Thermal behaviour properties and corrosion resistance of organoclay/polyurethane film

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Abstract. Organoclay/polyurethane film composite was prepared by adding organoclay with different content (1, 3, and 5 wt.%) in polyurethane as a matrix. TGA and DSC showed decomposition temperature shifted to a lower point as organoclay content change. FT-IR spectra showed chemical bonding of organoclay and polyurethane as a matrix, which means that the bonding between filler and matrix occured and the composite was stronger but less bonding occur in composite with 5 wt.% organoclay. The corrosion resistance overall increased with the increasing organoclay content. Composite with 5 wt.% organoclay had more thermal stability and corrosion resistance may probably due to exfoliation of organoclay.

1. Introduction

Among all the available nano fillers, those derived from layered silicates (nanoclays) are the most studied for polymer nanocomposites. By adding small amounts of nanoclay into polymer, it is possible to achieve consistent increments of some properties such as elastic modulus and strength, flame retardancy, lower gas permeability, improved solvent, and heat resistance [1-3].

Thermal stability is defined by specific temperature or temperature time limit within which the material can be used without excessive loss of its properties. Thermal decomposition of polyurethane (PU) has been known as the complex heterogeneous [3]. The thermal decomposition of PU (their degradation attributed to absorbed thermal energy) and corrosion resistance are important phenomenon from both fundamental and industrial applications. The understanding of degradation processes allows determination of optimum conditions for designing PU in order to obtain high-performance polymer materials.

Organoclay such as montmorillonite have been researched for more than 10 years as a filler for polymer based composite [4-5]. Exchanging cations present in clay by Na⁺ could allow water to increase interlayer spacing up to several hundred angstrom [6-7]. Modifications of montmorillonite by means of organic modifiers such as alkylammonium to improve the compatibility between hydrophilic organo-montmorillonite and hydrophobic polyurethanes are often used [8, 9]. These organic chains having positively charged ends can be bonded to the surface of the negatively charged silicate layers resulting in an increase of the interlayer gap [10-11].

Composite on polyurethane and montmorillonite particles have been widely investigated [8,10] and frequently enhanced advanced properties such as mechanical, water vapor permeability, water permeability properties due to exfoliation dispersion, and high surface area [11-14].

The presents paper will discuss the characterization of nanocomposite clay-polyurethane. Polyurethane was obtained from commercial product with aluminum addition. Addition of aluminum...
differs it with others PU. Thermal stability and corrosion resistance were studied with different content of organoclay. With unique properties of organoclay, we expect that the thermal stability and corrosion resistance changed due to different content of organoclay.

2. Experimental procedure

PU was obtained from commercial product with aluminum addition. The composition of the PU are diisocyanate (MDI), MDI based polyisocyanate, 4,4’– diphenylmethane, aluminum, aromatic solvent blend, and isobutyl acetate. Figure 1 shows the urethane groups –NH–(C=O)–O– link the molecular units.

![Urethane groups](image)

**Figure 1.** The urethane groups –NH–(C=O)–O– link the molecular units.

Organoclay was procured from commercial product. The composite were prepared by stirring PU solution with various content of clay: 1 wt.% (PClay1), 3 wt.% (PClay3), and 5 wt.% (PClay5). Then composite were deposited on low carbon steel plate using High Volume Low Pressure (HVLP) method. Then the films were taken from the substrate to be characterized. Thermogravimetry (TGA) was used to measure the weight loss of the clay-polyurethane composite under nitrogen atmosphere. Samples were heated from 30 °C room temperature to 800 °C at heating rate 10 °C/min. Differential Scanning Calorimetry was used to obtained information heat needed or loss during heating or cooling rate of 10 °C/min from 30 °C temperature to 800 °C. The salt spray according to ASTM B-117 test was also used for 72 hours to provide information of corrosion resistance. The samples were also investigated by FTIR spectrometer in the wave number range of 300 – 4000 cm⁻¹. Morphology of the samples was investigated by optical microscope before and after salt spray test.

3. Results and discussion

3.1. TGA analysis

The study of the decomposition of PU is often difficult. PU degrades with the formation of various gaseous products and a number of decomposition steps are typically observed in thermogravimetric analysis (TGA). TGA also provide information of lost mass during heating as function of temperature of the samples. Figure 2 shows TGA curve as a function of time. According to figure 2 there are two step of degradation. The first (onset temperature) is round 260 – 290 °C and the other stage (end-set temperature) is between 420 – 450 °C. The first stage is major stage which the sharp degradation occurred. In the second stage, the composite with different content clay displayed higher thermal resistance than pure PU. The smallest lost mass is PU and the lost mass increases with increasing clay content. It seems that the onset temperature become sharp and slightly shifting to the higher temperature with increasing clay content, but the end-set temperature remain more or less unaltered.
Figure 2. TGA curve of the samples clay/PU with various content of clay. These are pure PU (P0), 1 wt.% (PClay1), 3 wt.% (PClay3), and 5 wt.% (PClay5).

3.2. DSC analysis

Figure 3 displays heat needed or loss versus temperature of the samples. Samples P0, PClay1, and PClay3 suddenly decreased in heat flow around 800 °C, but PClay5 was better in thermal stability. Some researchers have shown that thermal-degradation behavior of PU and its composite at high temperatures may provide a fingerprint of the materials that may not only inform us the material characteristics or the filler type but also its processing and quality of the end products [15]. The complexity of the PU’s or its composite’s thermal stability and degradation drives researchers to do further study.

Figure 3. DSC curve of the samples clay/PU with various content of clay.
3.3. **FTIR analysis**

Figure 4 shows FTIR patterns of the pure PU (P0) and its addition with various clay content. The transmittance as a function of wave number of PU with 5 wt.% clay (PClay5) showed the best transmittance for wave number 500 – 4000 cm\(^{-1}\). Stretching frequency of OH functional group is observed at 3349 cm\(^{-1}\) [15]. The peaks at 1596 and 1460 cm\(^{-1}\) occurred due to the stretching frequency of C=C in the aliphatic chain and aromatic ring respectively. The bands appearing at 1167 cm\(^{-1}\) and 1041 cm\(^{-1}\) correspond to Si-O-O and Al-O-Al stretching frequency, respectively [16]. The addition of 5wt.% organoclay showed less chemical interaction comparing to others samples. But the better thermal stability of PClay5 may occur due to phenomena of exfoliation of organoclay [17].

![Figure 4. FTIR curve of the samples clay/PU with various content of clay.](image)

3.4. **Morphology and salt spray analysis**

Durable corrosion protection is very essential in many industries. A high quality elastic PU coating system using raw materials is required to protect the material from corrosion environment. Therefore, PU with different clay contents were subjected for corrosion test using salt spray. Figure 5 shows surface morphology of the samples before and after salt spray test to understand corrosion resistance of PU coating. The samples P0, PClay1 and PClay3 have surface morphology smoother than PClay5 before salt spray test. After salt spray test, the surface morphology changed. We observed that samples PClay1 and PClay3 are rougher than PClay5. We suggested that PClay5 is more resistance than the others.

![Figure 5. Surface morphology of the samples before and after salt spray test.](image)
4. Conclusion
Organoclay/PU composite with different clay content have been investigated. PClay5 have more thermal stability and good corrosion resistance than PO, PClay1 and PClay3. It revealed that addition of clay modify the properties of pure PU thus it was suitable for coating materials. The exfoliation of organoclay in PU matrix indicated a good interaction between organoclay and PU.

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Figure 5. Surface Morphology of clay/PU composite with different clay content (a) before and (b) after salt spray.