/ reprocessed high density polyethylene (rHDPE)/ nanoclay composites was investigated. The bagasse flour content was constant at 50%, the maleic anhydride content was constant at 3%, and the nanoclay (Cloisite 30B) content was set at three different levels: 0%, 2%, and 4%. The materials were mixed in a co-rotating twin-screw extruder; afterwards, the specimens were fabricated using an injection molding method. The water absorption and mechanical properties, such as flexural and tensile strength, flexural and tensile modulus, and notched impact strength, were measured. The nanoclay dispersion was examined by X-ray diffraction. The results indicated that tensile and flexural modulus increased with an increase in nanoclay content. Also By increasing the nanoclay content at 2 wt.%, the tensile and flexural strengths of the composite were increased. However, the addition of 4 wt.% nanoclay resulted in reductions of these properties. Water absorption decreased with increasing nanoclay content. The structural examination of the bagasse polymer composite with X-ray diffraction showed that the nanoclay was distributed as an intercalated structure in the polymer matrix, and the d-spacing of layers decreased with increasing nanoclay content. Scanning electron microscopy (SEM) showed that 2% nanoclay samples with lower and more uniform pores compared at 4% nanoclay samples, respectively.

Keywords: Nanoclay, reprocessed high density polyethylene, scanning electron microscopy, X-ray diffraction.

INTRODUCTION

Wood-plastic composites (WPC) are a group of materials made from a combination of wood fiber (or flour) and a thermoplastic resin, together with varying amounts of additives (Kiaei *et al.* 2014).

Many research organizations and institutions have conducted or are currently conducting research on wood-plastic composites (WPCs) that will provide more durable and cost-competitive products using waste materials. The reutilization of waste materials in the production of WPCs can have advantages to the economy, environment, and technology (Danesh *et al.* 2012).

Bagasse is the residue left over after sap extraction from crushed sugar cane stalks. Approximately 320 kg of bagasse is produced per metric ton of processed sugar cane (Lee and Mariatti 2007). Meanwhile, it is one of the most important agricultural fiber and lignocellulosic wastes. It is regularly cultivated in tropical countries, specifically, Brazil, India, Cuba, and some areas of Iran (FAO 2006). Approximately 3,4 million tons of bagasse is produced annually in Iran (Najafi *et al.* 2009). Today, bagasse is used sustainably as a major raw material for fuel, as well as for pulp and paper production, in addition to being a reinforcement material in value-added composite panel production (Lee and Mariatti 2007).

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The environmental problem nowadays is a factor of extreme importance in the industrial world, particularly in the case of plastic processing companies, as efforts are mainly focused on the reduction and recycling of wastes generated during transformation processes and also after product end use (Chianelli-Junior *et al.* 2013).

Nanoscience and nanotechnology have opened up a new way of developing WPCs (Lu *et al.* 2006). In particular, nanotechnology offers ways to improve the mechanical and physical properties of WPCs using nano-sized fillers (Ashori and Nourbakhsh 2009). The use of small amounts of montmorillonite-structured clays is enough to improve the overall properties of a polymer matrix at a relatively low cost (Pascual *et al.* 2009, Ratnayake and Haworth 2006). Wu *et al.* (2007), have claimed that the addition of only 2% nanoclay to a spruce HDPE wpc will increase the flexural strength and tensile strength by 24% and 13%, respectively. The incorporation of NC in the composites further reduces the impact and tensile strength, lower elongation, and increases the modulus of both the nanocomposites and the composites with PE matrix. However, NC would improve the water absorption and water loss of PE composites. Surfactants play an important role in this function by their morphological structures as well as chemical reactions (Gu *et al.* 2010). Wang *et al.* (2005), studied the thermal properties, mechanical, and morphological of composites reinforced with nanoclay particles. They found that these fillers cause better dispersion of the particles in the polymerized matrix and raise the tensile modulus, tensile strength, and hardness of the composite due to their exfoliated structure. The aim of this study was to investigate the effect of montmorillonite clays on the morphological and mechanical properties of WPCs.

EXPERIMENTAL

Materials

Natural Fiber

The bagasse flour was received from a manufacture (Dez Choob-Plastic Company, Khozestan, Iran). Particles pass through a 40 mesh and retained on 70 mesh was used.

Polymer

The polymer matrix high density polyethylene (HDPE) with trade name 5620 was supplied by Arak Petrochemical Company in Iran. It had a density of 0,956 g/cm^3 and a melt flow index (MFI) (190°C/2,16 kg) of 20 g/10 min. Then HDPE was recovered twice. In a twin-screw extruder at a temperature of 180 ° C and speed 100 rpm.

Coupling Agent

Polyethylene modified with maleic anhydride (MAPE) with a density of 0,965 g/cm^3 (MFI of 7 g/10 min, 1 wt% maleic anhydride) was used as the coupling agent. It was acquired from Solvay Company, Belgium.

Nanoclay

A commercial nanoclay product Cloisite-30B), with a density 1,98 g/cm3 and particle shape (Spherical) was ordered from Southern Clay, Inc. (Texas, USA). It was incoporated at three different levels: 0%, 2%, and 4%. Cloisite-30B is a natural montmorillonite clay modified with a quaternary ammonium salt, having a d-spacing of 18,5 Å and modifier concentration of 90 meq/100 g clay.

Methods

Processing of the composites

Before sample preparation, the bagasse flour was dried at 70 ± 5 °C for 24 h. Bagasse flour, nanoclay, reprocessed high density polyethylene (rHDPE), and MAPE were weighed and bagged according to the formulations given in table 1 and then mixed in a co-rotating twin-screw extruder (Collin) at the Iran Polymer and Petrochemical Research Institute. Screw speed of 60 rpm at 185 °C. Bagasse flour, granules of reprocessed high density polyethylene, and a coupling agent were properly mixed with the nanoclay and then poured into the funnel of the extruder. The compounded materials were then ground using a pilot scale grinder (WIESER, WGLS 200/200 model). The resulting granules were dried at 105 °C for 24 h. Test specimens were prepared with an injection molding machine (Imen Machine, Iran) at 190 °C and a pressure of 80 MPa according to standard ASTM D638. The specimens were stored in controlled conditions (50% relative humidity and 23 °C) for at least 40 h prior to testing.

Table 1. Composition of the studied formulations.

Sample code	rHDPE (Wt%)	Bagasse Flour (Wt%)	Nanoclay (Wt%)	Coupling Agent (Wt%)
0Nc	47	50	0	3
2Nc	45	50	2	3
4Nc	43	50	4	3

Measurement of mechanical properties

Tensile strength and tensile modulus were measured according to the ASTM D 638 standard using an Instron Universal Testing Machine (model 1186) at a speed of 5 mm/min. The dimensions of the standard dumbbell (dog-bone) samples for the tensile tests were 145 x 10 x 4 mm (length x width x thickness).

Flexural strength and flexural modulus were measured according to the ASTM D 747 standard using an Instron Universal Testing Machine (model 1186) at a speed of 2 mm/min. The dimensions of the specimens for the flexural tests were 105 x 13 x 5 mm (length x width x thickness).

Notched impact strength was measured according to the ASTM D 256 standard using a Zwick Universal Testing Machine (model 5102). The dimensions of the specimens for the notched impact tests were 60 x 12 x 6 mm (length x width x thickness).

For each treatment level, five replicates were measured for each property and the average values were reported.

Measurement of water absorption

Water absorption tests were carried out according to ASTM D7031-04. The dimensions of the specimens for the water absorption tests were 20 x 20 x 20 mm. Five specimens of each formulation were selected and dried in an oven for 24 h at 102 ± 3 °C. The weight of dried specimens was measured to a precision of 0,001 g. The specimens were then placed in distilled water and kept at room temperature. The weight of the specimens was measured after 30 days.

X-ray diffraction

X-ray diffraction (XRD) analysis was carried out with a Seifert-3003 PTS (Germany) with Cu*Ku* radiation (λ=1,54 Å; 50 kV, 50 mA) at room temperature. The scanning rate was 2°/min. The XRD was used to investigate the intercalation or the exfoliation, behavior of the nanoclay by estimating the distance between the silicate platelets (*via* Bragg's Law). The samples were scanned over the range of 2θ = 1° to 10°. The dimensions of the specimens for the XRD analysis were 10 x 10 x 4 mm (length x width x thickness).

Scanning electron microscopy

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

Statistical Analysis

Data analysis was performed using SPSS Statistical Software (IBM Software, Armonk, New York) in terms of one-way analysis of variance. The average values were compared and classified using the Duncan test at the 95% confidence level.

RESULTS AND DISCUSSION

The F-value and significance level are summarized in table 2.

Table 2. Analysis of variance (F-value and significance level) of nanoclay in the nanocomposite.

Nanoclay (%)	Tensile Strength (MPa)	Flexural Strength (MPa)	Tensile Modulus (MPa)	Flexural Modulus (MPa)	Impact Strength (J/M)	Water Absorption (%)
0	$19,85^{a}(0,65)$	$24,28^{a}(0,52)$	$2089^{a}(71,2)$	$1612^{a}(101)$	28,79(0,52)	$5,23^{c}(0,25)$
2	$21,52^{b}(0,3)$	$25,74^{c}(0,88)$	$2324^{b}(108)$	$1715^{b}(63,9)$	28,9(0,97)	$4,82^{b}(0,12)$
4	$21,08^{b}(0,94)$	$25,18^{b}(0,39)$	$2360^{b}(42)$	$1756^{b}(87,2)$	29,91(0,12)	$4,57^{a}(0,08)$
F-Value	38,820*	35,265*	41,966*	16,341*	$0,402^{ns}$	53,861*

* 95% significance level; ^{ns} no significance
(small letters indicate the Duncan ranking of the averages at a 95% confidence interval.)
Values in parentheses are standard deviation

Mechanical Properties

The effect of nanoclay on the tensile and flexural strengths, as well as the tensile and flexural modulus, was found to be significant at the 95% level, while the notched impact strength was not significant at the 95% level. The mechanical properties of the composites are dependent on the interface and inter-phase interactions between the wood flour and the polymer matrix. The effects of the nanoclay content on the mechanical properties of reprocessed nanocomposites are shown in Table 2. For the composites, the tensile and flexural strength increased with increasing nanoclay content at 2 wt.% and then decreased when the nanoclay was increased at 4 wt. % (Table 2). Effects of the addition of nanoclay at 2 wt.% can be attributed to the strong interaction between the matrix (polymer) and silicate layers due to formation of hydrogen bonds (Yeh and Gupta 2010) and the formation of intercalation or exfoliation structure, in the nanocomposite (ZiaeiTabari *et al.* 2011, Han *et al*. 2008). The decrease in tensile and flexural strength at 4 wt. % nanoclay may be related to the formation of agglomerated clay tactoids (Chen *et al.* 2007, Samal *et al.* 2008). Another reason for the higher strengths from the addition of the nanoclay at 4 wt.% could be related to the absorption of the coupling agent by the nanoclay (Yeh and Gupta 2010).

Increasing the nanoclay content at 4 wt.% increased the tensile and flexural modulus and notched impact strength (Table 2). The large aspect ratio and high interfacial contact area of the nanoclay filler can improve the tensile and flexural modulus (Ramos Filho *et al.* 2005, Advani 2007). The increment of the modulus depends on the dispersion of nanoclay in the composites. Thus, one reason for the increased modulus in these nanocomposites could be the better dispersion of the nanoclay through the reprocessed high density polyethylene. This can, in turn, lead to reduced values of viscosity and molecular weight due to the greater MFI during the recycling process (Elloumi *et al.* 2010).

Water Absorption

The effect of nanoclay on water absorption was found to be significant at the 95% level. Table 2 shows the water absorption of the samples *versus* nanoclay content. For all of the samples, the water absorption decreased as the nanoclay content increased. Accordingly, increasing the nanoclay amount caused a reduction in the 720-h water absorption and had a positive effect on reducing the long-time water absorption rate in WPCs. Generally, water absorption in WPCs is governed by two mechanisms: the hygroscopic nature of the fillers/fibers and the penetration of water into the composites (diffusivity) via gaps and flaws at the interfaces between the fibers and the plastic matrix (Ghasemi and Kord 2009, Eshraghi *et al.* 2013). Because the composite microvoids and the lumens of the fibers were filled with nanoclay, penetration of water into the deeper parts of the composite was inhibited (Ashori and Nourbakhsh 2011).

X-ray Diffraction

The clay dispersion processes were studied by X-ray diffraction (XRD). The XRD patterns of the nanoclay and the WPCs with different nanoclay loadings are shown in Fig. 1. By considering Bragg's law, we have estimated the distance between silicate platelets and compared it with the basal plane distance of Cloisite 30B to determine whether intercalation or exfoliation occurs:

$$2d \sin \theta = \lambda n \qquad (1)$$

where d is the distance between the crystallographic planes, θ is the half-angle of diffraction, n is an integer, and λ is the wavelength of the X-ray radiation.

The $2\theta = 4{,}75°$ peak is related to pure clay with $d_{001} = 18{,}58$ Å. In the sample with 2% nanoclay, the peak shifted to a lower angle ($2\theta = 1{,}83°$; $d_{001} = 48{,}22$ Å), which implied the formation of intercalation morphology. The peak related to 4% nanoclay appeared at $2\theta = 1{,}95°$; $d_{001} = 45{,}25$ A°. These data showed that the order of intercalation was higher at 2 wt.% nanoclay than at 4 wt.% nanoclay concentration. Thus, one reason for the achievement of an intercalated structure in these nanocomposites could be better dispersion of the nanoclay throughout the reprocessed high density polyethylene. This can in turn lead to reduced values of viscosity and molecular weight due to the greater MFI during the recycling process (Elloumi *et al.* 2010). These results are in agreement with those of Kord (2012) and Khademi Eslam *et al.* (2013).

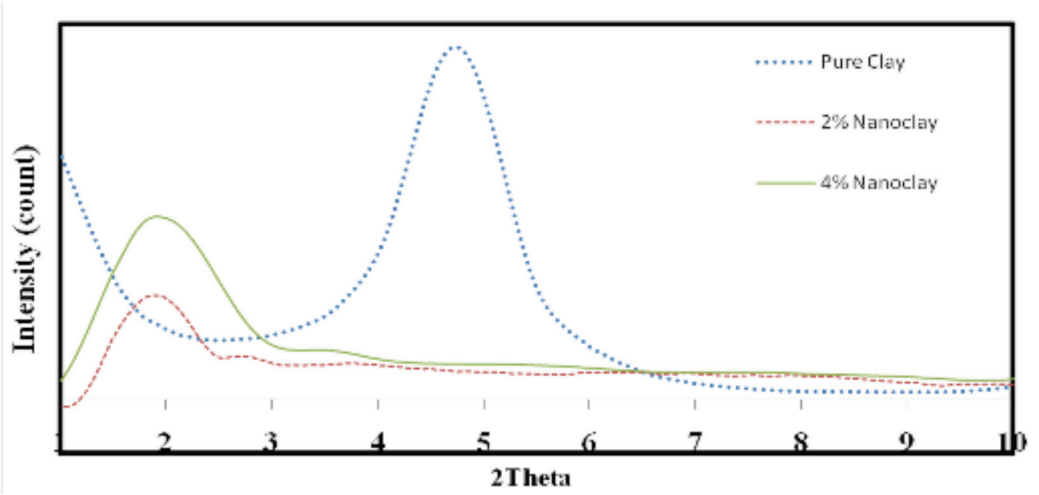

Figure 1. XRD patterns of the nanoclay content at 2θ = 1 to 10°.

Scanning electron microscopy

Based on the images taken by a SEM, one could find proper distribution and consistency between the filler and the matrix. The obtained micrographs confirmed the results of mechanical and physical tests on the composites. The created voids imply a weak connection area between the fibers and the matrix. It means that the fibers are detached from surface of the matrix by introduction of stress and pressure due to the weak connections they have with the matrix. Since the nanoclay is absorbent of the coupling agent (Yeh and Gupta 2010), once a larger amount of the nanoclay is used (4 wt%), further addition of the nanoclay will increase the absorption of the coupling agent, too. In this case, the coupling agent does not establish a proper connection between the matrix (polymer) and the lignocellulosic material. As evident from figure 2c, presence of the larger particles on the fracture area with 4 wt% nanoclay is indicative of the weaker connection between the bagasse flour and the polyethylene matrix. A comparison between this fracture area and the one obtained from a sample with 2 wt% nanoclay showed that the smaller ad finer pores in these samples bear a more appropriate connection between the polymer and the lignocellulosic material (Figure 2b). There is close correlation between mechanical and physical properties of the composites and their microstructure (Naeemian 2008). Since the nanoclay is absorbent of the coupling agent, further introduction of the nanoclay will increase number of the pores and thus, reduce tensile/bending strength upon using 4 wt% nanoclay in the composite. Fink *et al.* (2000) and Huda *et al.* (2006), examined morphology of the lignocellulosic/polypropylene fibers by SEM photography.

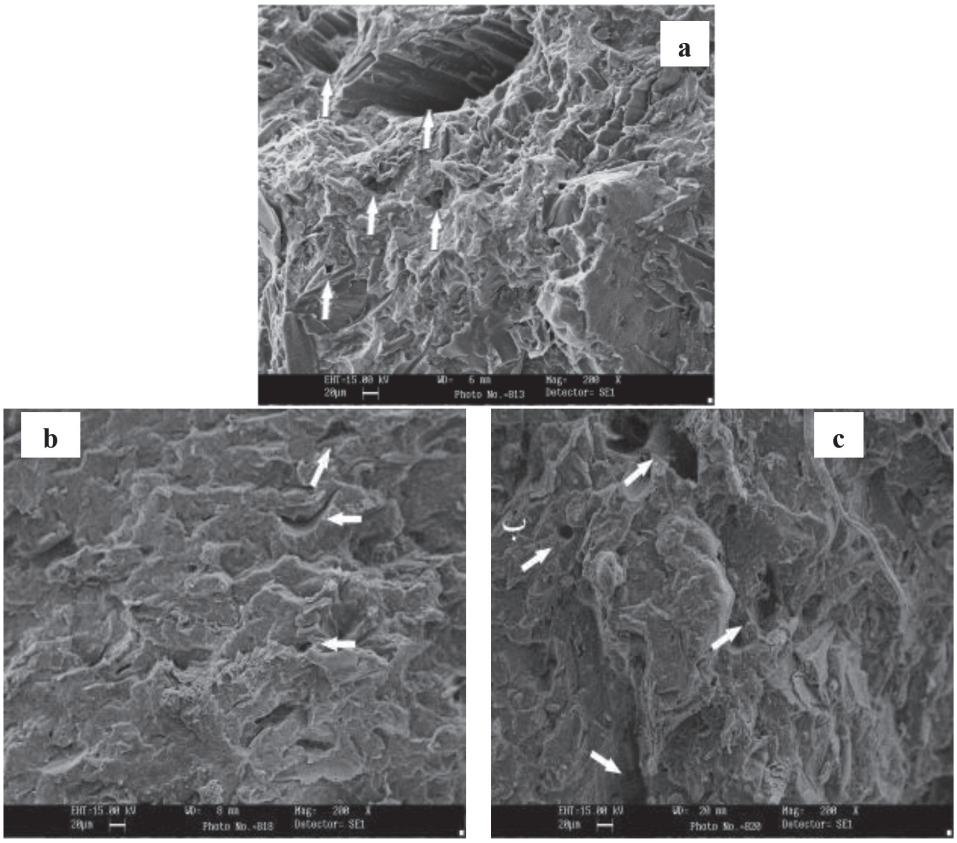

Figura 2. SEM micrograph of the fracture surfaces in the composites (a) 0wt% nanoclay, (b) 2wt% nanoclay, and (c) 4wt% nanoclay.

CONCLUSIONS

Increasing the nanoclay content from 0 to 4 wt% increased the amount of tensile and flexural strengths, tensile and flexural modulus and notched impact by 6,2; 3,7; 12,9; 8,9 and 7,6% respectively; the amount of water absorption was decreased by 12,6%.

By increasing the nanoclay content at 2 wt.%, the tensile and flexural strengths of the composite were increased. However, the addition of 4 wt.% nanoclay resulted in reductions of these properties.

By increasing the nanoclay content at 4 wt.%, the tensile and flexural modulus and notched impact strength of the composite was increased.

Increasing the nanoclay content at 4 wt.% decreased the water absorption of the composite.

Morphological studies of the nanocomposite using XRD spectra showed that an intercalated structure was created in the composite material. The order of the intercalation for samples containing at 2 wt.% nanoclay was higher than that containing at 4 wt.% nanoclay. The d-spacing of layers decreased with increasing nanoclay content.

Scanning electron microscopy (SEM) showed that at 2 wt% nanoclay samples with lower and more uniform pores compared at 4 wt% nanoclay samples, respectively.

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