Thermal behaviour and corrosion resistance of nano-ZnO/polyurethane film

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Abstract. Hybrid materials Nano-ZnO/polyurethane film was prepared with different zinc oxide (ZnO) content in polyurethane as a matrix. The film was deposited on low carbon steel plate using high volume low pressure (HVLP) method. To observe thermal behaviour of the film, the sample was investigated using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Fourier transform infrared spectroscopy (FTIR) was used to see whether any chemical reaction of ZnO in polyurethane occurred. TGA and FTIR results showed that the decomposition temperature shifted to a higher point and the chemical reaction of zinc oxide in polyurethane occurred. The surface morphology changed and the corrosion resistance increased with an increase of ZnO content.

1. Introduction
Polyurethanes (PUs) are commonly used in many applications such as adhesives, coatings, fibers, foams, paint, rubbers, thermoplastic elastomers, and composites [1 – 4]. Monomers can be flexibly chosen from many varieties of diisocyanates, polyester and chain extenders, as well as various types of molecular architectures that provide PUs with good properties such as abrasion resistance, mechanical properties, toughness, and chemical resistance [5 – 7]. However, there is still room to improve properties of PUs with emphasis on their mechanical properties and hydrophobicity. These can be achieved by varying microstructures of PUs or incorporating inorganic fillers. For example, organic-inorganic nanocomposites were developed to combine the required properties of PUs and also those of inorganic fillers [8 – 13] such as clay, silica, ZnO, and other nano-sized layered silicates. Significant improvements in performances such as mechanical properties, thermal stability have been achieved.

Present work deals with synthesis of nano zinc oxide-polyurethane composite with different nano-ZnO (1, 3 and 5 wt.%) content. Nano ZnO was produced by sol gel method. ZnO nanoparticles, which have high surface to volume ratio and more chemically reactive, were expected to modify the properties such as thermal behaviour and corrosion resistance of polyurethane as a matrix.

2. Experimental procedure
PUs was obtained from commercial product. The composition of the Polyurethane are diisocyanate (MDI), MDI based Polyisocuanate, 4,4’-Diphenylmethane, aluminum, aromatic solvent blend and isobutyl acetate. Figure 1 shows the urethane groups –NH–(C=O)–O– linking the molecular units. Nano-zinc oxide was synthesized from Zn (CH₃COO)₂.2H₂O by sol-gel method. An appropriate amount of zinc acetate Zn(CH₃COO)₂.2H₂O were dissolved in ethanol. The resulting solution was stirred at 80 °C for 2 hours until gel was formed. The obtained gel was then dried in an oven at 150 °C.
for 1 hour and then ground with mortar and pestle to obtain fine powder. The powder was then sintered at 600 °C for 2 hours [13]. The composite were prepared by stirring polyurethane solution with various content of ZnO 1, 3 and 5 wt.%. The solution was deposited on low carbon steel plate using high volume low pressure (HVLP) method. The obtained films were taken from the substrate to be analyzed.

![Figure 1. The urethane groups –NH–(C=O)–O– link the molecular units.](image)

Thermogravimetry (TGA) was used to measure the weight loss of the nano-ZnO-polyurethane composite under nitrogen atmosphere. Samples were heated from room temperature to 800 °C at heating rate of 10 °C/min. Differential Scanning Calorimetry (DSC) was used to obtain information how the samples interact with calor at rate of 10 °C/min from room temperature to 800 °C. We did not use heating and cooling method to test the thermal stability due to permanent decomposition of the samples and limitation of the instruments. The samples were also investigated using Fourier transform infrared spectroscopy (FTIR) in the range of 300 - 4000 cm\(^{-1}\). The method involves transmittance measurements. The resolution was set to 2 cm\(^{-1}\), so that the spectra will be obtained at intervals of approximately 1 cm\(^{-1}\). Morphology of the samples was observed by optical microscope and electron microscope. The samples were also subjected to salt spray according to ASTM-B117 for 72 hours. The samples were placed in closed testing chamber and exposed by fog or mist of a salt water (5% NaCl) solution. Information of the samples' corrosion resistance was obtained by observing its morphology.

3. Results and discussion

3.1. Thermogravimetry (TGA) analysis

TGA provides information about thermal stability of a material. The TGA curves of ZnO-polyurethane composite are shown in figure 2. It shows weight loss at temperature from room temperature to 800 °C. Onset decomposition temperature increases with increasing nano ZnO content. Temperature changes from 250 °C, 270 °C, 280 °C, and 291 °C with an increase in ZnO content. It suggests that the thermal stability of polyurethane also increases with increasing ZnO content. The end-set temperature remains the same, i.e. 424 °C, for various nano-ZnO content. It can be suggested that addition of ZnO cause an increase in thermal stability. PZnO 1 wt.% and PZnO 3 wt.% are more stable than PU (pure polyurethane without addition of ZnO) and PZnO 5 wt.%. A decrease in thermal stability may be due to agglomeration of ZnO in the matrix.

3.2. Differential Scanning Calorimetry (DSC)

DSC provides information heat absorb (endotherm) or loss (exotherm) during heating or cooling. The samples were heated in nitrogen atmosphere at heating rate 10 °C/min. Figure 3 shows DSC curve of four composite samples. It shows that during samples decomposition, heats released or absorbed are not significant. Samples PU and PZnO 5 wt.% show sudden exothermic heat for decomposition. It
shows that PZnO 1 wt.% and PZnO 3 wt.% have more thermal stability than PU and PZnO 5 wt.%. Therefore, this evidence is consistent with results from TGA analysis.

**Figure 2.** TGA curve of PU with various ZnO content (0, 1, 3 and 5 wt.%).

**Figure 3.** DSC curve of polyurethane without and with ZnO (0, 1, 3, and 5 wt.%) content.

### 3.3. Fourier transform infrared spectroscopy (FTIR) analysis

FTIR analysis was used to determine the functional groups of the samples. Figure 4 shows transmittance variation of polyurethane without and with ZnO. Stretching frequency for OH functional group is observed at 3350 cm$^{-1}$ [8]. The peaks at 1598 and 1460 cm$^{-1}$ are due to stretching frequency of C=C in the aliphatic chain and aromatic ring, respectively. The spectra show band around 2164 cm$^{-1}$ which is for NCO group. The bands appearing at 1168 cm$^{-1}$ and 1039 cm$^{-1}$ correspond to Si-O-O stretching frequency and Al-O-Al stretching frequency, respectively [9]. According to the literature, the most affected functional groups by the ZnO filler are the N-H and C=O band at wave number 3521 cm$^{-1}$ and 3358 cm$^{-1}$ [10]. Samples PU and PZnO 5 wt.% have less intense transmittance than samples PZnO 1%wt and PZnO 3%wt. These trends are in line with DSC and TGA characterization.

### 3.4. Morphology and salt spray analysis

Figure 5 shows morphology of the nano ZnO powder used in preparing ZnO-polyurethane composite. The shape of the particle is rod-like with 30 nm in diameter and 200 nm in length. Due to nanoscale size of the particle, the powder have high surface to volume ratio which lead to more chemically reactive.

**Figure 4.** FTIR curve for composite with different ZnO content.

**Figure 5.** TEM image of ZnO powder.
Figures 6 and 7 show surface morphology of the samples before and after salt spray test. It is shown that samples PZnO 1 wt.% and PZnO 3 wt.% have smoother surface morphology compared to PU and PZnO 5 wt.% (figure 6). Rougher surface was found in samples with higher ZnO content due to agglomeration of ZnO. After salt spray test for 72 hours, sample surface shows different roughness compared to initial condition (Figure 7). Sample roughness indicated that samples PZnO 1 wt.% and PZnO 3 wt.% have better corrosion resistance than samples PU and PZnO 5 wt.% The smooth morphology in PZnO 1 wt.% and PZnO 3 wt.% can be related to interaction of ZnO with polyurethane which were shown in FTIR pattern.

**Figure 6.** Surface Morphology of ZnO-Polyurethane composite with different ZnO content before salt spray test.

**Figure 7.** Surface Morphology of ZnO-Polyurethane composite with different ZnO content after corrosion.

4. Conclusion
Nano ZnO/polyurethane composite with different ZnO content have been successfully prepared. Samples PZnO 1% wt and PZnO 3% wt seem to have higher thermal stability and corrosion resistance than samples PU and PZnO 5 wt.%. There may be chemical interaction of ZnO and polyurethane due to nano-scale size of ZnO. The composite ZnO and polyurethane may be used as a coating material to protect material from corrosion.

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