Thermal behaviour properties and corrosion resistance of carbon/polyurethane film

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Abstract. Carbon/polyurethane film composite were prepared by adding carbon with different content in polyurethane as a matrix. The materials were characterized by means of thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FT-IR), Optical microscope and salt spray test. TGA and DSC results showed decomposition temperature shifted to a lower point and the FT-IR spectra showed chemical reaction of carbon/polyurethane matrix. The corrosion resistance overall decrease with the increasing carbon content.

1. Introduction
Efforts to use Carbon as a filler added to the polymer have been carried out to determine and obtain the desired material properties. Adding carbon to polyurethane is possible to obtaining material such as heat resistance, flame retardance and proper of mechanical properties [1-4].

To obtain polymer materials with performance related to heat resistance and corrosion resistance, it is necessary to understand the decomposition of polyurethane materials. Thermal decomposition of polyurethane is recognized as a heterogeneous complex [5]. Thermal decomposition of polyurethane (heat energy feature absorbed into its degradation) and corrosion resistance are important occurrence of fundamental and industrial practice. To obtain high-performance polymeric materials, understanding the degradation process allow the determination of optimal conditions for designing polyurethanes. Specific temperatures or temperature limits where the material can be used without losing its properties are often called thermal stability.

Research of Carbon as a filler of polymer (as a base of composite) have been conducted [6-8]. Carbon works well as a filler in a polyurethane matrix that has the results of thermal resistance and good electrical conductivity [9]. Research of composite polyurethane filled by carbon was conducted on wear resistance of polyurethane/carbon with pigment concentration and NCO/OH ratio as parameters that affect the potential of wear resistance and the result found that the most effective factor in wear resistance is type polyols due to CO’s potentiality to form hydrogen bonds with hard segments of polyurethane and also that the weight of carbon pigments has an average effect on wear resistance [10].

Research to improve advanced properties such as mechanics, permeability and surface area in polyurethane / carbon composites has been frequently and widely investigated. The addition of carbon nanotubes or graphite in an effort to improve thermal mechanical properties can also increase the
mechanical strength of about 20% by adding up to 0.05% carbon nanotube and also increase resistance to fire [1-11].

This paper describes the results of the characterization of carbon-polyurethane nanocomposite. Polyurethane used is a commercial product with the addition of aluminum. The addition of this aluminum makes it different from other polyurethane. Observations on thermal behavior and corrosion resistance were carried out based on different carbon content and it was estimated that there was a change in thermal behavior and corrosion resistance due to changes in carbon content.

2. Experimental
Polyurethane used is a commercial product where there is an additional aluminum which makes it different from other polyurethane. The Polyurethane composition consists of diisocyanate (MDI), MDI based Polyisocuanate, 4,4′ – Diphenylmethane, Aluminum, Aromatic Solvent Blend and Isobutyl Acetate. Figure 1 show 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

Carbon used as fill material is a carbon allotrope, which is graphite. Micro-carbon comes from pure carbon graphite which is then made in powder size with a diameter of 30 Mesh (0.23 inch or 595 microns) by mashing using mortar. The composite were prepared by stirring polyurethane solution with various content of Carbon, 1%, 3%, 5%wt. The mixing of fillers begins by preparing each ingredient according to the percentage fraction of mass and mixtures needed.

The method used to mix fillers into polyurethane as a matrix by the mixing method for obtaining carbon/polyurethane. The melt mixing method was chosen because the process is simple by mixing the fillers into the liquid polyurethane matrix so that a dispersed particle composite is formed. The mixing process was carried out using a magnetic stirrer at Cimet SP131635 Barnstead Thermolyne Magnetic Stirrer (Apogent Technologies Inc., US) with a stirring speed of 500 rpm for 120 minutes.

Furthermore after stirring process, sample was printed on the aluminum plate (diameter of plate 23 mm) using gun spray which exposed by High Volume Low Pressure (HVLP) method. HVLP method is one method of making composite-based open mold, namely the printing process carried out in an open space, does not need to be in a vacuum chamber. The solution of the polyurethane matrix and its filler put into a spray gun and then sprayed evenly onto the mold. The spray gun used has a strong air pressure of 15 Psi. During the spraying process, it is assisted by a small spatula to flatten the mixture of ingredients on the plate so that no air is trapped in the matrix and filler solution. After the sample thickness is in accordance with the desired amount of 0.35 mm, the sample is dried at room temperature for 24 hours. After drying, the layer is removed from the mold and prepared for testing.
Thermogravimetric analysis (TGA) and Differential scanning analysis is carried out to obtain information of mass loss during the heating period which is needed to see process of decomposition. We expected that thermogravimetric analyzer can obtain information of polyurethane degradation through forming various products and a number of decomposition processes. TGA describes information on loss of assumption during heating as a function of temperature of the sample. DSC is in the same process to identify the thermal stability of the test sample when temperature increases. The pattern of data displayed after the DSC test can represent the state of the test material such as decomposition, oxidation, dehydration or crystallization. These conditions are some thermal resistance analysis parameters of each sample. TGA and DSC test used 6000 Simultaneous Thermal Analyzer (STA) (Perkin-Elmer Inc., USA) with a test temperature range of 30 - 800 °C at heating rate 10°C/minute.

To identify of organic material, Fourier Transform Infrared Spectroscopy (FTIR) analytical technique is applied. The FTIR technique measures the absorption of wavelengths of infrared light emitted by the material being tested. This infrared absorption band shows the structure and components of certain molecules. FTIR testing was carried out using Spectrum Two FTIR Spectrometer L160000A (Perkin Elmer Inc., USA). This non-destructive test uses specimens measuring 2 cm x 2 cm starting from radiation wavelengths of 300 - 4000 cm⁻¹.

Corrosion resistance testing is carried out by the salt spray method according to ASTM B117 standards. For the salt spray test a sample measuring 2 cm x 2 cm was prepared. This method was chosen because it is the right and efficient method for carbon/polyurethane samples. In this method the sample is sprayed with 0.5 M NaCl solution with the spraying period every 3 hours in a total 72 hour test time.

Optical Microscopy was carried out using Zeiss Axio Lab.A1 (Carl Zeiss Co., German). For the Optical Microscopy test a sample measuring 2 cm x 2 cm was prepared which was observed using 100 times magnification. This test was carried out to observe the morphology of the composite layer of composite samples at the initial state of the sample before salt spray testing and sample conditions after the salt spray test was carried out.

3. Results and Discussion
3.1. Thermogravimetric (TGA) analysis
Thermogravimetric analysis is carried out to obtain information of mass loss during the heating period which is needed to see process of decomposition. We expected that thermogravimetric analyzer can obtain information of polyurethane degradation through forming various artifact and a several processes of decomposition. Thermogravimetric analysis describes information on loss of mass during heating as a function of temperature. Figure 2 display TGA curve as a function of temperature.
Figure 2 show degradation of sample in two step, the first step is round 270-300 °C (onset temperature) then the second step is round 390-430 °C (endset temperature). The first stage is the main stage where there is a sharp decline, while in the second stage the composite with different content carbon, the smallest loss of mass occurs on PC5 following PC1 and PC3.

3.2. Differential Scanning Calorimetry (DSC) analysis

Figure 3 display heat consumed or loss versus temperature of the composite samples. The graph obtained a poor value in the PC3 and the trend on the graph has not looked good. DSC test results are always related to how the bonds in the material chain are. The crosslinking or cross-linking in the chain will affect the temperature response. There is a melting temperature shift and crystallization temperature caused by crosslinking which results in reduced chain flexibility and inhibits the movement of polymer chains, so that thermal transitions occur at high temperatures [12].

Samples PC1, PC3 dan PC5 show that heat flow suddenly decrease on around 300°C, however P1 is more excellently in thermal stability
Figure 3. DSC curve of Carbon/Polyurethane composite sample with various content of Carbon

The study of the behavior of thermal degradation that has been carried out by several researchers shows that at high temperatures it can give fingerprints of the material that do not have to be only with the characteristics of the original material, the kind of fillers but also with the processing and final quality of end products [13]. Due to the complexity and degradation of polyurethane has provided motivation for researchers to investigate it endlessly.

3.3. Fourier Transform Infrared (FTIR) Analysis
Figure 4 show FTIR pattern of the carbon/polyurethane composite samples. The transmittance as a function of wave number of. Pure Polyurethane show the excellence transmittance for wave number 500-4000 cm$^{-1}$ than PC1 and PC5.
Figure 4. FTIR curve of the carbon/polyurethane composite samples
Carbon/Polyurethane with various content of Carbon

Hydrogen bond in Figure 4 can be seen from the N-H and O-H bonds around 3200 - 3400 cm\(^{-1}\) and 1600 - 1700 cm\(^{-1}\). At other peaks that indicate the existence of carbon bonds are shown in Figure 4 the N-H region of the urethane chain in the PC1 is deeper and larger than the other PC sample variations, it can be interpreted that the PC1 bond is stronger.

3.4. Salt spray and Morphology analysis
Long-term corrosion protection is very important and is needed in many industries. Specifically when facing with steel structures due to they are permanently and for the long time exposed to water in the form of sheet pile walls, water gates, barrages, dams and breakwater structures. A huge quality elastic polyurethane coating system based on raw materials is required. Composite of Polyurethane with various carbon contents were subjected to salt spray. Figure 5 and 6 show surface morphology of the carbon/polyurethane composite samples before and after salt spray test to find corrosion resistance properties.

Figure 5. Surface Morphology of the carbon/polyurethane composite sample with various Carbon content before corrosion
Carbon / polyurethane composite samples P0, PC1 and PC3 can be seen that have a smoother of surface morphology than PC5 before the salt spray test. After the corrosion test, the surface morphology seemed to change. It seems that samples PC5 and PC3 are more rough than PC1 and P0. It seem that P1 is more resistance than the others.

4. Conclusion
Carbon/Polyurethane composite with various Carbon content have been prepared. The study obtain that PC1 have more a better thermal stability and good corrosion resistance than PC3 and PC5. It seem that addition of carbon was decreased the properties of pure polyurethane and it is probably was not good to use as a coating materials.

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