Corrosion Resistance, Dielectric and Thermal Resistance Properties of Hybrid Polyurethane/Carbon/Nano-Zinc Oxide

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Abstract. Hybrid materials polyurethane films were prepared with different content of carbon, and carbon/zinc oxide as filler components in polyurethane matrix. The films were deposited on low carbon steel plate using high volume low pressure (HVLP) method. To observe corrosion resistance of the films, the samples were examined by salt spray method. Dielectric properties were obtained by resistivity valued method. Thermal resistance was investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD) used to see functional groups and phase composition of carbon and zinc oxide (ZnO) in polyurethane matrix. After ZnO and carbon addition, we observe changes in surface morphology and more resistant to corrosion. Dielectric test showed that only carbon dispersed in polyurethane matrix have higher dielectric value at higher frequency. TGA and DSC confirmed composites with carbon and ZnO as filler that has highest temperature decomposition.

1. Introduction

Polyurethanes (PU) have high performance properties coating materials and have widely used for surface protection, such as marine, piping, construction, automotive and mining vehicle [1], [2]. Hybrid inorganic/organic materials provide excellent properties due to the rigidity and high thermal stability. Nowadays, carbon and zinc oxide has been often used in this type of hybrid material as filler [3], [4]. These materials are interesting due to their wide range application such as in UV shielding, photoluminescence, visible light transmission and significant IR reflectance, etc. [5]. Hybrid materials with carbon and ZnO as filler for coating applications shows better properties, such as antibacterial, super hydrophobic, excellent adhesion and flexibility [4], [6], [7].

In this paper, composite nano-ZnO/carbon-PU with different content ZnO and carbon were investigated. The choice of ZnO and carbon as a filler was expected to exhibit shifts in melting temperature and chemical reaction between the filler and the matrix. This phenomena is expected leading to change in the properties of the hybrid coating.

2. Experimental Methods

PUs were obtained from commercial product. The composition of the polyurethane 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.
Carbon and ZnO was procured from commercial product with size 592 micrometer and 30 nm. The composite were prepared by stirring polyurethane solution with various content of carbon and ZnO 5 wt%. Then composite were deposit on low carbon steel plate using high volume low pressure (HVLP) method.

Phase and structure identifications were carried out by using X-ray diffractometer. The diffraction angle 20 ranges from 10° – 90° and radiation CuKα = 1.5408 Å. Thermogravimetry analysis (TGA) was used to measure the weight loss of the Carbon/ZnO-PU composite under nitrogen atmosphere. Samples were heated from temperature 30 to 800°C at heating rate 10°C/min. Differential scanning calorimetry (DSC) was used to obtained information how the samples interact with heat at rate 20°C/min from room temperature to 800°C. The samples were also investigated by Fourier transform infra-red (FTIR) spectrometer in the range of 300–4000 cm⁻¹. Morphology of the samples was observed by optical microscope. The samples were also subjected to salt spray according to ASTM B-117 for 72 hours to get information of corrosion resistance.

3. Results and Discussion

3.1. X-ray diffraction (XRD) analysis

Figure 2 shows X-ray diffraction pattern of carbon and polyurethane, written as PU/C and PU/C/ZnO. The phase presents in the composite are polyurethane, carbon graphite and ZnO. The presence of peaks of the aluminum phase in the polyurethane matrix composition confirms that there is aluminum in the form of granules that fill the pores in the foam-shaped polyurethane. The aluminum was added during the synthesis of polyurethane. XRD patterns show the carbon, ZnO and Al signatures. The amorphous feature (broad peak) at low frequency at PU has lower intensity when the filler carbon (PU/C) and ZnO (PU/C/ZnO) were added. This probably occurs due to the polyurethane changes from hard polyurethane to soft polyurethane. In this research, we did not measure the change in average molecular mass.

3.2. FTIR analysis

FTIR analysis was used to determine the functional groups of the samples. The changes in any functional groups will indicate the chemical reaction between filler and matrix. Figure 3 shows the FTIR of the composite. The two types of composites frequencies of O–H and N–H occur around the peaks of 3200–3300 cm⁻¹. The frequency of C–H is present around the wave number 3000 cm⁻¹ while for C–OH at about 1200 cm⁻¹. The bonding vibration N=C=N occurs at wave number 2300 cm⁻¹. And the urethane double bond C=O and other double bonds such as C=C and C=N are at 1500 – 1400 cm⁻¹. The peak frequency number 1039 cm⁻¹ shows the Al–O–Al bond. The vibrations of the C–O–C

![Figure 1. The urethane groups –NH–(C=O)–O– link the molecular units](image-url)
bonds as characteristic of the urethane chains there are at a frequency of 1000 –1100 cm$^{-1}$ and for aromatic chain vibrations C=C–C and C–H are respectively located at 1597 and 1200 cm$^{-1}$ [8].

The most influential bonds on ZnO filler material are N–H and C=O at wave number 3521 and 1592 cm$^{-1}$ [9]. Other hydrogen bonding information can be obtained from the N–H and C=O stretching vibrations near 3200–3400 cm$^{-1}$ and 1600–1700 cm$^{-1}$. Transmission analysis of waves 1071.47 cm$^{-1}$ is an aliphatic bond for N–H vibration. This N–H bond is characteristic of the polyurethane material, as well as the hydrogen bond indicating Bulk's properties of polyurethane. And the effect of this hydrogen bond makes spectroscopy a generated to become larger and the bonding frequency of the compound shifts over a certain range [10]. Overall FTIR pattern of N–H hydrogen bonds and carbon bonds in figure 3 shows that PU/C/ZnO has stronger bonds than PU/C.

![Figure 2. XRD pattern of PU, C, PU/C and PU/C/ZnO](image)

![Figure 3. FTIR pattern PU, C, PU/C and PU/C/ZnO](image)
3.3. Dielectric analysis

Figure 4 shows the graph of the AC frequency relationship with the dielectric function at room temperature. The value of the dielectric functions was obtained from the relation of voltage and current as function of the frequency on the specimen material [11]. Overall, the maximum dielectric function value obtained for PU/C/ZnO composite is 224 at 50 kHz. But in higher frequency range (400 kHz – 1 MHz) composites with carbon filler material shows flat curve. It is shown on the graph that the PU/C has the highest dielectric coefficient among any other sample. This is in accordance with the previous results that less than 3.5 wt% of carbon graphite concentration as a filler material is already able to form a good conductive network [12]. Error may happen because of the presence of a cavity formed between two aluminum plates and specimens, caused by the rough surface of the specimen itself. The cavity directly affects the sample capacitance test results.

3.4. Thermogravimetry analysis (TGA)

Thermogravimetry describes how much the mass of material remains after heated at certain temperatures. The TGA curves of Carbon/ZnO–PU composite are given in figure 5. Thermal decomposition properties of polyurethane and its composite show similar pattern but a little different rate of decomposition [13]. TGA curve showed that the thermal stability of PU/C/ZnO was higher than PU/C and even compared with the unmodified PU. The incorporation of carbon and ZnO delayed the thermal degradation process of the polyurethane.

In general, the mass change of a solid material occurs when there are physical process such as absorption of water and chemical changes such as decomposition into others chemical compound.

Decomposition occurring on the specimen divided into two stages, namely the first stage and the second stage. In general, decomposition that occurs in the first stage is decomposition of the hard segment (isocyanate) of polyurethane chain. Decomposition in the second stage occurs in the soft segment (polylol) of polyurethane chain which consisting of C–H and O–H bonds. The type of the longitudinal chain, the formation of the urethane chain, affects the overall degradation process and the presence of selected catalysts also improves thermal endurance properties of polyurethane chain [14].

3.5. Differential scanning calometry (DSC) analysis

DSC provides information heat needed or loss during heating or cooling. The samples were heated in nitrogen atmosphere at rate 20°C/min from room temperature to 800°C.

Figure 6 shows clearly between polyurethane with and without carbon and ZnO. Without carbon and ZnO, PU exhibits exothermic reaction before 800°C (black line), but when carbon and ZnO are added, PU exhibits small endothermic reaction (red and blue lines). The samples PU/C and PU/C/ZnO are more stable than polyurethane without carbon and ZnO. DSC characterization results are related to

![Figure 4. Dielectric function curve of the samples polyurethane with various carbon and ZnO](image)

![Figure 5. TGA curve of the samples polyurethane with various carbon and ZnO](image)
how the bonds in the material chain. The presence of crosslinking or chemical reaction of PU with the filler on the interface will affect the temperature response. There is a shift in melting temperature and crystallization temperature caused by crosslinking which affects the reduced chains and inhibits the movement of the polymer chain, so that thermal transitions occur at elevated temperatures [8].

3.6. Optical microscope analysis and corrosion resistance
Analysis on the surface due to corrosion test were conducted by using optical microscope with 400 times magnification with two categories, there are observation of sample at the initial state (figure 7) and on the condition after being treated with salt spray test (figure 7) for 72 hours.

From morphology of PU/C and PU/C/ZnO composites showed the agglomeration of carbon and ZnO as filler increase. The surfaces look rough, which will affect the ability of corrosion resistance. This is certainly due to the unevenness of the dispersion of the filler material in polyurethane matrix. In addition, the liquid composite mixture must go through a perfect process in application before it is dried. If during application there is air or oxygen trapped together with the mixture, the result of composite sample will be damaged. In other words, after the mixture dries and forms a layer will be some visible bubbles cause by uneven surface.

Figure 6. DSC curve of the samples polyurethane with various carbon and ZnO

Figure 7. Surface morphology of PU with different carbon and ZnO content initial state

Figure 8. Surface morphology of PU with different carbon and ZnO content after corrosion
Corrosion test were conducted by using salt spray test method with ASTM B117 standard. The result of salt spray test was shown in figure 7. In the Galvanic corrosion review based on standard series of potential energy of metal, zinc (Zn) -0.76eV and aluminum (Al) -1.66eV electrodes. Based on the Galvanic corrosion principle the electrodes with smaller potential values will oxidize and transfer electrons to electrodes with a greater potential standard value [15]. This is related to the purpose of research that is to produce a coating solution that has better corrosion resistance properties.

4. Conclusions
Nano-ZnO/C-PU with different ZnO and carbon content have been successfully synthesized. Influence of carbon and ZnO on dielectric, thermal resistance show clear increase due to chemical reaction of PU with filler at the interface. Increasing the number of filler risk the agglomeration led to the decrease of corrosion resistance. It seem that the composite have been improved its properties as coating materials.

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