Thermal behavior, dielectric and corrosion resistance of polyurethane/carbon/nanoclay hybrid materials

I H Ramadhan, B Soegijono, O Kurniawan, E Virgawati and I Mudzakir
Department of Physics, Faculty of Mathematics and Natural Sciences (FMIPA), Universitas Indonesia, Kampus UI Depok, Depok 16424, Indonesia

Corresponding author’s e-mail: bambangs@sci.ui.ac.id

Abstract. Recently, research on hybrid materials of Polyurethane/Carbon/Nanoclay are challenging because of their applications. In this study, these materials were fabricated with various amounts of carbon and organoclay (1, 3, and 5) wt.%). The samples were characterized by thermogravimetry analysis, differential scanning calorimetry, optical microscope, RLC meter, Fourier transform infrared spectroscopy (FTIR) and salt spray test. The results showed that the samples with 5 wt.% carbon/organoclay have higher dielectric constant. Thermal behavior of the samples depends on the content of the filler. Salt spray test showed that the samples with 1 wt.% carbon/organoclay have higher corrosion resistance.

Keywords: polyurethane, organoclay, corrosion resistance

1. Introduction
Polyurethane (PU) has various unique properties such as good elasticity, elongation, tensile strength, highly resistant against abrasion, great resistant towards weather, exceptional luster, color retention and good resistant against corrosion characteristics [1–2]. But in harsh conditions, PU fails to provide satisfactory thermal and mechanical resistance performance, so we need to induce such structural properties in PU through mixing into composites to offer a great performance even in the extreme environmental circumstances. It was noted that the synergistic influence among filler and matrix (PU) increases its ability to stabilize, solubilize, as well as improve the properties of thermal, mechanical, electrical and optical [3–6].

Good thermal stability, environmentally friendly and easily synthesized is regarded as the hallmarks of conducting polymer materials in general. The invention of conducting polymer nanocomposites has revolutionized polymer applications due to their advantages such as high load ratio, high efficiency, light weight and low cost [6–7]. Conducting polymer such as carbon nanotubes (CNT), graphene, and graphite were carried out in a good dispersion of mixtures [8], and also shows good dielectric properties [9]. They provide optimum effect in a sufficiently small amount (0.5–5) % as fillers in a polymer matrix to form composites in the production of various electronic and optical devices such as sensors, actuators, light-emitting diodes, coatings and others [6,10,11].

Other materials that can be used in the development of PU polymer composites are clay. Clay might serve a crucial role in regards to provide a barrier and high impedance properties for coating systems. In other words, clay increases corrosion protection by preventing corrosive media from penetrating through layers. Optimization and new properties of clay/polymer nanocomposites compared with pure polymers, and many new nanocomposites based on polymers/clay have been investigated [12–16]. The integration of
organoclay into the PU matrix generates the better coating properties namely, adhesion, hardness, barrier properties, thermal resistance, and resistant to corrosion [3,17]. Composite of polyurethane with filler carbon and organoclay were fabricated to obtain a good corrosion resistance and thermal stability hybrid material.

2. Experimental procedure
The precursor was polyurethane methylene diphenylene diisocyanate (MDI) with aluminum addition from the commercial product, MDI based polyisocyanate composition, 4,4’-diphenylmethane, aluminum, aromatic solvent blend and isobutyl acetate. The urethane group –NH–(C=O)–O– link molecular units is shown in figure 1. Carbon was used for graphite filler as one of the allotropes of carbon. The carbon was grounded to the size of 30 mesh to obtain microcarbon. Organoclay was also used as filler from the commercial product. The composite was prepared by mixing PU, carbon and organoclay with various compositions of 1, 3, and 5 wt %, respectively then stirred at 500 rpm for 120 minutes.

Thermogravimetric analysis (TGA) was used to identify the weight loss of the composite as function of temperature and differential scanning calorimetry (DSC) was applied to obtain evidence about heat stability throughout the heating process at 20 °C/min from 30 °C temperature to 950 °C. Fourier transform infrared spectroscopy (FTIR) was also employed to see the functional groups of composite at the wavenumber range of 500–4000 cm⁻¹. Dielectric test was used to see dielectric value of the sample with frequency 100 kHz to 1 MHz. Optical microscopy (OM) was used to analyze morphological changes of samples before and after salt spray tests.

3. Results and discussion

3.1. TGA analysis
TGA pattern offers the evidence of weight loss throughout the heating process as the function of the sample’s temperature as shown in figure 2. Figure 2 shows there are two degradation steps, the initial stage is around 340–370 °C and the second is around 680–720°C. The initial stage is the main stage which has high degradation percentage (45–55) % from 230 °C onset temperature until 420 °C endset temperature. The second stage is minor stage with degradation percentage (5–15) % from 610 °C onset temperature until 790 °C endset temperature. The end of second stage samples displayed higher thermal resistance than pure polyurethane.

Polyurethane has the lowest final weight and the final weight increases with the increase of Carbon/Clay content. It seems the onset temperature is shifting to the higher temperature with the increase of carbon/clay content. The significant difference at the second stage indicates chemical interaction on the surface filler with the matrix. Composite with 3 wt.% carbon/clay shows the highest thermal stability. It probably occurs due to agglomeration of clay or carbon when the content increases. If the agglomeration exists, the chemical interaction between matrix and the surface of the filler decreases.

3.2. DSC analysis
DSC pattern indicate the need or excess heat as temperature function of the samples as shown in figure 3. PU pattern shows a sharp decrease indicating no sufficient resistance against thermal condition, but with the addition of carbon/clay, the pattern becomes relatively stable. It indicates that the sample has thermal stability due to the cross-linking characteristics of the matrix increasing thermal stability by the addition of fillers [18], and as it is seen from figure 3, the best thermal stability is the sample PCClay3.
3.3. FTIR analysis

FTIR transmission pattern as wave number function is shown in figure 4. PU with 1 wt % of carbon/organoclay shows the optimum transmittance for wave number 500–4000 cm\(^{-1}\). Stretching frequency of OH functional group was observed around wavenumber of 3050–3720 cm\(^{-1}\). At wavenumber of 2800–3000 cm\(^{-1}\), there was a peak of stretching C-H bond. The C=O (amide I) vibration was identified.
3.4. Dielectric analysis
The dielectric value of the sample is found on a linearly inclined curve at frequency 400 kHz–1 MHz in which the values are averaged as shown in figure 5. PCClay5 shows a big difference dielectric value at 100–200 kHz, but the real dielectric value or the dielectric constant is obtained from the average dielectric value of the curve that has been relatively stable. Dielectric constant of the frequency of PU, PC, PClay and PCClay sample comparison which shows a significant difference from the PCClay sample because the highest dielectric constant value reaches 7.8 x 10^3 when the frequency is 50 kHz. Inset in figure 5 is a magnification of figure 5 at a frequency of 400 kHz to 1 MHz. The value of the dielectric constant of a sample is taken on a dielectric curve that is relatively linear, then each point is summed and then the average value is determined. After the calculation above is obtained the value of the dielectric constant of the PU sample, PC, PClay, and PCClay respectively are 24.12; 50.25; 42.92; 125.95. Organoclay is dielectric material [20], so it is clear that the increase of the content of clay exhibits the increase of dielectric constant.

3.5. Optical microscopy and salt spray analysis
Figure 6 and figure 7 show surface morphology of the samples of before and after corrosion using 100 x magnification of optical microscopy. Figure 7 shows that PU and PCClay1 have smoother surface...
4. Conclusions

Polyurethane/carbon/organoclay composite with various contents of Carbon and Clay have been prepared. PCClay3 provides a higher thermal stability than the other sample. But, PCClay1 has the highest transmittance and good corrosion resistance. On the other hand, PCClay5 has the best dielectric value. Polyurethane/carbon/organoclay composite is possible to be applied as anticorrosive coating for material and also has good thermal and dielectric properties.
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