Preparation and Characterization of Polyurethane/Carbon/Organoclay Composite for Coating of Aluminum Conductor Overhead Lines

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Electrical transmission overhead lines use an aluminum conductor in services. However, protection of the aluminum conductor from corrosion has to be considered. Hence, an extensive experimental work was done to prepare the composite coating of the aluminum conductor. Three types of polyurethane composites were fabricated with different fillers (5 wt% carbon and 5 wt% organoclay) and were characterized. The composites were polyurethane/carbon (PC), polyurethane/organoclay (PClay), and polyurethane/carbon/organoclay (PCClay). Thermogravimetry analysis and Fourier transform infrared spectroscopy were conducted to obtain thermal properties and chemical bonding of the composites. To obtain the corrosion resistance, salt spray tests were applied. To obtain hydrophobicity properties, the contact angle between water and the composites was measured. Measurements of composites relative permittivity was conducted to obtain dielectric properties. A water vapor permeability test was conducted to obtain the rate of water/gas vapor discharge. Finally, an adhesion test was conducted to obtain adhesion performance according to the ASTM D3359 standard. Based on characterization, PCClay had better characters to be used as an overhead aluminum coating material followed by PC and PClay.

Keywords Polyurethane; Composite; Thermal resistance; Corrosion resistance; Dielectric

I. INTRODUCTION

High voltage electrical transmission lines worldwide use aluminum conductor overhead lines as the main conductive material. Because of their complex operation environment, in-service aluminum conductor overhead lines are prone to corrosion. They may cause problems of safety, reliability, and service life of the transmission lines [1, 2].

Efforts to reduce the rate of corrosion and degradation of the conductors can be done by preventing direct contact between the atmosphere/air and the conductor by coating the conductor. Materials that are widely applied as coatings are polymeric materials, especially nanotechnology polymers. Nanotechnology polymers are the results of a broad area of interdisciplinary research in the design of the manufacture, development, processing, and application of polymeric materials, and the materials are filled with particles less than 100 nanometers [3, 4]. Polyurethane is a highly versatile polymeric material that has special characteristics and can be modified and adjusted both physically and chemically by adding filler material and synthesis process. Because of its properties, this material is widely applied in various fields including automotive, textile construct, and biomedicine. However, it also has limitations including resistance to fire and heat [5–8]. The controlled degradation and adjustable material are the advantages of polyurethane. In several research, to improve several properties such as elastic modulus and strength, flame retardant, reduce gas permeability, increase solvent, and heat resistance, small amounts of nanoclay are added into polymers. A heterogeneous complex
is known as thermal decomposition of polyurethanes [9]. Thermal decomposition and corrosion resistance of polyurethanes are some of the important and fundamental phenomena in various applications. To determine the most optimal conditions for designing the best performance of polymer materials, a comprehensive understanding of the degradation process is important information.

Adding various fillers such as organoclay and carbon into Polyurethane has been done to achieve desired polyurethane properties [3, 10]. Research of polyurethane and montmorillonite composite materials has been carried out in depth and their material properties have been improved such as mechanical steam permeability and water permeability due to dispersion and height [11, 12]. A research showed that polyurethane/organoclay composite materials succeeded in improving the fire resistance properties compared to ordinary polyurethane [13]. Increasing the concentration of organoclay fillers in polyurethane also has an impact on thermal stability and corrosion resistance. Addition of carbon nanotubes or graphite to improve thermal mechanical properties can also increase mechanical strength and fire resistance [14–16].

This paper describes a characterization of polyurethane/carbon/organoclay (PCClay) based on different carbon, organoclay, and carbon/organoclay contents on thermal resistance, corrosion, dielectric properties, hydrophobicity, adhesion, and water vapor permeability to obtain a coating material for aluminum conductor overhead transmission lines.

II. EXPERIMENTAL

A. Materials

Polyurethane comes from commercial products. The polyurethane composition consists of disiocyanate (MDI), and MDI is based on polyisocyanate, 4,4’-diphenylmethane, aromatic solvent blend, and isobutyl acetate. Figure 1 shows the molecular unit of the urethane group $-{\text{NH-}}-{\text{O}}-{\text{C=O}}$.

The type of carbon used as filler material is carbon graphite powder with a diameter of 30 mesh (0.023 in or 595 μm). Organoclay was a commercial product (NANO-LIN DK), which was made from high purified smectite that exhibited ultra-fine phase dimensions. Based on the product information on the package, the size of nanoclay was typically in the range 1–100 nm. When fully dispersed, the average thickness of platellite was around 25 nm, and the aspect ratio was 100–1000.

B. Preparation of polyurethane based composite

1. Composite of polyurethane/carbon/organoclay

Three types of polyurethane composites were fabricated with different fillers (5 wt% carbon and 5 wt% organoclay). The composites were (1) polyurethane/carbon (PC), (2) polyurethane/organoclay (PClay), (3) polyurethane/carbon/organoclay (PCClay). Table 1 shows the composition of the samples coated on aluminum substrates.

2. Mixing and coating preparation

The mixing process were carried out using a magnetic stirrer at cimet SP131635 barnstead thermolyne magnetic stirrer (Apogent Technologies, USA) with a stirring speed of 500 rpm for 120 min. After stirring process, samples were molded into the aluminum plate of 415.6 mm$^2$ with a thickness of 0.35 mm and were dried at ambient temperature for 24 h. After drying, the layer was removed from the aluminum plate and prepared for testing.

C. Characterization

X-ray diffraction (XRD) analysis was employed to identify compositions and the phase of the composites using the PANalytical materials research diffractometer (Malvern Panalytical, UK).

To analyze and identify the chemical bond of the composites, fourier transform infrared spectroscopy (FTIR) analytical techniques were applied using an FTIR

Table 1: Composition of polyurethane base composites.

<table>
<thead>
<tr>
<th>Composition (wt%)</th>
<th>Polyurethane</th>
<th>Microcarbon</th>
<th>Organoclay</th>
<th>Total (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P0</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>PC</td>
<td>95</td>
<td>5</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>PClay</td>
<td>95</td>
<td>0</td>
<td>5</td>
<td>100</td>
</tr>
<tr>
<td>PCClay</td>
<td>90</td>
<td>5</td>
<td>5</td>
<td>100</td>
</tr>
</tbody>
</table>

Figure 1: The molecular units of the urethane group [3].

Figure 2: Parallel capacitor principle for a dielectric test.
spectrometer L160000A (PerkinElmer, USA) with radiation wavelengths of 4000−400 cm−1.

Agilent/HP 4284A was used to measure dielectric properties as a function of the frequency with a range between 50 kHz and 1 MHz. The samples were placed between aluminum plates as electrodes. The relative permittivity (ε') were obtained by calculating the permittivity value (ε) divided by the permittivity value in vacuum (ε0).

\[ \varepsilon' = \frac{\varepsilon}{\varepsilon_0} \]  

The permittivity value was obtained by calculating the capacitance, the area, and the sample thickness based on the basic principle as shown in Figure 2.

\[ C = \varepsilon \frac{A}{d} \]  

In Eq. (2), C is capacitance (F), ε is the permittivity of the material (F m⁻¹), ε0 is the vacuum permittivity (8.85 × 10⁻¹² C² N⁻¹ m⁻²), A is an area of the sample (mm²), and d is a sample thickness (mm).

Thermogravimetric analysis (TGA) and differential scanning analysis were carried out to obtain information of mass loss during heating. Thermogravimetric analyzer provides information of degradation in terms of temperature through the decomposition processes. Thermal analyzer 6000 simultaneous series (STA) (PerkinElmer, USA) with temperature range of 50−950°C was used for the TGA test.

The salt spray method to investigate corrosion resistance was carried out according to the ASTM B117 standard. The samples were sprayed with 0.5 M NaCl solution with the spraying period of every 3 h, totaling 72 h of the test time. Optical microscopy was carried out using Zeiss Axio Lab. A1 (Carl Zeiss, Germany) with 400 times magnification.

Hydrophobic observations were carried out by measuring the angle of the water droplet on the surface of the samples. The photos were taken using Canon 1000D EOS Camera. The hydrophobic criteria were determined by the value of the angle θ as seen in Figure 3.

In this research, adhesive power measurements were carried out using the ASTM D3559 standard. Furthermore, a water vapor permeability test was conducted to measure the composite materials’ rate of water/gas vapor discharge. The test was conducted for 13 days by measuring permeability of the samples using the gravimetric method. In this method, a desiccant was placed in a tube with a size of 21 × 150 mm covered with a sample material. Due to the desiccant’s ability to absorb water vapor, the material performance could be detected by measuring the weight of the desiccants. Observations were carried out every day by weighing and recording the weight of the desiccants. The absorber used in this test was silica gel with properties that could absorb moisture.

### III. RESULTS AND DISCUSSION

#### A. XRD analysis

XRD patterns are presented in Figure 4. The data shows that polyurethane (P0) gave a broad structure in the range of 10°−25°, which is a typical form of the XRD pattern of polymer materials. In the XRD pattern of PC, an element of graphite was identified by two hkl indices, i.e., (002) and (004) with angles of 27° and 55°, respectively. In the XRD patterns of PClay and PCClay, the content of nanoclay was not identified. This probably occurred due to the small amount of nanoclay as a filler. In the XRD graph of polyurethane, it seems smoother due to the amorphous form of polyurethane while carbon is crystalline.

#### B. TGA

TGA described information of mass loss of the sample during heating as a function of temperature. A TGA curve of polyurethane and those of the samples are given in Figures 5 and 6, respectively. Decomposition of the samples occurred in two stages; the first stage occurred on the hard segment (isocyanate) of the urethane chain, and the second stage decomposition began to disconnect the bond of a polyurethane soft segment (polyol) chain consisting of bond −CH and −OH.

**Figure 4:** XRD patterns of the composites.
The peak temperature ($T_m$) is the temperature at which the phase changes the sample in the TGA. An onset temperature ($T_o$) is the temperature used as the identification standard of the beginning of the transformation. The onset temperature is produced from the intersection of a linear line with a curve that falls linearly and roughly. An endset temperature ($T_e$) is the temperature used as the identification standard of the end of the transformation. The endset temperature is produced from the intersection of a linear line with a linear upward curve as shown in Figure 5. The width of the curve describes the amount of heat absorbed by the sample to carry out the transformation. Table 2 shows the results of $T_o$, $T_m$, and $T_e$ of composites for the first stage ($T_o1$, $T_m1$, and $T_e1$) and the second stage ($T_o2$, $T_m2$, and $T_e2$).

The first stage decomposition for the PC composite occurred at temperatures around 320–420°C. In the second stage, the decomposition of the sample (PC) occurred at 650–790°C. For the PClay sample, the first stage of decomposition occurred at 330–420°C. For the PCClay sample, the first stage occurred at 310–420°C and the second at 620–795°C. By adding carbon, clay, or both carbon and clay to polyurethane, the second-stage decomposition does not occur until 620°C. The second-stage decomposition of PCClay at temperatures above 700°C is due to carbon reacting with oxygen to form CO$_2$, resulting in a decreased mass of carbon. Thus, the decrease in the mass of the PCClay composite above 700°C is due to carbon but not due to clay. PCClay was not better than PC in terms of the second-stage decomposition. This may be because, compared to mixing polyurethane and carbon or polyurethane and clay, there is a different reaction if carbon and clay are simultaneously mixed with polyurethane. This is still unconfirmed in this study. The graph shows that the PC composite was better than other composite samples.

### C. FTIR analysis

Referring to the previous research of the reaction between hydroxyl and isocyanate [18], the FTIR analysis was monitored in the range of 400–4000 cm$^{-1}$. It mentioned that the most important characters were located at 3050–3720 cm$^{-1}$ for $-\text{NH}$ stretching vibration, 2800–3000 cm$^{-1}$ for $-\text{CH}$ stretching vibration, at 1665–1780 cm$^{-1}$ for C=O stretching vibration, at 1500–1590 cm$^{-1}$ for C–N, N–H, and C–C, and at 1200–1292 cm$^{-1}$ for C–N [18].

Figure 7 shows FTIR pattern of the samples, and the data confirmed the previous research. The hydrogen bonds were seen from the N–H and O–H bonds at 3200–3400 cm$^{-1}$ and 1600–1700 cm$^{-1}$. Other peaks indicated the existence of carbon bonds in the N–H region of the urethane chain in the PC composite. The stretching frequency of the OH functional group was observed at 3349 cm$^{-1}$ [19]. The peaks at 1596 cm$^{-1}$ and 1460 cm$^{-1}$ were due to the stretching frequency of C=C in the aliphatic chain and the aromatic ring, respectively. The bands appearing at 1167 cm$^{-1}$ and 1041 cm$^{-1}$ corresponded to the Si–O–O stretching frequency [20].
The addition of organoclay showed less chemical interaction compared to other samples. However, the better thermal stability of PClay may probably due to the phenomenon of organoclay exfoliation [21].

PClay showed the best transmittance for the wave number region between 500 cm$^{-1}$ and 4000 cm$^{-1}$ following P0, PC, and PCClay.

### D. Salt spray test

Figure 8 shows the morphology of the samples before and after the salt spray test. In the PClay and PCClay samples, agglomeration was detected, unlike in PC and P0 samples. PC and PCClay composites showed agglomeration on several sides. The salt spray test represented the corrosion resistance of PC and PCClay that had less amounts of agglomeration, meaning a greater potential for corrosion resistance.

After the salt spray test, the surface of the PC sample was rougher than those of the PClay and PCClay samples. On the opposite surface, the morphology of the PClay sample was smoother than the others. It means that the PClay composite had better corrosion resistance.

### E. Dielectric analysis

The relative permittivity properties of the sample were investigated in the frequency range between 50 kHz and 1 MHz at room temperature. The permittivity was obtained from the composite samples which were placed between two aluminum plates as the capacitor effect [22].

The variation of the relative permittivity is presented in Figure 9. In general, all of the composite samples showed good performance of the relative permittivity at 50 kHz. The relative permittivity of PClay is lower than that of P0 up to...
250 kHz but is superior to the relative permittivity of P0 above 250 kHz. The composite of PCClay also shows good performance of the relative permittivity. Addition of carbon in polyurethane gave a better permittivity than addition of clay, but PCClay was the best composition in view of the permittivity value that increased sharply compared to the others.

F. Hydrophobicity analysis

The chemical nature is a key point to develop a hydrophobic surface, and the concept of wetting is important to the determined degree of hydrophobicity. The degree of wetting (or wettability) is determined by the balance between adhesive and cohesive forces. The adhesive force between liquid and solid materials causes the liquid droplet to spread, while the cohesive force within the liquid causes the liquid droplets to be balled up, i.e., avoiding the contact with the surface.

The observation of hydrophobicity of the composites is shown in Figure 10. The contact angles between water and P0, PC, PClay, and PCClay were 48.5°, 57°, 56°, and 57.5°, respectively. All of the composites are categorized as being hydrophilic.

G. Adhesion test

The adhesion test measurement was carried out using the ASTM D3359 standard to assess the performance of the composite materials on their adhesion to the coated material. The result of the test was compared to the standard ASTM D3359 classification as shown in Table 3.

Figure 11 shows the surfaces of the composite layers after the adhesion test. The coatings seemed to be still in good condition nor bear defects on the coating area. Referring to the ASTM D3359 standard, the composites P0, PC, PClay, and PCClay were included in the 5B classification or very good.

H. Water vapor permeability

As a solvent of polyurethanes, isobutyl acetate, which is a derivative of petroleum, was utilized in this experiment. Measurements of water vapor permeability aims to obtain information on the ability of the composite to resist the penetration of water molecules and the possibility of the water vapor entering due to porosity of the composites. The measurements of water vapor permeability were expected to provide an overview of which composite material had the best water vapor permeability. Figure 12 presents the properties of water vapor permeability for the composites. The addition of carbon to polyurethane increased the absorption of moisture. This result confirmed the salt spray test result that carbon filler increased corrosion. It is expected that the increase of water vapor permeability was due to porosity.

I. Result of characterization in term of composite as coating for conductor

To determine which one was the best composite, the score of the characterization results of each composite was calculated. The scores were obtained from the results of each characterization/testing as described in Table 4; score 0 = poor, 1 = fair, 2 = good, and 3 = very good.

Table 3: Classification of the adhesion base on ASTM D3359.

<table>
<thead>
<tr>
<th>Classification</th>
<th>% Area removed</th>
</tr>
</thead>
<tbody>
<tr>
<td>5B</td>
<td>0% (None)</td>
</tr>
<tr>
<td>4B</td>
<td>Less than 5%</td>
</tr>
<tr>
<td>3B</td>
<td>5–15%</td>
</tr>
<tr>
<td>2B</td>
<td>15–35%</td>
</tr>
<tr>
<td>1B</td>
<td>35–65%</td>
</tr>
<tr>
<td>0B</td>
<td>Greater than 65%</td>
</tr>
</tbody>
</table>

Figure 12: Water vapor weight of the composites.
The characterization of PCClay composite was investigated to get the best variation of composite for the aluminum conductor coating. TGA analysis, FTIR, the salt spray test, the hydrophobicity test, and water vapor permeability test were conducted to obtain the performance of corrosion resistance. The thermal stability performance in the TGA analysis showed that PC was better, followed by PCClay and PClay. The thermal stability performance was needed in the operation of the aluminum conductor overhead lines due to the climate condition. In the FTIR analysis, the PClay composite was better than the others for transmittance. PClay had a stronger bond than the others. The salt spray test was conducted to obtain the performance of corrosion resistance. The salt spray test showed that PClay was better in corrosion resistance than the others. Meanwhile, the best relative permittivity showed that PCClay was better than the others. Even though all of the composites were hydrophilic, PCClay gave a higher contact angle than the others. For water vapor permeability, polyurethane without the fillers gave a better performance, and for the adhesion performance, all of the composites were included in the 5B classification or very good. Based on the characterizations, the PCClay composite have the best characteristics (scored 15) to be used as a coating material for overhead aluminum.

**References**

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