INFLUENCE OF NANOPARTICLE \( \text{CaCO}_3 \) ADDITION TO THE PHYSICAL AND MECHANICAL PROPERTIES OF POLYPROPYLENE-\( \text{CaCO}_3 \) COMPOSITE

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Abstract. Influence of Nanoparticle \( \text{CaCO}_3 \) Addition to the Physical and Mechanical Properties of Polypropylene-\( \text{CaCO}_3 \) Composite. This research was carried out to study the effect of adding \( \text{CaCO}_3 \) nanoparticle on the physical and mechanical properties of polypropylene-\( \text{CaCO}_3 \) composites. It was characterized by several parameters such as tensile strength, hardness, and thermal analysis including both melting point and heat of fusion using Differential Scanning Calorimetry (DSC). Based on XRD results, the particle size of \( \text{CaCO}_3 \) after 24 hours of milling was 39 nm. There are various compositions of polypropylene-\( \text{CaCO}_3 \) composites (PP MF35: nano-\( \text{CaCO}_3 \)) made in this study, namely 40%:60%, 35%:65%, 30%:70%, and 25%:75%. The results showed that the tensile strength of the PP MF35-\( \text{CaCO}_3 \) composites decreased with increasing nano-\( \text{CaCO}_3 \) content. Meanwhile, the hardness of the nanocomposites increased with increasing nano-\( \text{CaCO}_3 \) content, but decreased the melting point and heat of fusions (\( \Delta H_m \)) of the nanocomposites. The infrared spectrum showed that the interaction between PP MF35 and nano-\( \text{CaCO}_3 \) was only physical interaction and there was no chemical reaction.

Keywords: polypropylene; nano-\( \text{CaCO}_3 \); tensile strength; composite.

1. Introduction

An increasing population is always followed by an increase in the necessities of life. This is what underlies the increasing need for plastic as a packaging of food, beverage and other necessities. By 2050, it is estimated that the world’s population will reach 9 billion and the level of plastic production will exceed 1 billion tons.

Plastic as a packaging has several advantages such as strong, light, transparent, stainless, easy to shape and to color and also has a low price. Plastics can be applied in various human life sector like household, automotive, agriculture and health [1]. Market demand for good quality goods at competitive prices and the increasingly rapid development of polymer technology have prompted scientists to make polymer-based plastics by mixing polymers with nano-sized fillers. In this research, a polymer composite was made by mixing polypropylene as a matrix and \( \text{CaCO}_3 \) as a filler.

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Polypropylene (PP) is a type of thermoplastic polymer, which is a linear hydrocarbon polymer formed by propylene monomers. In this study, polypropylene was used because it is widely used as a raw material of packaging for food, beverages and other applications [2]. One of the fillers that can be applied is CaCO$_3$. It is used because the presence of CaCO$_3$ in nature is abundant, cheap, inert and it has high melting point. The economic price of the filler causes the final product price to be lower, so that economically, it will benefit producers and consumers [3]. CaCO$_3$ as a filler is made in nanometer size. Because the smaller the size of filler particle, it is expected that the more filler can interact with the matrix, so that the less polymer matrix is applied. Moreover, it caused changes in the physical and mechanical properties of polypropylene. It can improve the physical and mechanical properties of polypropylene [3]. Based on previous research, the addition of micro-sized CaCO$_3$ reduces the mechanical properties of PP-CaCO$_3$ composites. Meanwhile, both tensile strength and flexural strength of Polyethylene-terephthalate (PET)/Polypropylene (PP)/CaCO$_3$ are increased after the addition of specific composition of CaCO$_3$. [5]. It also improved the melting point of polypropylene [6]. Therefore, the effect of nano-sized CaCO$_3$ on properties of PP MF35-CaCO$_3$ nanocomposites was investigated in this study [4–6].

2. Experimental Methods

2.1. Materials
The polypropylene with melt flow of 35g/10 min is a product of PT TRI POLYTA INDONESIA, Tbk, Cilegon – Banten. Calcium carbonate (pro analyzed) used the (MERCK catalog) as a filler, Yasicha brand mica plastic and nitrogen liquid.

2.2. Experimental Procedure

2.2.1. Manufacture of Nano-sized CaCO$_3$
High Energy Mill (HEM, brand SPEX Centripep 8000-series Mixer/Mills) is used to manufacture nano-sized CaCO$_3$. First of all, CaCO$_3$ and sphere go tri with weight ratio of 1:2 was put into vial and then milled with HEM to obtain a nanometer size. After that, the milling process was carried out with different time variations such as 0, 6, 12, 18 and 24 hours on different samples.

2.2.2. Synthesis of PP MF35-CaCO$_3$ Composite
First of all, laboplastomill (Toyoseiki brand, Japan) is cleaned with acetone to avoid impurities during material synthesis. Then, mix the melted polypropylene 35 with nano-sized CaCO$_3$ in laboplastomill at a temperature of 1800$^\circ$C for 10 minutes with a rotating speed of 40 rpm. The variations of CaCO$_3$ are 60, 65, 70, and 75wt% and the propylene of 25, 30, 35, and 40wt%. After mixing homogeneously, then the mixture was made a film using Hydraulic Hot Press at a temperature of 1800$^\circ$C for 5 minutes and a pressure of 150kg/cm$^2$. Then the film molding tool is put into the cold pressing machine (a/s 16 Tons Hydraulic Press).
2.2.3. **Characterization.**

The manufacture of nano-sized CaCO$_3$ is carried out using High Energy Mill (HEM) for 24 hours to minimize the particle size of material. The particle size of CaCO$_3$ after milling for 24 hours were measured using X-Ray Diffraction (XRD-PAN Analytical 610) with Cu–Kα source at wavelength (λ) = 0.154 nm). Infra-red (IR) spectrum for identification of functional groups and metal oxide bonds was measured by means of Fourier Transformation Infra-Red (FTIR) type Tensor 27 Bruker. Samples in powder form as much as 5 mg were mixed with KBr then crushed and homogenized and then pressed to form pellets. Samples were irradiated with IR in the wave number range of 500 cm$^{-1}$ to 3000 cm$^{-1}$.

![Figure 1. Specimen of the tensile test.](image)

Tensile strength specimens were produced by using the TKC series-vertical injection mold machine, following the ASTM D638 standard. The tensile specimen size was 19 mm wide, 113 mm length, and thickness 4 mm (Fig. 1). Five samples were tested for each composition. The experiment was carried out on Strograph R1, Toyoseiki (Japan) with longitudinal extension, a high resolution (1.8 μm). Some basic specifications are described as follows: The maximum test power was 20 kN, in range of speed 0.001-1600 mm/min, speed accuracy ± 0.1 % test speed, the operating temperature at 5-50°C, data acquisition speed 1000 Hz. SEM characterization was carried out to determine the morphology, microstructure and particle size distribution of the CaCO$_3$, the test was carried out with a magnification of 5000 times using a SEM- JEOL 6510 LA.

### 3. Result and Discussion

3.1. **Manufacture of Nano-sized CaCO$_3$**

The manufacture of nano-sized CaCO$_3$ is carried out using High Energy Mill (HEM). In HEM, there is a process of CaCO$_3$ attrition. The attrition method is a method in which micrometer-sized material is hammered into a particular ball milling in order to minimize the particle size of material [7]. So that finally we get a material with a smaller particle size (in nanometers).

The results of the measurement of the x-ray diffraction pattern from the mechanical milling process which are expected to form CaCO$_3$ nanoparticles are shown in Figure 2. Figure 2 shows the x-ray diffraction pattern with milling time variations of 0, 6, 12, 18, and 24 hours. Phase
identification shows that the sample after milling has an unchanged phase, in other words, that milling does not find any foreign phase. In this research, particle size analysis used X-ray diffraction using the Scherer method in which the crystalline scale is determined based on the reaming of the X-ray diffraction peaks that appear. Based on this method, the more small-scale crystals, the wider the diffraction peaks will be. The relationship between scale crystals and X-ray peak diffraction width can be seen with the Scherer equation [8]:

\[ D \approx K \frac{\lambda}{B \cos \theta_B} \]  

Where D is crystallite size in nano-meter; \( \kappa \) a constant whose value depends on particle shape; \( B \) is FWHM (Full Width at Half Maximum); \( \lambda \) is the wavelength of incident beams in nm and \( \theta \) is Bragg’s angle. Based on result of gauging at milling 24 hours, we obtained that the average D value of CaCO\(_3\) after milling for 24 hours was about 39 nm.

![X-ray diffraction pattern of CaCO\(_3\) milling time variation](image)

Figure 2. X-ray diffraction pattern of CaCO\(_3\) milling time variation.

### 3.2. Analysis of Mechanical Properties (Tensile Strength)

The tensile was the tensile properties that were determined using five samples for each composition to study the effect of CaCO\(_3\) on tensile properties. Tensile strength specimens were produced by using the TKC series-vertical injection mold machine, following the ASTM D638 standard. Tensile strength can be determined by applying force to the test material until it breaks. Tensile strength, which is a measure of the ability of a polymer to withstand pulling stresses is usually measured by pulling a dumbbell specimen [9,10].
Based on the results above, it is known that the tensile strength decreased with the increasing of nano-sized CaCO$_3$ filler content. Meanwhile, it decreased due to uneven distribution of nano-sized CaCO$_3$. This is because nano-sized CaCO$_3$ filler has very small particles, so that the nano-sized CaCO$_3$ tends to clump and form a larger drain structure or known as agglomeration which has an impact on the decreasing of tensile strength [9,11]. The tendency to form very large agglomerates is due to electrostatic forces between CaCO$_3$ particles. Particles with a diameter of less than 1 µm have a relatively high tendency for agglomeration to occur.

Polypropylene MF35/nano-CaCO$_3$ composite have tensile strength with higher level if compared to PP MF35-CaCO$_3$ composite at the same concentration. PP MF35-CaCO$_3$ composite at concentration of CaCO$_3$ equal to 60% have the tensile strength at about 148kg/cm$^2$. Meanwhile, tensile strength of PP MF35/nano-CaCO$_3$ composite at concentration of CaCO$_3$ 60% is about 181kg/cm$^2$. The increase of tensile strength is equal to 18%. This caused by filler nanometer CaCO$_3$ which has big equi-amplitude surface district so that it will give more contact between filler and matrix resulting mechanical properties of polymers composite to increase [12].

### 3.3. Analysis of Physical Properties

#### 3.3.1. Hardness

Hardness is the resistance to local deformation that is often measured as the ease or difficulty for a material to be scratched, indented, marred, cut, drilled, or abraded. In this research, hardness was measured by Shore A.

Based on the table, the hardness of the composites increased with the increasing of nano-CaCO$_3$ composition because the addition of CaCO$_3$ can increase the molecular weight of the polymer so that it can also increase the solidity of polymer. Consequently, it increased the crystallinity of polymer [13].

### 3.3.2. Analysis of Thermal

The analysis of thermal properties includes melting point (Tm) and heat fusion ($\Delta$Hm) using Differential Scanning Calorimetry (DSC, Perkin Elmer Brand) method. Melting point describes the phase transformation from solid to liquid without undergoing a transformation of the composition. Melting is basically the separation of polymer chains in a crystalline region which allows the polymer to flow.

**Table 3. Melting Point of PP MF35/Nano-CaCO$_3$**

<table>
<thead>
<tr>
<th>No.</th>
<th>Sample</th>
<th>Heat of Fusions (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>PP MF35 40% + 60% nano-CaCO$_3$</td>
<td>160</td>
</tr>
<tr>
<td>2.</td>
<td>PP MF35 35% + 65% nano-CaCO$_3$</td>
<td>158</td>
</tr>
<tr>
<td>3.</td>
<td>PP MF35 30%+ 70% nano-CaCO$_3$</td>
<td>159</td>
</tr>
<tr>
<td>4.</td>
<td>PP MF35 25%+ 75% nano-CaCO$_3$</td>
<td>156</td>
</tr>
</tbody>
</table>

**Tabel 4. Heat of fusion of composite PP MF35/nano-CaCO$_3$**

<table>
<thead>
<tr>
<th>No.</th>
<th>Sample</th>
<th>Heat of Fusions (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>PP MF35 + 60% nano-CaCO$_3$</td>
<td>25</td>
</tr>
<tr>
<td>2.</td>
<td>PP MF35 + 65% nano-CaCO$_3$</td>
<td>22</td>
</tr>
<tr>
<td>3.</td>
<td>PP MF35 + 70% nano-CaCO$_3$</td>
<td>20</td>
</tr>
<tr>
<td>4.</td>
<td>PP MF35 + 75% nano-CaCO$_3$</td>
<td>14</td>
</tr>
</tbody>
</table>

Based on the Table 4, the melting point of nanocomposites decreased with the increasing of nano-CaCO$_3$ filler content. This is because the polymer chain was physically degraded and was released to the wall together with the filler, causing the breakdown of the polymer molecular chain bonds. The addition of filler to polymer matrix shows that the interaction of filler with the amorphous part of PP MF35 was also increasing, so that it reduced the crystallinity of PP MF35 and its melting point [14].

The reduction of heat fusion occurred due to the higher concentration of nano-CaCO$_3$ in the composites. As a result, the concentration of PP MF35 in the composite reduced, then it also reduced the required energy to break polymer chains of PP MF35 when it changed from a solid to liquid state.
3.3.3. Analysis of Functional Groups with Fourier Transform Infra-Red (FT-IR)

FT-IR analysis is applied to identify organ compounds based on readings of the functional
groups of the compounds in the form of spectrum read on the graph. Polypropylene, CaCO₃, and
PP/nano-CaCO₃ composites were identified for functional groups using FT-IR.

Based on spectral data, we see the absorption peak at wave number around 3382 cm⁻¹ which
is a stretching vibration absorption of primary NH₂, NH stretching vibration absorption at wave
numbers around 1570 cm⁻¹, and aliphatic CH vibration absorption at wave numbers around 2800 -
3000 cm⁻¹. Si-OC vibrations identified in the wave numbers 1100 and 1085 cm⁻¹. O-CH₃ vibrations
identified in the wave numbers 1450 and 1434 cm⁻¹. CH₂ bending vibrations identified in the wave
numbers around 1485 and 1150-1162 cm⁻¹ while the C-CH₃ bending identified in the wave
numbers 1382, 1337 and 958 cm⁻¹.

<table>
<thead>
<tr>
<th>No.</th>
<th>Group</th>
<th>Wavenumber (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>C-H stretching</td>
<td>2800-3000</td>
</tr>
<tr>
<td>2.</td>
<td>CH₂ bending</td>
<td>1162</td>
</tr>
<tr>
<td>3.</td>
<td>CH₃ bending</td>
<td>1382, 1337 and 958</td>
</tr>
</tbody>
</table>

3.3.4. Distribution Nano-CaCO₃ in Polymers Composite

Figure 1 showed the morphology of CaCO₃ which was observed using Scanning Electron
Microscopy (SEM). CaCO₃ undergoes agglomeration due to its small scale. Based on figure 1, the
cupola of volume diffraction composition of PP MF-35/nano-CaCO₃ (40wt%/ 60wt%) looks a bit
slippery, rather flat, rather dense and looks rather compact when compared to the addition of
volume diffraction greater than 60wt%. With the addition of the diffraction percentage of the
CaCO₃ filler composition into the nanocomposite, the real composition will be greater and larger
chambers. Meanwhile, its distribution is more coarse, uneven, and not compact. This is due to the
influence of nano-CaCO₃ which tends to agglomerate [15].
Based on XRD results, the particle size of CaCO₃ after 24 hours of milling was 39 nm. The tensile strength of the PP MF35-CaCO₃ composites decreased with the increasing of nano-sized CaCO₃ filler content. Meanwhile, the hardness of the nanocomposites increased with the increasing of nano-sized CaCO₃ filler content, but both the melting point and the heat of fusions (ΔH_m) the nanocomposites decreased. The infrared spectrum showed that the interaction between PP MF35 and nano-CaCO₃ was only physical interaction and there was no chemical reaction occurred.

4. References


