THE EFFECT OF ADDITION BY BUTYLATED HYDROXYTOLUENE (BHT) ON PHYSICAL PROPERTIES OF GEOMEMBRANE FROM RECYCLED HIGH DENSITY POLYETHYLENE (HDPE) PLASTIC WASTE

Veren Fransiska¹, Intan Syahbanu¹*, and Adhitiyawarman¹

¹ Department of Chemistry, Faculty of Science, Tanjungpura University, Pontianak, 78124, West Kalimantan, Indonesia

*Corresponding author: intan.syahbanu@chemistry.untan.ac.id

DOI: http://dx.doi.org/10.26418/indonesian.v6i1.62725

ARTICLE INFO

ABSTRACT

Recycled High Density Polyethylene (HDPE) has been prepared for geomembrane construction material. The aim of this research was to study the effect of Butylated Hydroxytoluene (BHT) addition as an antioxidant on the characteristics of the resulting geomembrane. Fourier Transform Infra Red (FTIR) analysis was carried out to examine functional groups of recycled HDPE and prepared geomembranes. Mechanical properties, permeability and hydrophobicity of geomembrane were observed to determined optimum BHT addition. The results of FTIR analysis on recycled HDPE showed the presence of functional groups at wavelengths 2912 and 2847 cm⁻¹ (C-H stretching); 1474 and 1467 cm⁻¹ (CH₂ bend); 721 cm⁻¹ (CH₂ Rock). After being formulated with other materials to obtain geomembranes, it was not found new peak indicating that the presence of BHT in geomembrane only physical interaction occurs. All of geomembranes had no permeability to water and reach 100% of hydrophobicity. The highest tensile test value was shown by geomembrane with 0.25 b/b% of BHT which about 21.235 MPa and 16.01 MPa for before and after soil burial test for four weeks, respectively. Perhaps might be due to the interaction between BHT at low concentrations which has lower polarity and HDPE which is nonpolar has better compatibility than at other concentrations.

© 2023 IJoPAC. All rights reserved

1. Introduction

Plastic material is difficult to decompose (non-degradable), resulting in high waste pollution by plastic waste in the environment. The publication of the Synthesis Report by the World Bank Groups¹ outlines the estimated waste accumulation from several cities in Indonesia to reach 0.87 tons/capita/day with the percentage of plastic waste reaching 13.16% or 0.15 tons/capita/day. Surveys conducted on river flows in several cities found that the composition of plastic bottles in plastic waste reached 1%, which means it reached 1.5 kg/capita/day and on an annual scale it
reached 547.5 kg of plastic bottle waste that pollutes the river environment [2]. One type of plastic that is often used is High Density Polyethylene (HDPE). The reuse of HDPE plastic waste can be processed into construction material products, namely Geomembrane [3], HDPE as geomembranes (specification GR1-GM13) are predicted to have lifetimes greater than 36 years, meanwhile the other material such as LLDPE (specification GR1-GM17) and fPP (specification GR1-GM18) are predicted to have lifetime approximately 36 years and 30 years [4].

Geomembrane is a geosynthetic construction material used in the foundation of dams, reservoirs and waterproofing in the foundation of road construction in the form of a sheet that acts to prevent the entry of water into the subgrade soil so that the levels in the subgrade soil do not change which results in roads built on subgrade soils becoming damaged [4–6]. The mechanical characteristics of the geomembrane are influenced by the natural properties of the polymer and the composition. One of important additive on geomembrane is antioxidant [7,8,9]. Antioxidants have a role to inhibit the degradation process due to oxidation that affects the mechanical strength of the material. One of common antioxidant is Butylated Hydroxytoluene (BHT). BHT as antioxidant has better stability (highest oxidation resistance; oxidation indeks [OI] is 0,21) and followed by HPAO (pentaerythritol tetrakis [methylene-3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate] (OI 0,29), Vitamin E (alpha tocopherol) (OI 0,29) and β-carotene (OI 0,35) on irradiated HXLPE (highly crosslink polyethylene) [11]. Besides, BHT concentration in polymer can influence the mechanical properties value [12].

Increasing BHT concentration on polypropylene-based plastic was inversely proportional toward the number of tensile strength, but it was better than the other antioxidant (BHA & TBHQ) [12]. Therefore, presence of antioxidants affects the mechanical properties of the material. Intend of this study was to investigate the effect of variations in the mass of Butylated Hydroxytoluene (BHT) additives towards mechanical characteristics of geomembranes produced from recycling HDPE plastic waste.

2. Method

2.1. Chemicals and Materials

Plastic waste based high density polyethylene (HDPE) such as bottle of shampoo, soap and yogurt were obtained from used household plastic. Toluene and glycerol were obtained from Merck (Darmstadt, Germany), while butylated hydroxytoluene from Sigma Aldrich (Missouri, USA) and Carbon black from CABOT (Cilegon, Indonesia). For deionized water was purchased from Cleo (Surabaya, Indonesia). n-hexane solvent used was technical grade while the other solvents were analytical grade and used without further purification.

2.2. Preparation and Characterization Method

2.2.1. Preparation of HDPE plastic waste

HDPE plastic waste samples were cut into small pieces and washed using tap water, then dried by drying for 12 hours. After that, the sample was weighed 20 g and placed in a flask equipped with a vertical condenser and a magnetic stirrer, then 400 mL of toluene was added. The sample was heated to a temperature of 120°C and maintained for 1 hour. After that, the solution was then cooled and dripped into the n-hexane solution as a non-solvent to re-precipitating the isolated HDPE plastic polymer. The precipitate formed were filtered and dried in an oven for 10 hours at 80°C.

2.2.2. Preparation of Geomembrane

The geomembrane was prepared by dissolving 0.1 g of 120 mesh Carbon Black as light stabilizing filler (Sahu), 0.125 mL of Glycerol and Butylated Hydroxytoluene (BHT) with a percentage of mass variation (%w/w) to polymer mass (HDPE) 0; 0.25; 0.5; 0.75 and 1 into 50
mL toluene solvent for 3 hours. After homogeneous solution was reached, add 5 g of extracted HDPE solids gradually while the mixture heated at 80°C for 2 hours until homogeneous. The mixture then casted in a flat glass with 20 x 20 cm in dimension. The casted mixture was air-dried at room temperature for 24 hours. The geomembrane sheet formed was then released by immersing it in water until it was replaced from the glass container. Fourier Transform Infra-Red (FTIR) analysis was carried out on isolated HDPE samples and geomembranes made at wave numbers 400 – 4000 cm\(^{-1}\). Geomembrane sheets were treated with soil burial test for 4 weeks to study the geomembrane resistance. Effect of Butylated Hydroxytoluene (BHT) additive with mass variation w/w% against polymer mass 0; 0.25; 0.50; 0.75; 1 were observed. Geomembranes were buried under soil about 30 cm from soil surface. Geomembranes without treated were used as a control.

### 2.2.3. Physical Characterization of Synthesized Geomembrane

Tensile tests were examined for geomembrane sheets before and after soil burial test. Geomembrane specimen were cut into a size of 10 x 2 cm. Both ends of the sample are clamped on the test equipment and pulled until break. Tensile strength data of geomembranes were recorded.

Permeability analysis was carried out using the Falling Head Test method. The geomembranes sheet were cut with a diameter of 5 cm in a circle and inserted into the tube. Then the water flows through the measuring pipe and allowed to pass through the geomembrane sheet. The permittivity and permeability value was calculated based on equation 1\[^{[13]}\] and followed by calculating the percentage of porosity owned by the geomembrane based on equation 2\[^{[14]}\].

\[
\begin{align*}
\text{Permittivity } \Psi (s^{-1}) &= \frac{k}{r} = 2.3 \frac{n}{A \Delta t} \log_{10} \frac{h_0}{h_f} \\
\text{Porosity } \epsilon (%) &= \frac{w_1 - w_2}{A \times l \times \rho w} \times 100%
\end{align*}
\]

Where \(k\) is permeability (m/s); \(r\) is thickness of the sample (m); \(a\) is area of water supply standpipe (m\(^2\)); \(A\) is total area of geomembrane test specimen (m\(^2\)); \(\Delta t\) is time change between \(h_0\) and \(h_f\) (m); \(h_0\) is head at the beginning of the test (m); \(h_f\) is the head at the end of test (m) (equation 1); \(w_1\) is mass geomembrane before soaked (g) and \(w_2\) after soaked (g); \(A\) is the geomembrane effective area (cm\(^2\)); \(l\) is the thickness of geomembrane (cm) and \(\rho w\) is the water density (g/cm\(^3\)) (equation 2).

Water Uptake analysis were carried out by cutting the geomembrane into a size of 1x1 cm for each variation. The mass of the geomembranes were then weighed before and after being soaked. Geomembranes were treated by immersion with distilled water for 24 hours to study water absorption. After soaking for 24 hours, the mass of the geomembrane was weighed again and the percentage of its resistance to water is calculated based on equation 3 and 4\[^{[15]}\].

\[
\begin{align*}
\text{Water Uptake (\%)} &= \frac{w - w_o}{w_o} \times 100\% \\
\text{Hydrophobicity (\%)} &= 100\% - \text{Water uptake}\%
\end{align*}
\]

Where \(w_o\) is mass geomembrane before soaked (g) and \(w\) after soaked (g).

### 3. Results and Discussion

#### 3.1. HDPE from Plastic Waste Characteristic
Plastic waste bottles of shampoo, soap and yogurt made from HDPE polymer were cutted into about 2x2 cm to increase reaction activity due to larger cross-sectional area \[16\]. The heated samples results in a milky white solution indicates that plastics waste were dissolved in toluene. Recycled HDPE were obtained by The recycled HDPE solution then undergoes a phase inversion after being poured into non-solvent n-hexane, resulting in recycled HDPE solids.

The recycled HDPE mass obtained was 73.711 grams with an average yield of 61.3%. The recycled HDPE is a white solid and has rigid and hard properties \[17\]. The recycled HDPE was analysed with an *Fourier Transform Infra Red* (FT-IR) instrument to observe functional groups, and compared with the results of pure FT-IR HDPE data. The FT-IR data showed absorption at wave numbers 2912 and 2847 cm\(^{-1}\) which refers to C-H stretching, then absorption at wave numbers 1474 and 1467 cm\(^{-1}\) which refers to CH\(_2\) bend compounds. Absorption peak at wave number 721 cm\(^{-1}\) refers to the CH\(_2\) Rock. Results of FTIR analysis compared with FTIR by Jung *et al* \[18\] showed on Figure 1 and Table 1.

![FTIR spectra](image)

(a) (b)

Figure 1. FTIR (a) HDPE recycled by researcher; (b) HDPE by Jung *et al* \[18\]

<table>
<thead>
<tr>
<th>Functional Groups</th>
<th>Wave Number cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Researcher</strong></td>
<td><strong>Jung <em>et al</em> [18]</strong></td>
</tr>
<tr>
<td>C-H <em>Stretching</em></td>
<td>2912</td>
</tr>
<tr>
<td></td>
<td>2847</td>
</tr>
<tr>
<td>CH(_2) <em>bend</em></td>
<td>1474</td>
</tr>
<tr>
<td></td>
<td>1467</td>
</tr>
<tr>
<td>CH(_2) <em>Rock</em></td>
<td>721</td>
</tr>
</tbody>
</table>

3.2. **Characteristics of Geomembrane from recycled HDPE with BHT Addition**

Geomembranes were prepared with variations in mass (%b/b) BHT as an antioxidant. BHT play role in inhibiting polymer degradation due to oxidation and affected the mechanical resistance of the geomembrane \[19\]. The resulting geomembranes sheet have rigid and hard properties. The average thickness owned is 0.4985 mm. The thickness that is owned is in accordance with the minimum geomembrane standard, which is a minimum of 0.36 mm in Pd T-
11-2004-B standard [20]. Rigid and hard properties of the geomembrane are supported by HDPE polymer base material which has rigid and hard properties [7,18]. The result is as follows

![Figure 2. Geomembrane with mass variation w/w% BHT (a) 1; (b) 0.75; (c) 0.5; (d) 0.25; (e) 0](image)

3.3. **FTIR Characterization of Geomembranes**

FTIR characterization was carried out with the aim of seeing changes in the peaks that appeared for each variation that indicated chemical bonds, or only physical. The FTIR data for each variation shows absorption at wave numbers 3441 – 3531 cm\(^{-1}\) (O-H Stretching) which refers to carbon black [22], then absorption at waves 2920 and 2848 cm\(^{-1}\) (C-H Stretching) which refers to HDPE compounds (Figure 3(a)). Then the appearance of peaks of 3026 – 3080 cm\(^{-1}\) (=C-H Stretch aromatic), 1400 – 1600 cm\(^{-1}\) (C-C stretch in the aromatic ring) and 698 – 756 cm\(^{-1}\) (mono-substituted aromatic ring) all of which refer to the presence of toluene compounds [15,19].

![Figure 3. (a) HDPE Compound; (b) Toluene Compound](image)

The presence of toluene on FTIR indicates that the geomembrane has a solvent residue that has not been removed. It can also be seen, with the addition of BHT for each variation, there was no shift change or the presence of a new peak indicating that the bonding occurred only physically. Figure 4 shows the FTIR spectra of geomembranes.

![Figure 4. FTIR Spectra of Geomembranes](image)
3.4. Tensile Strength Characterization of Geomembrane

Tensile strength characterization was carried out on geomembranes with the aim to examine the effect of mass percentage of BHT on the mechanical properties of geomembranes before and after soil burial test for 4 weeks. The results show that the tensile strength of the geomembrane at 0 and 4 weeks has the highest resistance at 0.25% BHT variation, which is 21.235 MPa and 16.012 MPa, respectively, this value continues to decrease with increasing BHT mass (Figure 5).

![Figure 5. Geomembrane Tensile Strength](image)

Tensile strength decreased with the addition of BHT after a variation of 0.25% was because BHT has low polarity, therefore at a small mass it is more effective in increasing compatibility with non-polar HDPE where this affects the mechanical properties of the resulting geomembrane [3,9,10] the 1% BHT mass variation, it was seen that the tensile strength value at week 4 was higher than the week without planting with a difference of 1.44 MPa. It is possible that at the time of making the geomembrane solution the variation was not homogeneous, because the more BHT was added, the blending between HDPE and BHT matrices became more difficult due to differences in the polarity of these compounds. BHT tends to be polar, while HDPE is non-polar due to its hydrocarbon chain. As a result, the mechanical properties of the geomembrane with a high BHT mass are lower than the variation with a smaller BHT mass. However, in the 1% BHT variation, it was found that after 4 weeks of planting there was an increase in the tensile strength value, the exact cause of this increase was not known, but it is suspected that this was caused by the presence of BHT compounds which caused a lot of cross-linking after some time so that the tensile strength value increased [20,21].

Previous analysis by Kocak, 2019 [26] which made a geomembrane with a thickness of 0.5 mm having antioxidant formulations of irganox 1330 (3500 ppm), irfagos 168 (500 ppm), chimassorb 944 (5000 ppm) and carbon black 2.5% obtained tensile strength results at breaking on the geomembrane reaching 30.6 MPa. The tensile strength value obtained from this study is close to that value, which is 21.235 MPa. The study also found that the tensile strength values after planting for 3 months increased up to about 10% due to recrystallization by increasing cross-linking during cultivation. Differences in mechanical properties can be caused by differences in
the formulation used, thickness of the geomembrane and the method of the geomembrane fabrication\textsuperscript{[23,24]}.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig6.png}
\caption{Percentage of Degradation Resistance (\%) of Geomembranes}
\end{figure}

In figure 5, has been show the percentage degradation resistance of geomembranes after soil burial for 4 weeks. Each of geomembranes have percentage degradation resistance value more than 95\%. The recycled HDPE naturally has good resistance during the treatment by 95\% the lowest resistance reached by geomembrane without BHT added. BHT added into geomembranes had improve it’s resistance to degradation in soil. BHT has slow down the degradation process, which geomembrane without BHT adding, has the lowest degradation resistance. Highest resistance was obtained by geomembrane with 0.5\% BHT added.

3.5. Permeability Characterization

Permeability characterization was carried out with the aim of analysing water seepage in the geomembrane layer using the Falling Head Test method \textsuperscript{[13]}. The geomembrane of each variation was cut into a circle with a diameter of 5 cm and placed under the cylindrical tube. The cylindrical tube has a height of 10 cm and a volume of 158,96 cm\(^3\) which is then filled with water. Observations were made for 30 minutes to see the water discharge coming out of a cylindrical tube whose bottom has been placed with a geomembrane.

Observations of each variation after 30 minutes showed that there was no water passing through the geomembrane (no change in water level). The result shows each of those geomembranes have permeability of up to 0 max so that no water escapes. It mean, addition of BHT in geomembran has no effect to the permeability's value. These results are in accordance with the expected Permeability values of geomembranes based on the standard of Pd T-11-2004-B, 0 max. This permeability value is also supported by the characteristics of the percentage of porosity possessed by the geomembrane through the calculation of the gravimetric equation reaching 0\% which indicates that the geomembrane does not have pores so it does not pass water \textsuperscript{[25,26]}.

3.6. Water Uptake Characterization (Hydrophobicity)

Water Uptake characterization was carried out with the aim of seeing the percentage of the geomembrane's ability to absorb water. This test was carried out by immersing the geomembrane of each concentration that had been cut 1x1 cm in water for 24 hours. The test results show that each geomembrane does not have the ability to absorb water with a hydrophobicity value reaching 100\%, it can be seen that there is no change in mass before and after immersion. This also supports the permeability properties of the geomembrane which has a value of 0 max in all
variations so that no water can escape or be absorbed by the geomembrane (Table 2) and these results as well show the addition of BHT in geomembranes has no effect.

This hydrophobicity is also supported by the functional groups possessed by the geomembrane, namely C-H stretching (2920 & 2848 cm⁻¹), =C-H aromatic stretch (3026 & 3080 cm⁻¹), C-C stretch (1400 – 1600 cm⁻¹) in an aromatic ring, and a mono substituted aromatic ring (698 – 756 cm⁻¹) which is a functional group with hydrophobic properties causing the geomembrane to have good hydrophobic properties.[31]

Table 2. Geomembrane Water Uptake (Hydrophobicity) Test Data

<table>
<thead>
<tr>
<th>Geomembrane (BHT%)</th>
<th>Mass before soaking (g)</th>
<th>Mass after soaking (g)</th>
<th>Mass transformation (g)</th>
<th>Hydrophobicity</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0,05</td>
<td>0,05</td>
<td>0</td>
<td>100%</td>
</tr>
<tr>
<td>0,25</td>
<td>0,04</td>
<td>0,04</td>
<td>0</td>
<td>100%</td>
</tr>
<tr>
<td>0,5</td>
<td>0,05</td>
<td>0,05</td>
<td>0</td>
<td>100%</td>
</tr>
<tr>
<td>0,75</td>
<td>0,06</td>
<td>0,06</td>
<td>0</td>
<td>100%</td>
</tr>
<tr>
<td>1</td>
<td>0,58</td>
<td>0,58</td>
<td>0</td>
<td>100%</td>
</tr>
</tbody>
</table>

4. Conclusion

FTIR characterization shown that the presence of butylated hydroxytoluene (BHT) antioxidant in geomembrane made from recycling HDPE plastic waste only had physical interactions. Tensile test shown geomembrane with a mass variation of 0.25% w/w% BHT has the highest value of 21.235 MPa (without planting) and 16.01 MPa (4 weeks planting). Compare to geomembrane that made from pure HDPE and different antioxidant, the tensile value from geomembrane made from recyling HDPE has lower value, but still can optimized by change the casting method and the formulation with other antioxidant which has better performance in geomembrane to support the performance of recycling HDPE as basic material of geomembrane. Other test such as permeability shown in each variation of geomembrane reach value of 0 and porosity 0%. These characteristics meet the requirements of Pd T-11-2004-B standard with the minimum permeability value of the geomembranes is 0 max. Characterization of water uptake (hydrophobicity) shown those geomembranes have water resistabce (hydrophobic) which is supported by the functional groups possessed by those geomembranes. Throught the result, it mean the addtion of BHT in geomembranes has no effect to hydrophobicity and permeability characterization.

References


