The Effect Of Antioxidants Of A-Tocopherol On The Characteristic Of Mechanical, Thermal, And Morphology Properties Of Polypropylene-Montmorillonite (PP-MMT) Nanocomposites

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Abstract. The purpose of this study was to determine the effect of α-tocopherol on the mechanical, thermal, and morphological properties of polypropylene-montmorillonite (PP-MMT) nanocomposites. The preparation of polypropylene-montmorillonite (PP-MMT-AO) nanocomposites was carried out on PP compositions; PP-g-MA; MMT-octadecyl amine: AO is 80;10;10;5 and the PP-MMT nanocomposite composition is PP; PP-g-MA; MMT-octadecyl amine: 80;10;10. The SEM results showed that polypropylene, MMT, and the antioxidant α-tocopherol could be exfoliated and intercalated to produce compatible nanocomposites. The mechanical and thermal test results showed that the PP-MMT-AO nanocomposite had higher mechanical properties and thermal stability than the PP-MMT nanocomposite. Based on the FTIR test and degradation test on PP-MMT and PP-MMT-AO films which were carried out for up to 15 days and 30 days showed that the PP-MMT-AO nanocomposite against UV light was given, this shows that α-Tocopherol can prevent oxidation reactions polypropylene.

Keywords: montmorillonite, polypropylene, PP-g-MA, antioxidant, α-tocopherol, nanocomposite, mechanical properties, thermal, morphology.

INTRODUCTION

According to reports from futurologists, plastic consumption will continue to increase and is estimated to increase by five percent annually. One type of plastic that is widely used for various purposes is polypropylene (PP). PP is a non-polar material and has several obstructions, both chemical and physical properties, which causes its use to be restricted. PP is commonly functionalized with various monomers including glycidyl methacrylate (GMA) and maleic anhydride (MA) [2,3]. In addition, PP also has weaknesses, namely low strength, and resistance to low temperatures. To overcome this problem, several researchers have also tried to improve its properties with a nanotechnology approach and the addition of fillers such as montmorillonite [4].

Montmorillonite (MMT) is a group of phyllosilicate minerals isolated from bentonite and can expand as well as can be intercalated with organic compounds to form organic-inorganic composite materials. In addition, this mineral also has a high cation exchange capacity so that the MMT interlayer space can accommodate large amounts of cations, making MMT a unique material. MMT is now a mineral of concern and is a very valuable mineral. MMT is widely used in various industrial applications because it has a high aspect ratio, morphology in a plate shape, abundant content, and only intercalated and exfoliated making it widely used as a nanocomposite filler to improve the properties of such nanocomposites [5]. In recent years, the demand for advanced engineering materials in various applications, such as the automotive, aerospace, and building sectors has continued to increase which has led researchers to constantly search for new materials or develop existing materials, which are based on cost analysis, development of techniques and performance requirements.
In addition, sunlight will have a bad effect on plastic. Ultraviolet radiation can break chemical bonds in polymers. This process is called photodegradation which eventually causes cracking, calcification, discoloration, and a decrease in certain physical properties. The addition of additives such as antioxidants and ultraviolet stabilizers can prevent premature damage. This can be caused by increasing the degradation temperature of a material. According to [6], an increase in the temperature of the material or composite is associated with an increase in the level of crystallinity of the composite. One of the antioxidants that can be added is α-tocopherol.

Several previous studies have explained that the addition of antioxidants to polypropylene nanocomposites causes the nanocomposites to be more stable from various environmental influences [7]. The use of antioxidants or stabilizers in polypropylene also provides effective stability to the polymer either during processing and fabrication or for long-term stability when the polymer product is subjected to various environmental influences, e.g. light, heat, and UV, and other external factors, such as pressure and wear and tear [8]. The presence of antioxidants as fillers in nanocomposites can also increase the tensile strength of nanocomposites, this can occur due to the formation of a good interfacial bond between the filler and the hydrophobic polymer matrix in the presence of a coupling agent [9].

**METHODOLOGY**

**Material**
The materials used in this research were commercial Polypropylene (PP), a Singapore product with a density of 0.896 gr/cm³ and melting temperature of 176 ºC, commercial PP-g-MA, USA product polypropylene that has been grafted with maleic anhydride (MA), with density 0.934 g/cm³, mp 156 ºC, Mn 3,900 (GPC), Mw 9100 (GPC), octadecyl amine (C₁₈H₃₉N, 90%) is a Japanese product, α-tocopherol, and nano montmorillonite isolated from bentonite from North Aceh.

**Methods**

**Isolation nano montmorillonite from bentonite of Aceh Utara.**
Montmorillonite produced from bentonite processing was taken as much as 6.48 gr, dissolved in 250 ml of water, and then ultrasonicated for 5 minutes to produce a homogeneous suspension. The suspension is then heated to 70°C while stirring with a magnetic stirrer. The obtained solids are heated in an oven at 100 ºC for 3 hours. Furthermore, the solids are crushed slowly so that they become powder [10,11]. This powder is an MMT nanoparticle [11].

**Montmorillonite modification with octadecylamine**
About 1000 mL of distilled water is infused in a 2 L beaker glass, then heated and defended at 80 ºC in a water bath. Then 20 grams of montmorillonite samples were put in the hot water and dispersed by stirring it at (300 rpm) for 1 hour. Meanwhile, a solution containing 7.5 g octadecyl amine with 4.2 mL of concentrated HCl was made in hot distilled water of 500 ml and maintained at 80 °C Then this solution was added to the montmorillonite solution above and stirred for 1 hour at a speed of 400 rpm. After this, the solids are filtered and washed several times with 1000 ml of hot distilled water using a filtration vacuum device. The resulting organoclay is dried in an oven maintained at 60 ºC for 36 hours, and a modified octadecyl amine MMT will be obtained.

**Preparation of Polypropylene-Montmorillonite- α-Tocopherol Nanocomposites**
The preparation of nanocomposite polypropylene-montmorillonite and variations of the addition of PP, PP-g-MA, and montmorillonite as well as antioxidants (α-tocopherol), can be seen in Table 1.

<table>
<thead>
<tr>
<th>No</th>
<th>PP (%)</th>
<th>PP-g-MA (%)</th>
<th>MMT-octadecyl amine (%)</th>
<th>The antioxidant of α-tocopherol (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>85</td>
<td>10</td>
<td>5</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>80</td>
<td>10</td>
<td>5</td>
<td>5</td>
</tr>
</tbody>
</table>
The nanocomposite processing process is carried out in an internal mixer. Pure PP, montmorillonite, and commercial PP-g-MA are included in the internal mixer, further added with antioxidants of α-tocopherol. This process is carried out at a temperature of 180 °C with a time of 10 minutes, the speed is set at a speed of 65 rpm. The resulting PP-MMT-AO nanocomposites are characterized by their morphology, thermal properties, and mechanical properties. The manufacturing process of these nanocomposites is carried out by varying the amount of montmorillonite and the amount of commercial PP-g-MA. The resulting nanocomposites were characterized by mechanical tests, FT-IR, DTA, and SEM.

**RESULTS AND DISCUSSION**

**Degradation Test of Polypropylene-Montmorillonite Nanocomposite**

The degradation test is carried out by irradiating using 400 W UV lamps as many as 4 pieces placed in an aluminum chamber measuring 80x60x60 cm and on each side of the bottom of the box a hole is made so that air is free to enter and exit. The film of PP-MMT-AO is placed in the middle of the box and the temperature of the box during irradiation is kept between 50 – 65 °C [12]. Irradiation is carried out for 15 and 30 days. The results of irradiation are analyzed with FTIR.

**Results of PP-MMT Nanocomposite Analysis**

The added antioxidant in the nanocomposite causes MMT to be distributed more evenly in the polypropylene matrix than without the addition of antioxidants. This will affect the characteristics of the nanocomposite, such as mechanical and thermal properties [3].

Figure 1. shows a photo of the film of PP-MMT nanocomposites [11] with or without antioxidants, which shows that the film color of the two nanocomposites is almost the same with or without antioxidants, and the surface of PP-MMT nanocomposites added with antioxidants are more homogeneous. The antioxidants are also compatible with the PP matrix, MMT, PP-g-MA, and octadecyl amine as modifiers

![Figure 1. Film of nanocomposites (A) PP-MMT (without antioxidants), (B) PP-MMT-AO (with antioxidants)](image)

**Mechanical Properties of PP-MMT Nanocomposites**

Figure 2 shows a graph of the relationship between the PP-MMT and PP-MMT-AO nanocomposites on the tensile strength, elongation, and modulus of elasticity of the nanocomposites. It can be seen that the mechanical properties of the nanocomposite added with antioxidants can improve the mechanical properties of the PP-MMT-AO nanocomposite, including higher tensile strength, elongation, and modulus of elasticity than PP-MMT (without antioxidants). This indicates that the antioxidant α-tocopherol is sufficiently compatible with the polypropylene matrix to improve the mechanical properties of the PP-MMT nanocomposites. In addition, even the distribution of antioxidants in the polypropylene matrix can also improve the mechanical properties of the nanocomposites. This is related to the occurrence of interfacial bonds between antioxidants and polypropylene [9].
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Figure 2. Graph of the relationship between nanocomposites of PP-MMT and PP-MMT-AO on the properties of tensile strength, elongation, and elastic modulus of nanocomposites

Results of thermal analysis of PP-MMT nanocomposites

Thermal analysis of PP-MMT nanocomposites was carried out using the Thermal Analysis Test (TGA-DTA). The data from the TGA curve is the point of degradation of the nanocomposite in the presence of antioxidants.

Table 2. Degradation temperature of PP-MMT nanocomposite

<table>
<thead>
<tr>
<th>No</th>
<th>Materials</th>
<th>Degradation temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PP</td>
<td>382</td>
</tr>
<tr>
<td>2</td>
<td>PP-MMT</td>
<td>445</td>
</tr>
<tr>
<td>3</td>
<td>PP-MMT-AO</td>
<td>446</td>
</tr>
</tbody>
</table>

Figure 3 is the TGA thermogram curve of PP-MMT nanocomposites, the degradation temperature of the nanocomposite increases in the presence of antioxidants of α-tocopherol. The degradation temperature of PP-MMT nanocomposites in the presence of antioxidants can be seen in Table 2.

Figure 3. TGA thermogram curve of (A) Pure Polypropylene Film, (B) PP-MMT, (C) PP-MMT-AO

FTIR Characterization of PP-MMT Nanocomposites

FTIR analysis is performed to see functional groups and the presence of interactions in nanocomposites. FTIR spectra of pure polypropylene nanocomposite PP-MMT in the presence of antioxidants and the absence of antioxidants can be seen in Table 2 and Figure 4.

Table 3 and Figure 4 explain that there has been an interaction between PP, PP-g-MA, MMT, and antioxidants. In the PP-MMT nanocomposite, it can be seen that there is a shift in wavenumber compared to pure PP wavenumber. The spectrum at 1456.03-1255.44 and 3763.95 -3144.15 cm\(^{-1}\) in PP-MMT respectively explain the presence of Si-O-Si groups and carbonyl groups (C=O) from MMT and also amine groups (NH) of octadecyl amine. In PP-MMT-AO there was also a shift in wave numbers and the spectrum at 1465.92 - 1358.99 and 2951.49 - 2838.13; 3828.61 - 3194.78 cm\(^{-1}\) respectively explaining the presence of phenyl groups, CH\(_3\), CH\(_2\), and OH from α-tocopherol.
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Table 3. FT-IR Spectrum of PP-MMT Nanocomposite

<table>
<thead>
<tr>
<th>PP (cm(^{-1})) / Functional groups</th>
<th>PP-MMT (cm(^{-1})) / Functional groups</th>
<th>PP-MMT-AO (cm(^{-1})) / Functional groups</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>3763.95 -3144.15 / Amine (NH) of Octadecyl amine</td>
<td>3828.61 - 3194.78 / Amine (NH) of Octadecyl amine</td>
</tr>
<tr>
<td>2950.42 - 2616.44 / Alkanes from PP</td>
<td>2722.58 -2131.33 / Alkanes from PP and oktadecyl amine</td>
<td>2951.49 - 2838.13 / Alkanes from PP and the mechanical and thermal properties of octadecyl amine</td>
</tr>
<tr>
<td>-</td>
<td>1774.66 -1711.34/ Carbonyl group (C=O) of MMT</td>
<td>1779.36 - 1711.31/ Carbonyl group (C=O) of MMT</td>
</tr>
<tr>
<td>1456.8 - 1329.92 / C-H alkanes from PP</td>
<td>1456.03-1255.44/ Si-O-Si from MMT or C-H alkanes from PP</td>
<td>1465.92 - 1358.99/ Si-O-Si of MMT</td>
</tr>
<tr>
<td>-</td>
<td>1167.10-1086.15/ Si-O-Si of MMT</td>
<td>1166.99-1041.88/ Si-O-Si of MMT</td>
</tr>
<tr>
<td>947.27 - 458.6 / Alkanes of PP</td>
<td>973.15-463.91/ Alkanes from PP and from oktadecylamine</td>
<td>998.12 - 519.15/ Phenyl group of α-tocopherol</td>
</tr>
</tbody>
</table>

Figure 4. FTIR spectra of nanocomposite films of (A) PP-MMT (without antioxidants) and (B) PP-MMT-AO (in the presence of antioxidants)

The PP-MMT-AO, nanocomposites that had been added with the antioxidant α-Tocopherol were then subjected to degradation tests in ultraviolet in the presence of oxygen for 15 days and 30 days. The degradation-tested FTIR spectra of the PP-MMT-AO nanocomposite can be seen in Figure 5.

According to [13], the degradation of a nanocomposite can be seen from the increase in the FT-IR spectrum at absorbances of 3200-3600 cm\(^{-1}\) and 1600-1800 cm\(^{-1}\) when compared to non-degraded nanocomposites. The spectra in Figures 4(A) and 4(B) did not differ especially at 3200-3600 cm\(^{-1}\) and 1600-1800 cm\(^{-1}\), this indicates that the two PP-MMT-AO nanocomposites were not degraded by UV light given. According to [8], degraded PP-MMT nanocomposites will produce or increase oxygen which is characterized by increased absorption in the wave number region of the hydroxyl and carbonyl groups.
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Based on the FTIR results, it proves that α-Tocopherol can prevent the degradation of polypropylene, this is because α-Tocopherol has an unobstructed OH group. According to [12], the unobstructed OH group is one of the functional groups of a compound that can prevent the formation of free radicals due to the breaking of the polymer chain to react further

Results of SEM analysis of PP-MMT nanocomposites with or without antioxidants

Figure 6(A) is the SEM of the PP-MMT nanocomposite film which shows the lack of distribution of MMT in PP, it can be seen that there is a small layer of silica from MMT on the surface of the nanocomposite film. Figure 6(B) is an SEM photo of the PP-MMT-AO nanocomposite film, showing a more even distribution of the Si coating of MMT in polypropylene in the presence of the antioxidant α-tocopherol. This indicates that there has been a good interfacial bond between MMT, tocopherol antioxidants, and polypropylene. In addition, the PP-MMT-AO nanocomposite exhibits a compact and smooth morphology, this is because the tocopherol antioxidant is really attached to the matrix and is also very firmly embedded in the matrix, which is related to the interfacial interaction between PP, MMT, and antioxidants [14].

CONCLUSION

Processing of PP-MMT nanocomposites can be done by adding PP-g-MA as a compatibilizer and modifying MMT with octadecyl amine, the results suggest that exfoliation and intercalation of PP in MMT can occur.

Based on the results of tensile tests and thermal tests on the two PP-MMT nanocomposite films, it was found that PP-MMT-AO nanocomposites have higher mechanical properties and thermal stability than PP-MMT nanocomposites.

Based on the results of FTIR, it is explained that in the film PP-MMT-AO, there has been an interaction between PP, PP-G-MA, MMT, and antioxidants

Based on the FTIR test and degradation test on PP-MMT and PP-MMT-AO films which were carried out for up to 15 days and 30 days showed that the PP-MMT-AO nanocomposite against UV light was given, this shows that α-Tocopherol can prevent oxidation reactions polypropylene, and this result is supported by TGA data, namely the degradation temperature of the PP-MMT-AO nanocomposite is higher than that of PP-MMT.
REFERENCE