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Synthesis of Zinc Oxide Whiskers with Hydrothermal Method for Composite Absorbent Material of Microwave of ZnOw/MWCNT/Epoxy

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ABSTRACT: *The MWCNT/ZnOw/epoxy composites have great potential as microwave absorbing material. The synthesis of ZnO whiskers (ZnOw) was carried out using precursors $ZnSO_4$ and Na_2CO_3 via hydrothermal method with temperatures of 120°C, 160°C, 200°C, and 240°C. X-ray diffraction (XRD) and scanning electron microscope (SEM) were applied to find out the morphology and structure of ZnOw powder. The best results of the XRD and SEM-EDX at hydrothermal temperature of 160°C showed the best crystallinity of ZnO compound, that is at 2θ values of 31.7°, 32.2°, 34.3°, 36.1°, 37.9°, 56.5°, 62.8°, 67.8°, 76.8° and 89.5° with a Miller index of 111, 100, 002, 101, 102, 110, 103, 112, 202 and 203, respectively. At 160°C, ZnO whiskers had a size of 97.7 nm, with a purity level of 72.6%. By adding 4% MWCNT, the result of synthesis via spray pyrolysis method (purity 90%) and 4% of epoxy, the ZnOw synthesised by hydrothermal method formed MWCNT/ ZnOw/epoxy composites. To determine the composite's microwave absorption capability, a vector network analyser was administered at hydrothermal temperatures of 160°C and 200°C. The MWCNT/ZnOw/epoxy composites had a reflection loss of –11.9 dB. This value exceeds the standard for microwave absorbing material which is –11.9 dB. Therefore, the composite has great potential as a microwave absorbing material.*

Keywords: Zinc oxide whiskers, hydrothermal, MWCNT, composites, ZnOw

1. INTRODUCTION

Anti-radar technology has been developed involving two primary methods. The first method is radar absorbing structure (RAS) which involves manipulating the object geometry shape.[1] The second method uses a radar absorbing material called radar-absorbing material (RAM), which is done by modifying the object-material.[1] To improve the efficiency of RAM, numerous studies have been conducted to obtain optimal materials for absorbing microwaves.[1]

Zinc oxide is a derivative compound of zinc elements that have good physical characteristics. Hence, it is often applied in various technology products such as thin layer technology, supercapacitors, anti-radar technology and electronic devices.[2] One form of zinc oxide that has a unique morphology is ZnO whiskers (ZnOw).[3] ZnOw has a resistivity value of 0.62–0.65 × 103 Ωm. Therefore, it is classified as a semiconductor material. This is one of the characteristics of microwave absorbing materials.[4]

The synthesis of ZnOw using the hydrothermal method has several precursors that can be used. For example, synthesis of ZnO whiskers used precursors Zn(OH) referring to Liu et al., used precursors $Zn(NO_3)_2$ referring to Shen et al., and used precursors $ZnSO_4$ (Wen et al.).[5–7] The higher the temperature used, the lower the hydroxyl group (OH-) gets, indicating a better crystal form of ZnOw. However, to support this study, the authors use a variation of hydrothermal temperatures referring to Wang et al.[8]

To improve the quality, ZnO whiskers' microwave absorption must be formed into composite MWCNT/ZnOw/epoxy.[9] For example, the composites of ZnO/MWCNT/epoxy have the reflection loss value of 23.00 dB with a small density of 0.14 g cm^{-3}.[10] Therefore, it can be lighter when applied as a RAM material. In this study, the authors use composite MWCNT/ZnOw/epoxy with a certain composition to obtain a material that has characteristics allowing for maximal absorption of the microwave. Here in this paper, we demonstrate the hydrothermal method to synthesise ZnO nanostructures. We also prepare the composites of ZnO/MWCNT/epoxy to increase the microwave absorbance.

2. EXPERIMENTAL

2.1 Materials

Zinc sulfate heptahydrate ($ZnSO_4$), sodium carbonate (Na_2CO_3) 0.25 mol l^{-1} and a solvent of distilled water (H_2O) are prepared.[7] The synthesis of MWCNT with purity 92% uses ferrocene and benzene. To form the ZnOw/MWCNT/epoxy, a poxy resin matrix is used. All chemicals are analytical grade reagent from Merck KGaA, Germany.

2.2 Synthesis of ZnO Powder Whiskers

Synthesis of ZnO whisker powder uses precursor materials zinc sulfate heptahydrate ($ZnSO_4$) 0.4 mol l^{-1} and sodium carbonate (Na_2SO_4) 0.25 mol l^{-1} and a solvent of distilled water (H_2O).[7] The synthesis maintains hydrothermal temperature 160^{O}C after about 6 h using Teflon-lined stainless stell autoclave. Then it is cleaned by distilled water (H_2O) and it is also dried at 60°C for about 6 h.[10]

2.3 Forming ZnOw/MWCNT/Epoxy Composites

ZnOw/MWCNT/epoxy composite consists of three main materials: 4% MWCNT that had been synthesised by spray pyrolysis method, the synthesis result of 90% ZnOw using the hydrothermal method, and 4% epoxies as matrix.[11] Composite MWCNT/ZnOw/epoxy is printed into 2.3 cm × 1.1 cm in width and thickness of 2 mm.

2.4 Characterisation

To find out the morphology and structure of ZnO whisker powder, X-ray diffraction (XRD) (Phillip analytical X-Ray B.V) with CuKα radiation (λ = 1.5418 Å) at 40 KV and scanning electron microscopy (SEM JEOL JSM-6390A). To find out the composite capability of MWCNT/ZnOw/Epoxy in absorbing microwaves, a vector network analyser is used.

3. RESULTS AND DISCUSSION

3.1 Morphological Analysis of ZnOw

To obtain the morphology and structure of ZnO whisker powder, XRD and SEM are used. The XRD is aimed to analyse qualitatively the ZnO whisker particles that use the hydrothermal process of the compound $ZnCO_3$.[12] To form the ZnO whiskers, $ZnSO_4$ and Na_2CO_3 are applied as the precursor in reaction to a test:

$$ZnSO_4 + Na_2CO_3 + 7H_2O = Zn(CO_3) + Na_2SO_4 + H_2O \quad (1)$$

$$Zn(CO_3) = ZnO+2CO_2 \quad (2)$$

The XRD uses five samples. The samples consist of ZnO confronted with hydrothermal processes at temperature of T = 160°C about 6 h and $ZnCO_3$ before hydrothermal. The results of the XRD can be seen in Figure 1.

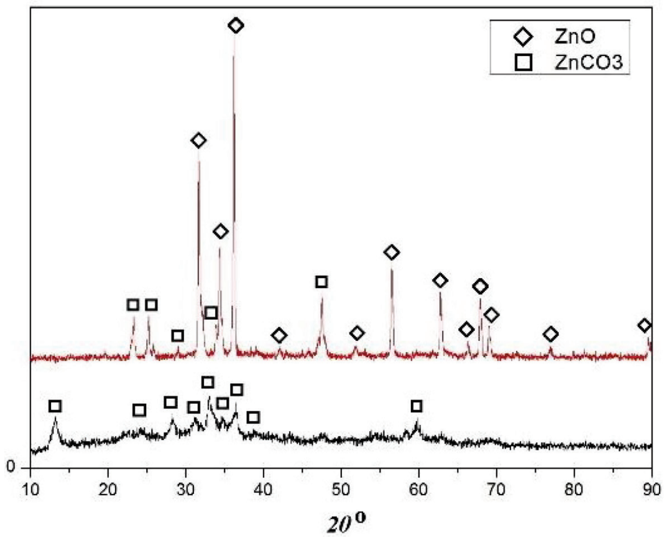

Figure 1: XRD analysis of ZnO and $ZnCO_3$ before the hydrothermal processing, where the compound that has been formed is $ZnCO_3$.

The results of XRD show some peaks corresponding to the values of the 2θ compound of $ZnCO_3$ in JCPDS database (PDF No.19-1458). The peak hydrothermal temperature of 160°C is indicated by the crystallinity of $ZnCO_3$ compound at 2θ values of 23.3°, 25.2° and 28.0° in directions to 111, 400 and 200. These results at the hydrothermal temperature of the 160°C show the peak corresponding to the values between at least the values of 2θ $ZnCO_3$ at JCPDS database (PDF No.19-1458) and the lowest intensity that shows the low crystallinity value of $ZnCO_3$. Besides the research by Wen et al. with hydrothermal temperature of 160°C, the results of crystallinity in this study are better due to the peak corresponding value of $Zn_5(CO_3)_2(OH)_6$ in JCPDS database (PDF No.19-1458) which is less and has lower intensity.[7]

The crystallinity level of ZnO is determined by analysing the peak corresponding to the value of 2θ ZnO compound in JCPDS database (PDF No.36-1451).[7] At hydrothermal temperature of 160°C, the peak indicates the crystallinity of the ZnO compound 2θ values of 31.7°, 32.2°, 34.3°, 36.1°, 37.9°, 56.5°, 62.8°, 67.8°, 76.8° and 89.5° in directions towards 111, 100, 002, 101, 102, 110, 103, 112, 202 and 203. These results show that the peak correspondence to the value of 2θ ZnO compound in JCPDS database is the highest intensity, which means the crystallinity value of ZnO compound is high.[7] Proper hydrothermal temperatures can affect the level of crystallinity of ZnO.[7] The results of crystallinity in this study are better due to the peak correspondence to the value of 2θ ZnO compound in JCPDS database (PDF No.19-1458) which is greater and has higher intensity.

The SEM shows that ZnO whiskers/ZnO root has been formed at hydrothermal temperature of 160°C for 6 h. At 160°C, the size of ZnO becomes 97.7 nm in length. The nanomaterials are less than 100 nm in length.[13] At 160°C, ZnO materials form nanomaterials. SEM is used to analyse the size and types of ZnO and MWCNT formed.[14] The SEM results can be seen in Figure 2.

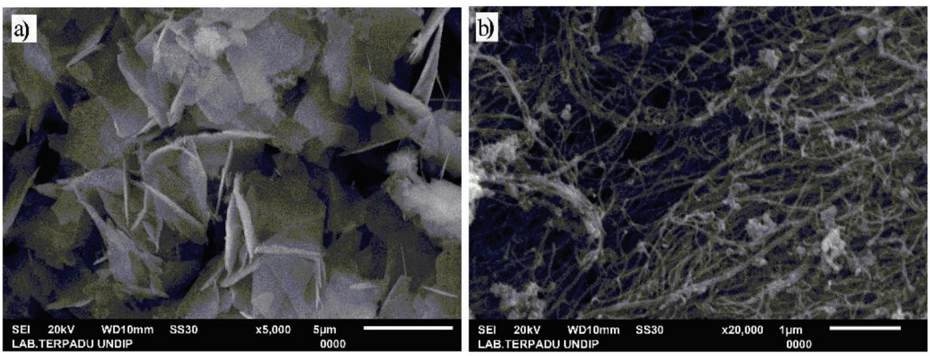

Figure 2: Test results of ZnO and MWCNT magnification 5000X with a) ZnO hydrothermal 160°C, and b) MWCNT.

SEM results show that the carbon nanotubes form well. The carbon nanotubes are synthesised using a spray pyrolysis process that has been formed based on SEM results that are part of MWCNT. SWCNT takes the form of rolled cylindrical sheets of graphite that are 0.2–5 µm in length and 1–2 nm in diameter.[15] An SWCNT consists of two parts: the side wall of the cylinder, and the peaks of the cylinder.[15] The form of MWCNT is the same as the form of SWCNT which consists of many rolls of 2–25 nm in diameter.[15]

3.2 Absorption Analysis of ZnOw/MWCNT/Epoxy Composite Waves

To study the composite capability of ZnOw/MWCNT/epoxy in absorbing microwaves, vector network analyser (VNA) is utilised.[25] The VNA test is used to find out the value of reflection loss, transmission loss and microwave absorption through compositing. Reflection loss is the main parameter to find out the anti-radar capability of composite MWCNT/ZnOw/epoxy. The reflection loss values can be seen in Figure 3.

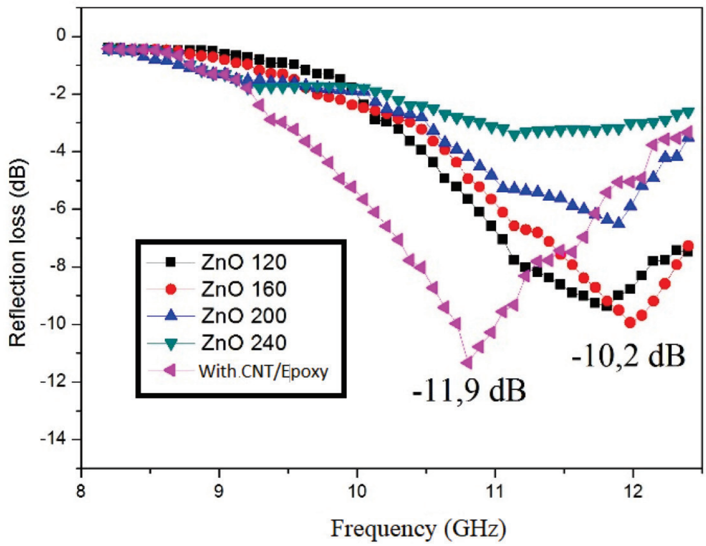

Figure 3: Reflection loss values of composite MWCNT/ZnOw/epoxy.

At hydrothermal temperature of 120°C, the reflection loss value is –2.1 dB. At 160°C, the value is–10.2 dB, while at 200°C, the value is –6.8 dB. At 240°C, the reflection loss is –8.9 dB. The reflection loss value of ZnOw/MWCNT/epoxies is –11.9 dB. Hydrothermal temperature of 160°C has the highest reflection loss value; EDX-tests of the results at hydrothermal temperature 160°C shows the highest content of C atoms, which is as high as 63.3%. According to Liu et al*.*, carbon is a dielectric material that has the capacity for polarisation and absorption of electromagnetic waves that converts them into heat energy.[7,16] When the electromagnetic waves hit the material, the polarisation occurs due to field of electric wave that creates an electric current, converting into heat through the Joule effect.[17] ZnO is a semiconductor material that has the ability to absorb electromagnetic waves by converting the energy of electromagnetic waves into heat energy.[17]

4. CONCLUSION

The results of the morphological analysis using XRD and SEM-EDX show that the material ZnO whiskers form well at hydrothermal temperature of 160°C. The results also show that the MWCNT material formed well. The test results of the anti-radar capability of composite MWCNT/ZnOw/epoxy that use VNA at a hydrothermal temperature of 160°C and MWCNT show that reflection loss values of composite MWCNT/ZnOw/epoxy are –10.2 dB and –11.9 dB, respectively.

5. ACKNOWLEDGEMENTS

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