Effect of Nanographene on Physical, Mechanical, and Thermal Properties and Morphology of Nanocomposite Made of Recycled High Density Polyethylene and Wood Flour

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The effects of the amount of nanographene on physical, mechanical, and thermal properties and morphology of the wood-plastic composites were investigated. This wood-plastic was made using recycled high density polyethylene (HDPE), nanographene, and wood flour. Four weight levels, 0, 0.5, 1.5, or 2.5 wt.% of nanographene, were combined with 70% polymeric matrix and 30% lignocellulosic material with an internal mixer. The results showed that by increasing the amount of nanographene up to 0.5% by weight, the flexural strength, flexural modulus, and notched impact strength of the composite increased. After adding 2.5 wt.% nanographene, these properties were reduced. By increasing the amount of nanographene, both the amount of residual ash and the thermal stability increased. Study of the images from scanning electron microscope (SEM) showed that the samples containing 0.5% of nanographene had less pores and were smoother than other samples.

Keywords: Recycled high density polyethylene; Nanographene; Wood plastic composites

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INTRODUCTION

Wood plastic composite (WPC) is a combination of polymer and cellulosic materials (Sanadi et al. 2001). WPCs generally can be considered to be environmentally friendly and require low maintenance compared to the wood. Wood plastic composites have a wood-like appearance, but they are much more efficient with respect to solid wood. The useful features of this composite include low moisture absorption, resistance to oxidation, resistance to diffusion and destruction by insects, low weight, high durability, high dimensional stability, desirable physical and mechanical properties, ease of cutting, and ability to apply decorative coatings. The use of wood and non-wood plant fiber as reinforcements in thermoplastics has increased dramatically in recent years (Caraschi and Leão 2002).

By using nanomaterials, the composite properties presently achieved in the industry can be improved, making it possible to produce new products with high-added value and more efficiency (Hemmasi et al. 2013).

A considerable amount of plastic wastes enters daily into the environment, and its recycling is important for the economy and the environment. Generally, polyethylene, polypropylene, polyethylene terephthalate, polystyrene, and polyvinyl chloride are the constituents of plastics in municipal solid waste (Najafi 2013).

Currently, approaches based on nanotechnology are being considered to reinforce composites. Among the different kinds of nanoparticles that are used in the manufacture of wood-plastic composites, in recent years, graphene is notable because of its exceptional
properties, including mechanical, heat, electrical, and optical characteristics (Dato et al. 2009; Cardinali et al. 2012; Cardinali et al. 2012; Sheshmani and Amini 2013).

The incorporation of nanomaterials in existing composites could improve their properties and produce new products with high added value and more efficiency (Wegner and Jones 2007).

Graphene is a two-dimensional allotrope of carbon made of a single layer of carbon atoms, which is formed by its sp² orbitals attached into a two-dimensional six-face crystal network (Stankovich et al. 2006; Vickery et al. 2009; Polschikov et al. 2013; Wang et al. 2013). Its intrinsic properties allow even small additions of graphene to significantly improve the properties of composites (Cardinali et al. 2012). Graphene’s superior properties compared with the matrix polymers in graphene/polymer nanocomposites results in high mechanical, heat resistance, gas permeability, electrical, and resistance against fire compared with pure polymer (Balandin et al. 2008; Ansari and Giannelis 2009; Potts et al. 2011). There is greater improvement and enhancement of mechanical and electrical properties of polymer-graphene composites than in clay nanocomposite or other nanocomposites (Kim and Macosko 2009; Kuilla et al. 2010).

Wood-plastic composites made from poplar wood flour, PP polymer material, and nanographene sheets proceed show increased connection and adhesion between particles and are improved by maleic anhydride grafted with polypropylene (MAPP) (Sheshmani and Amini 2013). These experiments showed that when the amount of 0.8 wt.% was used, the torsional and tensile properties reached their maxima. This was attributed to a lack of proper transfer of stress and agglomeration when using the amount of 3 to 5% by weight, such that physical and mechanical properties of structures reached their lowest values. Moreover, adding of this amount of graphene reduced water absorption and thickness swelling to 35% and 30%, respectively.

Chaharmahali et al. (2014) examined the effect of graphene nanoparticles on the physical and mechanical properties PP and bagasse fiber composites. Most of the strength was obtained in the samples made with a 0.1% graphene, and increase of fiber from 15 to 30% increased the flexural and tensile properties but decreased the resistance to impact. Also, at the level of 15% of the fibers, adding graphene improved the durability against thermal degradation of composites, but diverse results were obtained at the level of 30%.

Chatterjee et al. (2013) examined properties of the tensile and crystallization of fiber polyamide 12 reinforced with graphene and carbonic nanotubes. The crystallization index of polyamide fibers increased after adding nanofillers due to their effect on nucleation. Also, flexural and tensile strengths as well as the relevant modules were increased by adding the nanofillers. The increasing modulus was very significant and meaningful.

This study investigated the effect of nanographene additions on the mechanical and thermal properties of wood-plastic composites.

**EXPERIMENTAL**

**Materials**

**Cellulosic fillers or fillers**

Filling material consisted of wood flour that passed through the sieve with a mesh size of 50 and remained on a sieve with a mesh size of 70. The prepared wood flour was dried for 24 h at 80 ± 3 °C.
**Polyethylene**

High density polyethylene (HDPE; HD5218, Arak Petrochemical Co., Arak, Iran) with a melt flow index 18 g/10 min and density of 0.956 g/cm³ was used as a polymer matrix. To recycle the plastic, the polymer was subjected to a three-stage thermo-mechanical degradation in a twin screw co-direction extruder (Brabender, Duisburg, Germany). After each extrusion, the output material was converted into granules by the cutters. The index of recycled HDPE melt flow according to ASTM D1238-04 (2004) was measured using a Gottfert / MI-4 device (Rheometer Manufacturers, Buchen, Germany).

**Coupling agent**

To create compatibility between wood flour and recycled polyethylene, tests were done with addition of 3% maleic anhydride grafted with polyethylene (MAPE; PEGW 220, Arya Polymer Product Co., Isfahan, Iran) with the index of melt flow 7 g/10 min and density 0.964 g/cm³.

**Nanographene**

Type AO-4 graphene nanoparticles were purchased from Graphene Supermarket Co (USA). Their characteristics are presented in Table 1.

**Table 1. Profile of Nanographene**

<table>
<thead>
<tr>
<th>Specific Surface (m²/g⁻¹)</th>
<th>Color</th>
<th>Purity (%)</th>
<th>Average Thickness (mm)</th>
<th>Length of Particles (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>More than 15</td>
<td>black</td>
<td>98.5</td>
<td>60</td>
<td>3-7</td>
</tr>
</tbody>
</table>

**Methods**

**Mixing of material**

The polymer matrix (recycled HDPE), wood flour, MAPE, and nanographene were mixed together as shown in Table 2. The materials were mixed in a HAAKE SYS 9000 internal mixer (De Soto, MO, USA) in Iran Polymer and Petrochemical Institute for 8 min with a mixing degree of 150 °C and stirring speed of 60 rpm to achieve constant torque. After mixing, the output was converted to granules by a WIESER material crusher (model WG-Ls 200/200, Germany).

**Preparation of samples**

A mini test press machine (Toyoseiki Company, Tokyo, Japan) was used to prepare samples for the flexural test, notched impact strength test, and thermogravimetric analysis (TGA) at 200 °C and 25 MPa pressure for 4 min. The samples were cooled to 80 °C while the press continued. To reach equilibrium moisture before mechanical tests, samples were stored for two weeks in a conditioning room (20 ± 2 °C and 65 ± 5% relative humidity).
Table 2. Components of Wood Plastic Composites

<table>
<thead>
<tr>
<th>Treatment Number</th>
<th>WF (wt.%</th>
<th>rHDPE (wt.%</th>
<th>NG (wt.%</th>
<th>M (wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>30</td>
<td>67</td>
<td>0</td>
<td>3</td>
</tr>
<tr>
<td>2</td>
<td>30</td>
<td>66.5</td>
<td>0.5</td>
<td>3</td>
</tr>
<tr>
<td>3</td>
<td>30</td>
<td>65.5</td>
<td>1.5</td>
<td>3</td>
</tr>
<tr>
<td>4</td>
<td>30</td>
<td>64.5</td>
<td>2.5</td>
<td>3</td>
</tr>
</tbody>
</table>

WF, wood flour; rHDPE, recycled high density polyethylene; M, MAPE; NG, nanographene

Measurement of mechanical properties

By using an Instron Universal Testing Machine (model 1186) with speed of 2 mm/min and ASTM D-638-10 (2010), Flexural strength and flexural modulus were measured. The specimen dimensions for the tests were 105 x 13 x 5 mm (length x width x thickness).

Also Zwick Universal Testing Machine (model 5102) and ASTM D-256-10 (2010) standard was used for Notched impact strength measurements. For this test the specimen dimensions were 60 x 12 x 6 mm (length x width x thickness).

Five replicates were used for a piece property in each treatment level and average values were reported.

Thermogravimetric analysis

TGA measurements were collected using a TGA Q50 thermal analyzer (PL-150, Agilent, Santa Clara, CA, USA) with 7 mg of the test sample in a temperature range of 25 to 700 °C with a heating rate of 15 °C/min.

Scanning electron microscope (SEM)

In this study, model of scanning electron microscope (AIS2100; Seron Technology Co., Korea), was used.

Statistical analysis

SPSS software (IBM Software, Armonk, NY, USA; version 11.5) was used to compare the statistical difference between the mean of results that obtained from variance analysis. If the differences in means were meaningful, Duncan’s multiple range test was used for means comparison.

RESULTS AND DISCUSSION

Melt Flow Index

The melt flow index measures the fluidity of a polymer, and changes in this value reflect changes in the polymer structure. After three rounds of recycling, the melt flow index of HDPE increased from 18 g/10 min for virgin polymer to 35.04 g/10 min. Increasing the recycling frequency influences the thermomechanical properties, reduces the crystallinity, and lowers average of molecular weight (increased melt flow index) of polyethylene (Incarnato et al. 2003).
Mechanical Properties

The effect of nanographene on the flexural strength and notched impact strength was significant at the 95% confidence level. Its effect on the flexural modulus was not significant (Table 3).

**Table 3. Analysis of Variance of Nanographene Effects on Mechanical Properties**

<table>
<thead>
<tr>
<th>Property</th>
<th>F-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flexural Strength (MPa)</td>
<td>39.155*</td>
</tr>
<tr>
<td>Flexural Modulus (MPa)</td>
<td>2.486 ns</td>
</tr>
<tr>
<td>Notched Impact Strength (Jm²)</td>
<td>59.59*</td>
</tr>
</tbody>
</table>

*significance level 95%; ns, not significant

The Effect of Nanographene on Flexural Strength

Changes in flexural strength in composites containing different amounts of nanographene are shown in Fig. 1. The highest (24.77 MPa) and the lowest (20.5 MPa) average flexural strength were observed with 0.5% and 0% nanographene, respectively.

![Fig. 1. Effect of nanographene value on flexural strength](image)

The flexural strength of wood-plastic composites increased up to 0.5 wt.% nanographene, then decreased with additional nanographene. This reduction was statistically meaningful. Rafiee et al. (2009) reported that with the addition of 0.1 wt.% graphene to the epoxy increases the elasticity modulus by 31% and the tensile strength by 14% compared with the initial epoxy, which is due to the high slenderness ratio and good surface adhesion of graphene-epoxy (Rafiee et al. 2009).

The mechanical strength of some composites can be increased by adding nanoparticles (Potts et al. 2011). Increased mechanical properties as a result of low levels of nanoparticles, such as graphene, is easily understood because nanoparticles transfer more tension and improve the connectivity of the composite components (Young et al. 2012). Due to its mechanical properties and very high surface areas, even small amounts...
of graphene mixed with the polymer can enhance the mechanical properties (Farsi and Younesi Kordkheili 2012). The method of adding and weight percent of graphene have a great impact on the final properties of the composites, as adding more than a certain level, causes the forming of plates over each other and reduction of adhesion between the components in the composite. Agglomeration may decrease the mechanical properties. Using low percentages of graphene sheets in composite is an advantage. With regard to the free surface of graphene sheets, it tends to link carbon nanotubes, and it is usually used at very low weights to avoid agglomeration and particles clinging to each other. Adding up to 0.8 wt.% graphene nanoparticles to wood fiber-recycled polypropylene composite increases its mechanical strength, but the properties are reduced by the addition of 5 wt.% graphene (Sheshmani et al. 2013).

The Effect of Nanographene on Flexural Modulus

Changes in the flexural modulus of composites with different levels of nanographene are shown in Fig. 2. The highest (1778.5 MPa) and lowest (1604.6 MPa) average flexural modulus were observed in the samples with 0.5 wt.% and sample 0 wt.% nanographene, respectively.

![Fig. 2. Effect of nanographene value on flexural modulus](image)

Increasing the amount of nanographene to 0.5 wt.% caused the flexural modulus to increase and then decrease. This reduction was statistically meaningful. By increasing graphene to 0.5 wt.% in epoxy resin, the modulus of elasticity is increased; with further increases (up to 2 wt.%), it is reduced (Moazzami Gudarzi and Sharif 2011). In another study, Sheshmani et al. (2013) showed that the highest modulus of elasticity was obtained at 0.8% graphene, and in higher percentages, the modulus was lower. The graphene modulus of elasticity (1 TPa) is significantly higher than the modulus of polypropylene and natural fibers. Adding graphene increases the modulus of wood fiber composite, but the decrease in the modulus at more than 0.5% can be attributed to non-uniform distribution and agglomeration of the particles. There are several factors affecting the performance of the graphene to improve the mechanical properties of nanocomposite, including steady distribution, alignment, and foliation of graphene layers in the matrix (Van Lier et al. 2000;
Xu et al. 2009; Balog et al. 2010). Failure to adhere to these factors reduces the mass and width to thickness of graphene layers, which reduces the modulus of elasticity.

**Fig. 3. Effect of nanographene value on notched impact strength**

**The Effect of Nanographene on Notched Impact Strength**

Changes in notched impact strength in composites with different levels of nanographene are shown in Fig. 3. The highest (32.61 J/m²) and the lowest (19.35 J/m²) average notched impact strength were observed in samples with 0.5 wt.% and 0 wt.% nanographene, respectively.

By increasing nanographene to 0.5 wt.%, the notched impact strength of wood-plastic composite increased and then decreased to the level of 2.5%. This reduction was not statistically meaningful. The reduction of impact strength was predictable because nanographene particles caused more embrittlement of composites and reduced their impact strength. Nanoparticles in the polymer matrix reduced mobility and possibility of their energy loss, increasing the energy absorbed by the composite and creating spots of stress concentration. These spots initiate failures and cracks (Han et al. 2008).

**Thermogravimetric Analysis**

The results of residual ash related to the thermal gravimetric analysis is shown in Fig. 4. By increasing nanographene, the amount of residual ash increased. Figure 4 shows a comparative graph of 30% wood flour calorimetric results at 0, 0.5, 1.5, and 2.5 wt.% nanographene. There were three thermal degradation ranges in the sample. In the first phase, by increasing the amount of nanographene, the samples were destroyed at a higher temperature. In the second phase, which is much more severe, by increasing the nanographene, samples began to accumulate damage at 350 °C. In the third phase, by increasing the amount of nanographene, destruction continues at 386 °C. At this point, the degradation temperature was less than the degradation temperature of other samples, but the temperature difference of destruction of samples was not significant. From 450 to 500 °C, degradation was more severe. Generally, in samples containing nanographene and wood, the loss of weight continued up to 500 °C, after which the weight loss was constant or very minimal. Moreover, thermal degradation and weight loss were initiated at a lower temperature; nanographene increased the thermal stability. The amount of remaining ash in the four composite samples using 0, 0.5, 1.5, or 2.5 wt.% nanographene were 6.03, 6.39, 7.27, and 8.26%, respectively.
Effect of Nanographene on Thermal Properties

Thermal stability of composites is one of the important parameters for process and applications of this class of materials. The production of some composites requires mixing fiber and matrix at high temperature. Thus, thermal degradation of lignocellulosic material causes adverse effects on the composite properties. The effect of graphene content on weight reduction of the composites in the 30% flour during heating (from 25 to 650 °C) is shown in Fig. 4. There was an initial weight loss below 165 °C due to the loss of moisture, which was a very low value that is not clear in the graph. The weight loss of composite without graphene was more uniform than in the other three samples, which was probably due to the positive impact of graphene on delaying the degradation of the polymer matrix material. The curves showed a two-step weight loss in the composites. The first stage, which occurred from about 300 to 500 °C, is related to the wood fibers; the second stage ranged from about 500 to 650 °C and was related to thermal degradation of polymers, which have a greater thermal stability than wood. The initial destruction started at 270 °C to 375 °C and continued to 375 °C, representing the destruction of wood flour. In the first stage, the weight loss or thermal degradation of the composites was decreased by increasing the graphene, which shows the positive impact of graphene on improving the heat resistance the composites. The second phase of degradation began after 350 °C, and it was mainly related to matrix decomposition. In this stage, the distance between graphs was also greater, because decomposition of matrix of graphene-based composites occurs at higher temperatures. The occurrence of this phenomenon is probably due to the fact that graphene particles act as obstacles and delay disintegration of generated volatiles. Adding nanographene particles to polypropylene improves its thermal resistance (Menbari et al. 2015).

In general, increasing nanographene increased thermal stability, resulting in a higher temperature of destruction and weight loss at a higher temperature, as previously reported (Zhu et al. 2001; Gilman et al. 2006). However, the effect of nanographene on thermal stability depends on the type of polymer and processing conditions; nanographene in higher temperature ranges also increases the thermal stability (Nourbakhsh et al. 2010). The most important effect of nanographene on the thermal stability is the formation of a non-burning coal-like layer. Due to the high specific surface and appropriate coverage area, nanographene has a significant role in the thermal stability (Khosravian 2010). The results
showed that the addition of nanographene increased the thermal stability. The samples underwent weight loss and were damaged at high temperature. This phenomenon is probably due to the release of chemicals that are used in modifying of nanographene and the increased ash originating from nanomineral compounds (Nemati et al. 2015).

**Morphology by means of SEM**

This study investigated the composites’ microstructure on the created fracture surfaces. Images obtained from a scanning electron microscope showed an appropriate distribution and compatibility between filler and matrix. Empty spaces indicate a poor connection between the fiber and the matrix, which then indicates that after application of stress and pressure, the fibers separated from its surface, due to having a weak connection with matrix. In this section, we have addressed the fracture surfaces of the constructed composites.

Fracture surfaces of composites show a nearly continuous environment in the presence of 3 wt.% coupling agent. Fibers, to some extent, were surrounded by the ground material and adhesion of these two phases is due to the fact that the fibers could not come out from their places (Figure 5).

As can be seen in Fig. 5, the polyethylene matrix surrounded the cellulose fiber and had good adhesion, but albeit to this good adhesion, small holes again can be seen.

Figure 5 shows images of fracture surfaces of 30 wt.% wood flour at 4 levels (0, 0.5, 1.5 and 2.5 wt.%%) of nanographene. Improvement of mechanical properties by adding nanographene has been shown, and this also was confirmed by scanning electron microscope images, where a significant improvement in the distribution and compatibility between fiber and matrix is visible. Figure 5A shows a sample that is without nanographene; portions of fibers protruding from the polymer matrix are visible. By implying a minimal loading, samples break and fibers are easily removed from the polymer matrix, resulting in pores at the fracture surface of samples. As can be seen in Fig. 5B, wood fibers adhered well to the polymer matrix and no separation of fiber from the matrix was observed, indicating good compatibility of composite’s components with each other. Strong adhesion at the interface between fiber and matrix polymer, related to encapsulation of polyethylene with fibers, was also confirmed by an improvement in mechanical properties. Figures 5C and 5D show that fracture surface of samples containing 1.5 and 2.5 wt.% nanographene had several cavities that reduce the mechanical properties. In fact, the addition of nanographene in large amounts caused their agglomeration. Agglomeration causes voids in the composite and reduction in mechanical strength compared with samples of nanographene filled with less percentages.

Study of fracture surfaces of composites showed that adding nanographene to recycled polyethylene-wood flour composite improved the adhesion between the polymeric matrix and prevented fibers from dissociating from the polymer during fracturing. However, a high percentage of nanographene causes flocculation and improper distribution of graphene particles and their adhering together, thus creating agglomerates and larger pores in the composites, which can be seen clearly in the fracture surface. There was a close correlation between the physical and mechanical properties of the composites and their microstructure. Properties of every reinforced plastic with particles depends on the type of reinforcing material, arrangement of the particles, and how to connect particles with polymeric phase.
In this study, review of the microstructure of composites on the fracture surfaces generated by electron microscopy was performed. The resulting micrographs confirmed somewhat the mechanical and physical tests of composites. The micrographs showed the distribution and relatively good compatibility between the filler and matrix. Voids indicate a poor connection between the fiber and the matrix and means that the stress and pressure due to weak connection to the matrix fibers were separated from the matrix level. In this study, fibers partly surrounded by matrix and adhesion between the two phases occurred because the fibers were not dislodged. In fact, perhaps recycling of the polymer and increasing of MFI resulted in better coverage of the particles, increasing the interfacial contact between them. By increasing MFI, stronger connections are created and the particles that come out of the ground polymer are reduced. Samariha et al. (2015) studied the morphology of bagasse/recycled high density polyethylene fiber composites by imaging with SEM. Micrographs showed orientation, distribution, and dispersion of reinforcements, and it was determined that presence of coupling agents improved transfer of stress between the matrix and fibers, as well as distribution and dispersion of reinforcements in recycled polyethylene matrix.

CONCLUSIONS

1. This study evaluated the effect of nanographene addition on the physical, mechanical, and thermal properties of nanocomposites made from wood flour and recycled polyethylene.
2. By increasing the amount of nanographene to 0.5 wt.%, the flexural strength, flexural modulus and notched impact strength of the composites increased. At 2.5 wt.% nanographene, these properties were reduced.

3. Increasing the amount of nanographene increased the amount of residual ash and thermal stability.

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Article submitted: August 20, 2016; Peer review completed: October 20, 2016; Revisions accepted: December 20, 2016; Published: January 10, 2017. DOI: 10.15376/biores.12.1.1382-1394