Characterization of Nanoparticles Fe$_3$O$_4$ Nanocomposite Blend with Thermoplastic HDPE

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Abstract
This study aims to determine the mechanical properties, morphology and thermal thermoplastic blends of High Density Polyethylene (HDPE) with a filler material Fe$_3$O$_4$ nanoparticles. The method is performed by mixing the ingredients on Internal Mixer tool types Labo Plastomill 30 R I50 models with variations in the quantity (2,4,6,8) wt% Fe$_3$O$_4$ nanoparticles with a size of 33.11 nm and 2% by weight Polyethylene Grafted Maleic Anhidride (PE-g-MA) and without PE-g-MA, with a chamber volume of 60 cc with a temperature of 150°C at a speed of 50 rpm for 10 minutes. The results of the mechanical properties obtained an increase in tensile strength maximum with increasing the quantity of nanoparticles Fe$_3$O$_4$ without and the compatibilizer PE-g-MA with optimal the quantity at 2% by weight, while the elongation at break decreased with increasing the quantity of nanoparticles Fe$_3$O$_4$, but the tensile strength better by using compatibilizer, as well as Young's Modulus, s increased with increasing magnetic nano particles, but in general without compatibilizer better. The results of the dispersion morphology of the occurrence of a homogeneous mixture and intercalates between HDPE thermoplastic matrix with Fe$_3$O$_4$ particles and homogeneous mixture. The addition amount of filler increases the thermal stability and crystallinity of composite.

Keywords: Fe$_3$O$_4$ nanoparticles, HDPE, PE-g-MA

1. Introduction
Nanoparticles become a very interesting study, because the material that is in nano size particles typically have the chemical or physical properties that are superior to large-sized materials. In this case these properties can be altered by controlling the size of the material, setting the chemical composition, surface modification and control the interactions between the particles.

Nano particles of magnetite (Fe$_3$O$_4$) for the last few years has been widely used in various applications, such as storing the information with a high density, the formation of an image with magnetic resonance imaging (MRI), a delivery system for medicines, cosmetics, dyes, as coatings to prevent corrosion, adsorption processes and as a filler for various applications nanocomposite.

Compatibility is the level of integration of a mixture, compatibilizer the specific compounds that can be used to integrate incompatible polymers into stable mixture through intermolecular bonds, (Liu, H. et al, 2008).

The addition compatibilizer polyethylene grafted maleic anhidride (PE-g-MA) is expected to improve the homogeneity and decrease the size of the mixing phase distributed HDPE, the use of PE-g-MA have been done due to very broad applications, such as blending, compatibilizer agent of the polar polymer, adhesive, and on nanotechnologies, (Jayathu.Z.E, et al, 2006).


This study aims to determine the mechanical properties, thermal properties, morphology of HDPE thermoplastic composites with nano filler Nano magnetic particles (Fe$_3$O$_4$), using compatibilizer PE-g-MA and without compatibilizer.

2. EXPERIMENTAL
Materials
Fe$_3$O$_4$ with 33.11 nm particle size of the preparation result (Bukit.N, et al, 2015), Thermoplastic HDPE produced Nusantara PT Titan Petrochemical, PE-g-MA Production Sigma Aldrich USA, HCl with Molarity 37% Sodium Hydroxide (NH$_4$OH) molarity 25% Merck KGaA 64271 Darmstadt Germany. Poly ethylene Glycol (PEG) – 6000
Equipment

The Preparation of Nanocomposite
The preparation of nanocomposite made by blend thermoplastic HDPE with Fe$_3$O$_4$ nanoparticles which have been prepared through coprecipitation method with the size (33.11 nm). As this mixing by using Labo Plastomill Mixer Internal models 30 R 150 with variations in composition (2, 4, 6, 8) wt% Fe$_3$O$_4$ nanoparticles and 2% by weight of PE-g-MA is shown in Table 1, with a chamber volume of 60 cc with a temperature of 150°C at a speed of 50 rpm for 10 minutes.

<table>
<thead>
<tr>
<th>Material</th>
<th>The Quantity blend (%) wt</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDPE</td>
<td>S1A  S2A  S3A  S4A  S1B  S2B  S3B  S4B</td>
</tr>
<tr>
<td>Nanoparticle Fe$_3$O$_4$</td>
<td>96   94   92   90   98   96   94   92</td>
</tr>
<tr>
<td>PE-g-MA</td>
<td>2     4     6     8     2     4     6     8</td>
</tr>
</tbody>
</table>

From internal mixer tool produced samples of granular. The resulting composite mold tool inserted into rectangular plate with a thickness of 1 mm, length 11 cm, width of 11 cm. Furthermore, the printing of the printing press and heat by means of Gonno Ramdia 152 mm Ramstroke 150 mm performed for 10 minutes consisting of time heating the mold 3 minutes of heating time material 3 minutes and press 4 minutes with 50 kgf/cm$^2$ at a temperature of printing 150°C, followed with cold pressure for 4 minutes with 50 kgf/cm$^2$ at a temperature of 22°C.

The mechanical properties of nanocomposite was tested using a Universal Testing Machine (UTM). Tests conducted using a standard JIS K 6781 with a pulling speed of 50 mm/min

3. RESULTS AND DISCUSSION
3.1 Analysis of Mechanical Properties
From the results of tensile test, it can display a graph the relationship between variations in weight percent filler with tensile strength for each sample using a compatibilizer PE-g-MA and without compatibilizer as in Figure 1 to 3

![Graph showing the relationship between the tensile strength with the quantity of magnetic nanoparticles](image-url)

Figure 1. Relationship Between the Tensile Strength with the Quantity of Magnetic Nanoparticles
As shown in Figure 1, the relationship of tensile strength to the quantity of filler where in the tensile strength without the use of compatibilizer value is higher compared to using compatibilizer and conversely in Figure 2. The relationship between the elongation at break of the quantity of nanoparticles which by using compatibilizer PE-g-MA is greater, this is due to the force anhydride in PE-g-MA is an important role in improving the mechanical properties of the mixture in the ultimate elongation, of the nature of PE-g-MA addition to depending on the degree of grafting MA, but it can also be determined by the distribution of Maleic Anhydride (MA) within the molecular chain polyethilen (PE). (Machado, et al, 2005).

The optimum value of tensile strength between the use of PE-g-MA and without PE-g-MA on the quantity of the filler (2%) by weight. This shows that the quantity of this nanocomposite has the best tensile strength. As for the elongation at break where the optimum value on the quantity of the filler (2%) by weight and the use of PE-g-MA.

From Figure 3, Young's modulus optimum is in the quantity of the filler (6%) weight without using PE-g-MA. From the figure shows that the quantity of the nano-particles as a filler in (8%) weight had better grades by using PE-g-MA. This shows a lack of atomic bonding between the particles and fillers for the nanocomposite and no spread of the particles evenly. Crystal phase difference between the filler with the thermoplastic matrix also affects the tensile strength is not good. So the results of tensile testing of nanocomposite HDPE / nano Fe₃O₄ with increasing magnetic particle quantity decreased tensile strength at above 8% by weight of the quantity. By using compatibilizer give better effect to the elongation at break of the composite, while the effect without compatibilizer tensile strength and Young's modulus.

Based on research (Ginting, M.E, et al, 2015), on the quantity of 2% by weight with compatibilizer PE-g-MA where its strength value of 23.97 MPa. When compared with the results of this study in the same the quantity using Fe₃O₄ Nano particles that is obtained at 20 636 MPa. This indicates that the bonding between atoms that occurs in every nanoparticles used as a filler in thermoplastics HDPE vary. Where there is a strong bond that occurs and there is a weak bonds. As for the results of tensile strength using nano-particle filler bentonite as filler material thermoplastic HDPE (Bukit.N, et al, 2013) on the quantity of 2% by weight to produce a tensile strength of 25 377 MPa. This is due to lack of bonding between Fe₃O₄ compared with thermoplastic matrix of silica and
bentonite and clay. In addition, clotting occurs due to nanoparticles, causing inequity spread of nanoparticles in which it also greatly affects the tensile strength of nanoparticles.

According to research (Feng et al, 2004), states that the nanometer-size reinforcing materials such as silica, calcium carbonates and clay, a material that can also function as a compatibilizer between polymer blends are not mutually dissolve. Figure 4 shows a sample form JIS K 6781 before was treated and after testing elongation at break.

![Sample Nanocomposite](image)

Figure 4. Sample Nanocomposite (a) before, (b) after the Tensile Test
3.2 Morphology Analysis

From the analysis of the mechanical properties of the mixture of nano Fe$_3$O$_4$ more than 8% by weight on the contrary have negative effects that lower the elongation at break but larger if without filler nano-particles, is probably caused by a decrease in the degree of spread of exfoliating particles of Fe$_3$O$_4$ on nanocomposite containing nano high particle (> 6% wt), it is their agglomeration or clotting nano particles as shown in photo scanning electro microscope (SEM) in Figures 5 and 6. this case led to a decrease in tensile strength.

Agglomeration Fe$_3$O$_4$ believed to be a stress concentration and becomes the beginning of the crack so that the power will go down. The same research (Z.A.Kusmono , et al, 2008) . Nano clay more than 4 phr contrary negative effect that lowers the tensile strength. This is likely due to a decrease in the degree of exfoliation deployment of Fe$_3$O$_4$ layer on the nano composites. Similarly, the results of research (T.Serki, et al, 2006), reported by the addition of compatibilizer will form the esterification reaction or hydrogen bonding at interfaces hydroxyl groups on the particle on one side and the carboxylic group in the compatibilizer which diffuses into the polymer matrix on the other side and a homogeneous mixture.
Figure 5. Nanocomposite Morphology of HDPE / Fe₃O₄ in the quantity (a) 2% , (b) 4 % , (c) 6% , (d) 8%

3.3 Analysis Thermal

Figure 7  Curva TGA Nanocomposite HDPE/PE-g-MA/ Fe₃O₄ in the Quantity Fe₃O₄ (2,4,6,8)wt %
Figure 8: Curva TGA Nanocomposite HDPE/Fe₃O₄ in the Quantity Fe₃O₄ (2, 4, 6, 8) wt%

Table 2: Weight Changes in Nanocomposite HDPE/Fe₃O₄ with and without Compatibilizer

<table>
<thead>
<tr>
<th>HDPE/PE-g-MA/Fe₃O₄ (wt %)</th>
<th>∆M (mg)</th>
<th>HDPE/Fe₃O₄ (wt %)</th>
<th>∆M (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>-11,788</td>
<td>2</td>
<td>-20,484</td>
</tr>
<tr>
<td>4</td>
<td>-16,153</td>
<td>4</td>
<td>-16,888</td>
</tr>
<tr>
<td>6</td>
<td>-15,390</td>
<td>6</td>
<td>-15,590</td>
</tr>
<tr>
<td>8</td>
<td>-15,315</td>
<td>8</td>
<td>-14,817</td>
</tr>
</tbody>
</table>

From Figure 7 and 8, and Table 2 shows the quantity of nanoparticles Fe₃O₄ 2% weight smaller mass reduction compared with 4% of 16.153 mg of a mixture of HDPE/PE-g-MA/Fe₃O₄, this is because the more content of nano-particles, the greater the decomposition process, so that the thermal stability as well. While on a mixture of HDPE/Fe₃O₄ without compatibilizer seen the quantity of nanoparticles Fe₃O₄ 2% by weight, 20.484 mg had a change of times greater than the on the quantity of 8% by weight ie 14.817 mg, the temperature melting point of HDPE about 140°C, with the addition of filler there is an increase in the melting point the filler particles Fe₃O₄ nanoparticles in the quantity of 4% wt. This is caused by the increased dispersion of the bond between face diatara filler material polyethylene and PE-g-MA and nano particles of Fe₃O₄, the same can be obtained from the study (Pracell, et al, 2006), the addition of compatibilizer PE-g-MA, which could improve crystallization composite polyethylene (HDPE), this is caused by branching chain between maleic anhydride and a better dispersion between PE-g-MA in polymer materials.

To be considered a worthy polymer is heat stable or heat resistant, the polymer should not decompose under the temperature of 400°C and maintain its characteristics at a temperature close to the decomposition temperature, from figure 7 and 8 at a temperature of 500°C all polymer materials already have decomposed the rest is Fe₃O₄ nanoparticles.

From the curve TGA decomposition occurs at a temperature of 495°C, changes the weight of the smallest 11.778 mg at 2 wt% Fe₃O₄ with compatibilizer PE-g-MA, while the top position in accordance with the curve TGA visible changes in the largest weight as much as 16.153 mg on the composition of 4% at 500°C rest is Fe₃O₄ nanoparticles. As for HDPE mixture with Fe₃O₄ decomposition occurs at a temperature of 490°C, the smallest changes in weight of 14.81 mg at 2 wt% Fe₃O₄ with compatibilizer PE-g-MA, while the top position according to the TGA curves visible changes as much as 20.484 mg biggest weight on the quantity of 2 % by weight at a temperature of 500 °C rest is Fe₃O₄ nanoparticles. This is consistent with the results of the study (Salmah, 2005) that the addition of fillers increase thermal stability and crystallinity of the composite.

4. ACKNOWLEDGEMENTS

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5. CONCLUSION

The results of mechanical properties obtained an increase in tensile strength maximum with increasing the quantity of nanoparticles Fe₃O₄ without compatibilizer or with compatibilizer PE-g-MA with optimal quantity at 2% by weight, while the elongation at break decreased with increasing the quantity of nanoparticles Fe₃O₄, but the power
breakdown better with using compatibilizer, as well as Young's modulus, s increased with increasing magnetic nano particles, but in general without compatibilizer better. The results of the dispersion morphology of the occurrence of a homogeneous mixture and intercalates between HDPE thermoplastic matrix with Fe₃O₄ particles and homogeneous mixture. The addition amount of filler increases the thermal stability and crystallinity of composites.

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