Studying the Effect of Size of Bagasse and Nanoclay Particles on Mechanical Properties and Morphology of Bagasse Flour/Recycled Polyethylene Composites

Amir Hooman Hemmasi,[a] Ismail Ghasemi,[b] Behzad Bazyar,[a] and Ahmad Samariha [a,]*

The effect of the size of bagasse and nanoclay on mechanical properties and morphology of bagasse flour/recycled polyethylene nanocomposite was studied. The content of bagasse flour was considered to be constant at 40%, with the size of the remaining flour on sieves of mesh 40, 70, and 100, and the accompanying nanoclay content being 0, 2, and 4 wt%, respectively. It was found that tensile strength, flexural strength, and tensile and flexural modulus were increased by decreasing the size of the particles to mesh 70. Notched impact strength was also increased by reduction of the flour dimensions. Increasing the nanoclay content up to 2 wt% led to enhanced tensile and flexural strengths as well as tensile and flexural moduli of the composite material. These properties were hurt by the addition of 4 wt% nanoclay. On the other hand, increasing the nanoclay content up to 4 wt% is expected to decrease notched impact strength of the composites. X-ray diffraction (XRD) data indicated that the order of intercalation was higher at 2 wt% nanoclay in comparison with the samples containing 4 wt% nanoclay, and the d-spacing of layers decreased with increasing of nanoclay particles content.

Keywords: Composite; Recycled polyethylene; Nanoclay; XRD; Tensile strength; Flexural strength

*Contact information: a: Department of Wood and Paper Engineering, Science and Research Branch, Islamic Azad University, Tehran, Iran; b: Department of Processing, Iran Polymer and Petrochemical Institute (IPPI), P.O. Box 14965.115, Tehran, Iran; *Corresponding author: a_samariha@yahoo.com*

INTRODUCTION

Lignocellulosic fillers in the form of flour are excellent candidates to substitute for conventional mineral fillers such as glass and talc in producing thermoplastic composite products, due to their being inexpensive and available. Generally speaking, all filler materials including both organic and mineral promote application of the plastics and reduce their production cost. Nanostructures are a new class of polymeric composites, in which structures composed of nanometer-size particles are used. Nanoclay is an example of these particles which improve properties of the polymeric composites as a result of their special dimensions and high aspect ratio in comparison with other fillers when used in relatively small proportions (4% to 5%) (Sun *et al*. 2007). Wu *et al*. (2007) have claimed that the addition of only 2% nanoclay to the composition of spruce wood flour/HDPE will increase tensile strength and flexural strength by 13% and 24%, respectively. Wang *et al*. (2005) have studied morphological, mechanical, and thermal properties of the composites reinforced with nanoclay particles. They found that these fillers cause better dispersion of the particles in the polymerized matrix and finally raise tensile modulus, tensile strength, and hardness of the composite thanks to their exfoliated structure. Application of bagasse in manufacturing composites has been addressed by numerous researchers, including Tehrani *et al*. (2008), Luz *et al*. (2007), Talavera *et al*.

(2007), Ashori and Nourbakhsh (2009), and Najafi and Khademi-Eslam (2011). However, no relevant work was found on the simultaneous effect of lignocellulosic material and nanoclay particles on the mechanical properties of the composites. Application of agricultural resides such as bagasse is significantly important in manufacturing wood–plastic composites in terms of environmental issues and optimal utilization of waste materials. Therefore, the current work tries to explore the effect of the size of bagasse flour and nanoclay content on the mechanical properties of bagasse flour/ recycled polyethylene/nanoclay composite.

EXPERIMENTAL

Materials

Bagasse flour was supplied by Dez Wood Plastic Company and used at the 40 wt% level in the composite. Effects of sizes of bagasse flour particles were examined by comparing subsamples remaining on sieves of mesh 40, 70, and 100.

Municipal solid-waste materials are not systematically separated in Iran, and retailers of once-used dishes are usually unaware of the constituents of these dishes and the possible existence of impurities in their constituents. Therefore, in an effort to avoid error and to increase accuracy, it was decided to prepare the matrix material (recycled polyethylene) in the laboratory rather than collecting used milk bottles. In this regard, high density polyethylene with code 5620 was purchased from Arak Petrochemical Co. (Iran) with 20 g/10 min MFI (Melt Flow Index) and a density of 0.956 g/cm^3. Then HDPE was recycled in a twin-screw extruder.

Maleic anhydride grafted to polyethylene (MAPE), provided by Solvay with a density of 0.965 g/cm^3 (MFI 7 g/10 min, 1 wt% maleic anhydride) was used as a coupling agent.

A commercial nanoclay product with trade name of Cloisite 30B was introduced from Southern Clay (Southern Clay Products Inc., Texas, USA) at the three levels of 0%, 2%, and 4%. Cloisite-30B is a natural montmorillonite modified with a quaternary ammonium salt, having a d-spacing of 18.5°A and modifier concentration of 90 meg/ 100 g clay.

Methods

A co-rotating twin-screw extruder (Collin) was used at the Iran Polymer and Petrochemical Research Institute. Bagasse flour, granules of recycled polyethylene, and a coupling agent were properly mixed with nanoclay and then poured into the funnel of the extruder. To make the final samples with the injection-molding machine, the produced nanocomposite mixture must first be transformed into granules. This was done in a pilot scale grinder (WIESER, WGLS 200/200 model). The yielded granules were dried in a laboratory oven and prepared for the injection stage. Test samples were made in a single-screw extruder equipped with a pressure molding system (Imen Machine, Iran). After molding, samples of tensile, flexural, and notched impact strengths were examined according to ASTM D 638, ASTM D 747, and ASTM 256 standards, respectively. X-ray diffraction (XRD) analysis was carried out with a Seifert-3003 PTS (Germany) with CuKa radiation (λ=1.54 ^{o}A, 50 kV, 50 mA) at room temperature. The scanning rate was 1°/min. The XRD were used to investigate the intercalation, or exfoliation, behavior of the nanoclay by estimating the distance between the silicate platelets (by considering Bragg's Law). The samples were scanned over the range of 2θ = 1° to 10°.

Statistical Analysis

Data analysis was run completely randomly. Finally, comparison and classification was implemented using the Duncan Multiple Range Test at a 95% confidence level, while SPSS software was used for statistical calculations, as shown by lower-case letters on the bars in each figure.

RESULTS AND DISCUSSION

The aspect ratios for bagasse flour in meshes 40, 70, and 100 were obtained as 3.29, 4.17, and 3.82, respectively. Bagasse flour was studied in three different levels of nanoclay particles and dimensions, namely 0%, 2%, and 4%. The value of F and significance level are summarized in Table 1.

Table 1. Analysis of Variance (F-Value and Significance Level) of the Results of Bagasse and Nanoclay Particles on Nanocomposite

Properties Variable	Tensile Strength	Flexural Strength	Tensile Modulus	Flexural Modulus	Impact Strength
Bagasse size	134.945*	58.987*	70.888*	112.799*	173.243*
Nanoclay	126.562*	92.761*	87.839*	36.431*	0.299^{ns}
Bagasse size* Nanoclay	0.385^{ns}	1.211^{ns}	0.208^{ns}	0.531^{ns}	2.126^{ns}
* 95% significance level ^{ns} no significance					

Figures 1 through 5 depict the effects of the size of bagasse flour and nanoclay on mechanical properties of the nanocomposite.

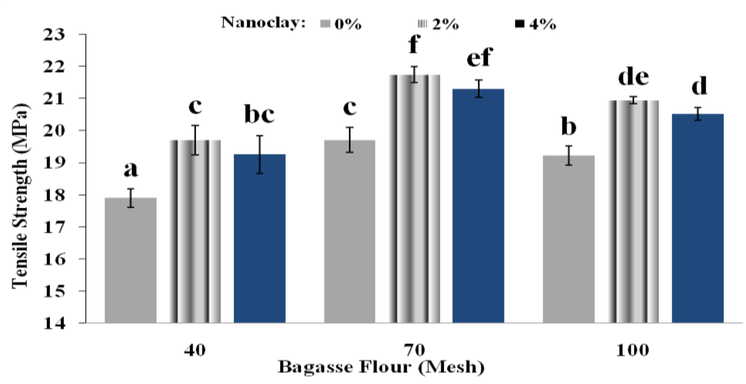

Fig. 1. Effect on nanoclay and size of bagasse flour on tensile strength of nanocomposite

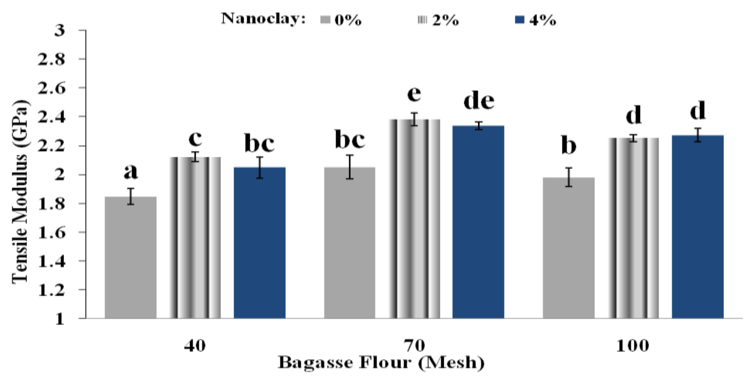

Fig. 2. Effect on nanoclay and size of bagasse flour on tensile modulus of nanocomposite

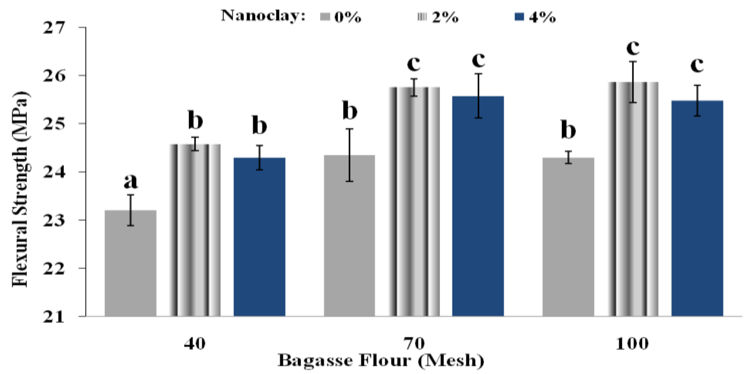

Fig. 3. Effect on nanoclay and size of bagasse flour on flexural strength of nanocomposite

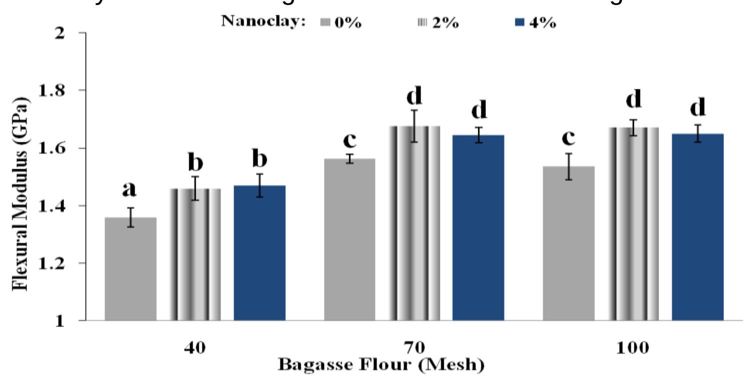

Fig. 4. Effect on nanoclay and size of bagasse flour on flexural modulus of nanocomposite

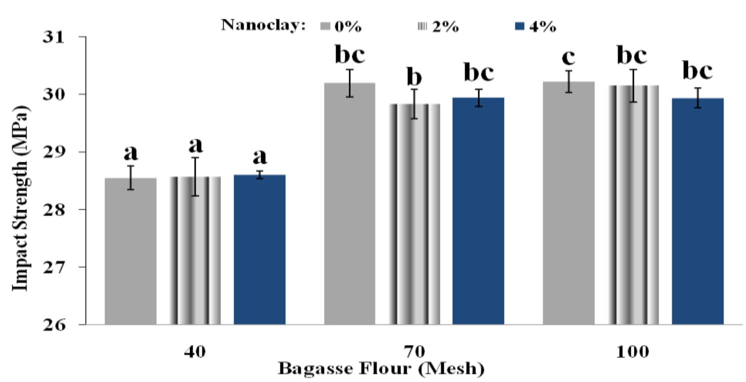

Fig. 5. Effect on nanoclay and size of bagasse flour on impact strength of nanocomposite

Effect of the Size of Bagasse Flour

The effect of the size of bagasse flour on tensile, flexural, and notched impact strengths as well as tensile and flexural moduli was found to be significant at the 5% level. Maximum tensile and flexural strength and also tensile and flexural moduli in the composite made from bagasse flour was obtained at mesh 70. The increased tensile strength and modulus as well as flexural strength and modulus of the bagasse flour at this size can be attributed to the greater ratio of length to diameter. The increased aspect ratio of the flour might further neutralize stress in the polymeric matrix (Nourbakhsh *et al*. 2010). However, minimum values of all these strengths were met for the bagasse flour of mesh 40. Notched impact strength was the highest in mesh 100. Moreover, further reduction of the particle size could transfer stress among the particles more homogeneously and cause greater strength in a smaller size of the particles. Meanwhile, finer particles would contribute to more uniform mixing of the lignocellulosic material and the polymeric matrix, while facilitating the finer particles passing through the injection orifice. Improved injection by the injection-molding machine may lead to increased strength (Gorjani and Omidvar, 2005). Similar results have also been reported by several researchers, including Shakeri and Omidvar (2006), Ghasemi *et al*. (2008), Bledzki and Gassan (1999), Stark and Rowlands (2003), Williams (2003), Febrianto *et al*. (2006), Nourbakhsh *et al*. (2010), and Huang *et al*. (2011).

Notched impact strength is increased for finer particles. In fact, the smaller particles in comparison with larger particles are more capable of creating an environment with a greater continuity and they can bear the applied stresses more properly. On the other hand, it can be argued that the larger particles may probably act as stress concentration points and create locations for crack initiation, which can simply lead to fracture of the composite. Furthermore, short fibers (small particles) incorporate a larger specific area due to their greater number. Thus, they show a more uniform dispersion and a better compatibility between the fibers and the matrix material (Caraschi and Lopes 2002). Moreover, particles of mesh 70 have a relatively higher aspect ratio and reduce the number of stress concentration points. The ascending trend of impact strength with smaller particles has also been addressed by other researchers, including Shakeri *et al*. (2006), Naeimian (2008), Wu *et al*. (2000), Yang *et al*. (2004), Cui *et al*. (2008), Basiji *et al*. (2010), and Huang *et al*. (2011).

Effect of Nanoclay

The effect of nanoclay on tensile and flexural strengths, as well as tensile and flexural moduli was found to become significant at the 5% level, while notched impact strength was not significant at the 5% level. The highest amount of tensile and flexural strengths and associated moduli was obtained for the composite made of 2% nanoclay. Minimum values of these strengths were met using 0% nanoclay. Effects of addition of the nanoclay up to 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), the large aspect ratio of nanoclay particles (Kord *et al*. 2008; Sun *et al*. 2007), and the formation of intercalation or exfoliation structure in the nanocomposite (Zhao *et al*. 2006). Meanwhile, heterogeneity and high ratio of surface to volume of the nanoclay with organic materials is also relevant in reinforcement capability of the nanoclay. Thereby, the nanoclay particles as reinforcement materials increase the interface area between the two phases (Wu *et al*. 2007).

Therefore, the obtained results demonstrate that all strengths of the composites were enhanced by addition of the nanoclay up to 2 wt%, in agreement with the results found by Kord *et al*. (2008), Kord (2011b), Tasuji *et al*. (2012), Nourbakhsh (2012), Chowdhury *et al*. (2006), Lei *et al*. (2007), Wu *et al*. (2007), Han *et al*. (2008), Ashori and Nourbakhsh (2009), Ziaei Tabari *et al*. (2011a), Danesh *et al*. (2012), and Kord (2012).

At the same time, increasing the nanoclay content up to 4 wt% will probably reduce all strengths of the composite owing to agglomeration and accumulation of the nanoclay particles and also to formation of interconnected masses at fracture points (Kord *et al*. 2008). Another reason for the higher strengths from the addition of the nanoclay up to 4 wt% could be related to absorption of the coupling agent by the nanoclay (Yeh and Gupta 2010). The coupling agent acts as a bridge between the matrix (polymer) and the filler/reinforcement material and increases their mechanical strengths *via* improving adherence between them (Mustapa *et al*. 2005; Hristove *et al*. 2004). When the amount of nanoclay in the composite structure is increased, they would attract much more coupling agent and avoid proper connection of the coupling agent with the lignocellulosic particles. This can degrade the strengths (Yeh and Gupta 2010).

The notched impact strength was also decreased by addition of the nanoclay up to 4 wt%. Since the nanoclay particles create stress concentration areas and crack initiation points, the impact strength of the composite is decreased by increasing the nanoclay content. In other words, the existence of the nanoparticles in the polymeric matrix will reduce mobility of the chains and their possible energy loss, while increasing the energy absorbed by the composite and creating stress concentration points. These points can act as locations for fracture and crack initiation (Han *et al*. 2008). Meanwhile, hardening of the polymeric chains due to addition of the nanoclay can be accounted for. That is why the notched impact strength is reduced by increasing the nanoclay content, which is in agreement with the results obtained by Kord *et al*. (2008), Tasuji *et al*. (2012), Nourbakhsh (2012), Chen *et al*. (2007), Han *et al*. (2008), Lei *et al*. (2007), Ashori and Nourbakhsh (2009), and Kord (2012).

X-ray Diffraction

X-ray diffraction apparatus was utilized in order to evaluate the nanoclay in the polymeric matrix. By XRD analysis one can measure the distance between nanoclay layers in addition to examining intercalation and exfoliation in the prepared nanocomposite samples. In a typical intercalated structure, the polymer is diffused into the layers of clay and increases the distance between them, but the layers are still spatially related and parallel to each other. However, in a typical exfoliated structure, the layers of clay are completely detached and dispersed throughout the polymer. Such a structure will cause the maximum reinforcement in the polymeric substrate (Medani 1999). The XRD patterns of Nanoclay and WPCs with different percentage of nanoclay loading are shown in Fig. 6. 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,

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

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

It can be seen that the $2\theta = 4.75^o$ peak was related to neat clay with d_{001}= 18.58 nm. The peak was shifted to smaller angles ($2\theta = 1.77^o$, d_{001}= 49.85 nm), ($2\theta = 1.81^o$, d_{001}= 48.75 nm), while it was shifted to ($2\theta = 1.69^o$, d_{001}= 52.21 nm) for composites having 2 wt% nanoclay in mesh 40, 70, and 100, and ($2\theta = 1.81^o$, d_{001}= 48.75 nm), ($2\theta = 1.91^o$, d_{001}= 46.2 nm), and ($2\theta = 1.73^o$, d_{001}= 51.01 nm) for composites which contain 4 wt% nanoclay in 40, 70, and 100, respectively, It can thus be inferred that an intercalated morphology had been formed. These data indicate that the order of intercalation was higher at 2 wt% Nanoclay in comparison with the samples containing 4 wt% Nanoclay (the tensile strength confirmed this fact). Thus, one reason for achievement of an intercalated structure in these nanocomposites could be better dispersion of the nanoclay through the recycled 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). The results of this part of the research are in agreement with those of Danesh *et al*. (2012), Kord (2011a), and Ziaei Tabari *et al*. (2011b).

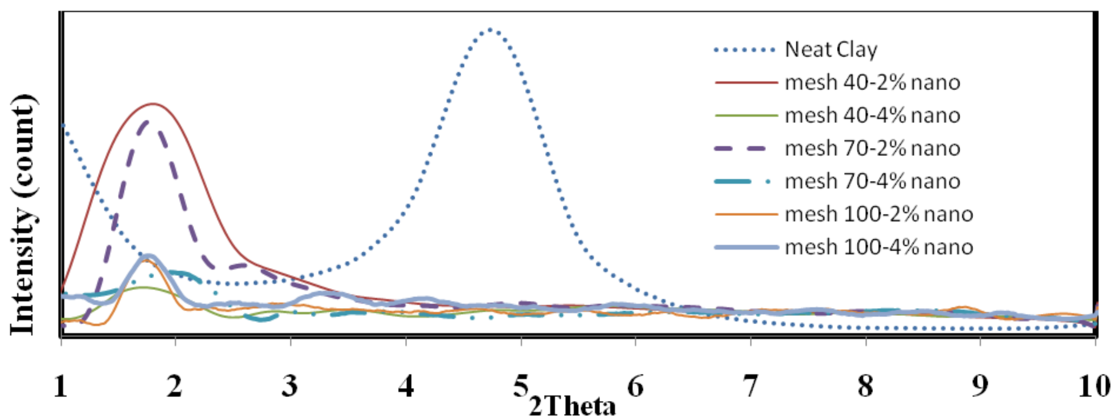

Fig. 6. XRD patterns of nanoclay content at 2θ = 1 to 10°

CONCLUSIONS

1. By reduction of the size of bagasse flour to mesh 70, tensile and flexural strengths as well as tensile and flexural moduli were increased due to the increased aspect ratio, while at mesh 100 the values of these strengths are decreased again due to further reduction of this ratio.
2. Notched impact strength was increased by reducing the size of bagasse flour particles.
3. By increasing the nanoclay content up to 2 wt%, tensile and flexural strengths as well as tensile and flexural moduli of the composite were increased. Afterward, by addition of 4 wt% nanoclay, these properties were reduced. On the other hand, the latter will also degrade notched impact strength of the composites.
4. Morphological studies on the nanocomposite by XRD spectra showed that an intercalation structure was created in the composite material, the order of intercalation for samples containing 2 wt% nanoclay was higher than that of 4 wt% nanoclay. The d-spacing of layers decreased with increasing of nanoclay particles content.

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