Multiwalled carbon nanotubes and zinc oxide using a high energy milling method for radar-absorbent

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Abstract
Radar is a technology that is always used by the military to detect an object because it can determine the shape, size, position, distance, and speed of an object. This enables the national defence system to have anti-radar technology to protect defence equipment or other important defence objects. One way that can be applied is using radar-absorbing material to coat the surface of the object. A good radar-absorbing material is made of a combination of dielectric materials with magnetic materials. MWCNT/ZnO composites were produced by a high energy milling method. The various milling times (0, 1, 3 and 5 h) using HEM on the microwave absorbing properties of the composites has an effect, which was studied. The experimental results show that the optimum microwave absorption ability is reached when the HEM process is carried out for 5 h with a thickness of 2.0 mm. The optimum return loss is $-26.4$ dB at a frequency of 11.2 GHz and the bandwidth correlative to the return loss is below $-10$ dB with a frequency greater than 1.5 GHz. When comparing MWCNT/ZnO without HEM treatment, the results show that HEM treatment can also increase microwave absorption properties.

1. Introduction
In the field of defence and security, radar has been used in almost all countries in the world. This condition requires the national defence system to have anti-radar technology to protect the main defence equipment or defence objects. One way that can be applied is by using a radar-absorbing material (RAM) to coat the surface of the object.

RAM must be dielectric and magnetic with a low coercivity [1–7]. RAM must also have the properties of high permeability and imaginary permittivity, high saturation magnetization, high conductivity and high Curie temperature. The electromagnetic wave absorbing material or RAM ideally has an effective return loss ($R_L$)$\leq -10$ dB, with material specifications that are lightweight, easy to design, inexpensive and stable against environmental influences [8–14].

Several studies on RAM have been carried out since the 1930s after the discovery of radar technology. Germany developed coating materials to camouflage its submarines. The material is a carbonyl iron powder-coated rubber sheet combined with a 3-inch-thick layer of resistive and rigid plastic sheet. The optimum result obtained for the return loss is $-20$ dB in the frequency range of 2 GHz to 15 GHz [15–17].

Research on RAM has developed every year; the basic materials and processing methods used are also increasingly diverse. Generally, RAM should be magnetic and dielectric. Ristiawan (2018) synthesized RAM with Zinc Oxide (ZnO) material. The precursors used in the manufacture of ZnO are ZnSO4 and Na2CO3 which are hydrothermally synthesized at a temperature of 160 °C, then mixed with 4% CNT and 4% epoxy. Optimum absorption is reached with a return loss value of $-11.9$ dB at a frequency of 10.8 GHz. This research was further developed by Subagio et al (2020) by synthesizing the MWCNT/ZnO material and by varying the MWCNT percentage of 1%, 3%, 5%, and 7% frequency The optimum composition of MWCNT/ZnO with 3% of MWCNT has a return loss value of $-31.4535$ dB at a frequency of 11.2 GHz on the electromagnetic wave. The
resulting effective absorption values are in the frequency range of 9.4 GHz to 10 GHz and 10.9–11.4 GHz (1.1 GHz) [18–20].

The high-energy-milling (HEM) method is one of the techniques used to produce a nanomaterial. Compared to other chemical and physical methods, the HEM method is simpler and faster; it can therefore produce large amounts of material. The HEM method does not require high temperature and pressure; it, therefore, uses less energy. In addition, the HEM method can also maintain the purity of the material being processed, because it does not add any catalyst [21, 22].

The purpose of this study was to synthesize MWCNT/ZnO using the HEM method for the MWCNT/ZnO mixture to become more homogeneous which will, in turn, increase the microwave absorption capability of MWCNT/ZnO.

2. Experimental

The material used in this experiment was a mixture of MWCNT/ZnO and was carried out using the high energy milling method. Multi-walled carbon nanotubes (MWCNT) were produced by the spray pyrolysis method and zinc oxide (ZnO) was produced by the hydrothermal method. The composition of the synthesized mixture was 3% MWCNT and 97% ZnO, which was the best composition between MWCNT and ZnO as researched by Subagio et al (2020).

The synthesis of the MWCNT/ZnO material was carried out using the HEM method, which is to mix ZnO and MWCNT to make it more homogeneous. The speed used was 500 rpm with milling time variations of 1 h, 3 h, and 5 h. The MWCNT/ZnO was analysed. This included a study of the surface morphology, which was analysed using a scanning electron microscope (SEM); the absorption properties were analysed using VNA.

For the analysis process using VNA, the sample has been placed instead of a mould with a size of 21 × 10 × 2 mm. This size corresponds to the size of the waveguide on the VNA for the frequency range 8 GHz to 12.5 GHz (X-band). The VNA analysis was performed to determine the value of return loss, permittivity, and dielectric tangent loss.

The impedance network on the VNA port resulted in a complex value called the Scattering parameter (S-Parameter). The waves were represented in s-parameters such as (S11 or S22) and (S12 or S21). The S-parameter was mathematically expressed as a tensor defined in the form of a matrix in equation (1) [23–27].

\[
S = \begin{bmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{bmatrix}
\]  

(1)

The Nicholson–Ross–Weir method was used to determine the electric properties from the S-parameter measurement data. The NRW method was used to obtain the electric properties as shown in equations (2)–(7) [23–27].

\[
X = \frac{S_{11}^2 - S_{21}^2 + 1}{2S_{11}} \tag{2}
\]

\[
\Gamma = X \pm \sqrt{X^2 - 1} \tag{3}
\]

\[
T = \frac{S_{11} + S_{21} - \Gamma}{1 - (S_{11} + S_{21})\Gamma} \tag{4}
\]

\[
\mu_r = \frac{1 + \Gamma}{\Lambda(1 - \Gamma)\sqrt{1 - \frac{1}{\lambda_0^2} - \frac{1}{\lambda_c^2}}} \tag{5}
\]

\[
\frac{1}{N^2} = \left(\frac{\varepsilon_r^*\mu_r}{\lambda_0^2} - \frac{1}{\lambda_c^2}\right) = -\left(\frac{1}{2\pi L\ln\left(\frac{1}{T}\right)}\right)^2 \tag{6}
\]

\[
\varepsilon_r = \frac{\lambda_0^2}{\mu_r}\left(\frac{1}{\lambda_c^2} - \frac{1}{2\pi L\ln\left(\frac{1}{T}\right)}\right)^2 \tag{7}
\]

where \(\lambda_0\) was the wavelength of the air, \(\lambda_c\) was the cutoff wavelength, \(L\) was the thickness of the material, \(\Gamma\) was the reflection coefficient, \(\mu_0\) was the magnetic permeability of air (4π × 10⁻⁷ H/m) and \(\varepsilon_0\) was the electric permittivity of air (8,854 × 10⁻¹² F m⁻¹) [23–27].

The complex values of permittivity were described by equation (8).

\[
\varepsilon^* = \varepsilon' + j\varepsilon'' \tag{8}
\]

The imaginary part (\(\varepsilon''\)) was sinusoidal and the real part (\(\varepsilon'\)) was cosine, so the electric properties of the material could be determined from the dielectric tangent loss. The dielectric tangent loss (\(\tan \delta\)) of material was
defined as equation (9) [23–27].

\[
\tan \delta_e = \frac{\varepsilon''}{\varepsilon'}
\]  

(9)

Microwave absorption performance is evaluated by return loss (RL). Return loss was obtained from the log value of the reflection coefficient (Γ), as stated in equation (10) [23–27].

\[
RL \ (dB) = -20 \log |\Gamma|
\]  

(10)

3. Results and discussion

3.1. Morphological analysis of MWCNT/ZnO

The HEM method of mixing MWCNT and ZnO was used to increase the homogeneity of the MWCNT/ZnO material. In figure 1, MWCNT looks like a wire, and ZnO in sheet form looks like agglomerated sheets. Some MWCNTs can combine and agglomerate with ZnO.

3.2. The MWCNT/ZnO Electromagnetic absorbing properties

Figure 2 shows (a) the real and (b) the imaginary parts of the permittivity of MWCNT/ZnO with the various milling times (0, 1, 3, and 5 h) in the frequency range of 8 GHz to 13 GHz. The real part of the permittivity (\(\varepsilon'\)) is also acknowledged as the dielectric constant of a material, expressing the amount of energy from the external electric field stored in the material [28]. Figure 2(a) shows that the real permittivity value is \(\varepsilon' < 1\), except for the 11–11.5 GHz frequency. The HEM method results in a shift in the location of the peak values and increases the permittivity of the real material. This can increase the number of energy from the external electric field that is absorbed into the material. It can be mainly ascribed to the polarization effect of the space charge and the dielectric relaxation [27].

The imaginary part (\(\varepsilon''\)) is a measure of the attenuation of the electric field, showing the amount of energy lost due to an external electric field [28]. Figure 2(b) shows the value of the imaginary permittivity \(\varepsilon'' < 1\). The HEM method causes the imaginary permittivity to be smaller. This shows that the energy lost due to the effect of an external electric field is decreasing. The decrease in the imaginary part of permittivity could be associated with the decrease in the electric conductivity of the material. The imaginary permittivity whose value is close to zero indicates that the material is close to lossless material properties, commonly called the loss factor [19].

The ratio of the two components of the real and the imaginary permittivity will produce a dielectric parameter called the dielectric loss tangent, as shown in equation (9). These parameters are used to determine the electrical properties of the material. Materials with good dielectric properties are materials whose conductivity is much smaller than the product of permittivity and angular frequency. This is indicated by a small tangent loss with \(\tan \delta \varepsilon < 1\). On the other hand, a good conductor has a large tangent loss with \(\tan \delta \varepsilon > 1\) [27].
Figure 3 shows that the HEM method can improve the dielectric properties of the MWCNT/ZnO material. This is evidenced by a decrease in the dielectric value of the tangent loss with a bandwidth of 1.7 GHz. The dielectric properties of the MWCNT/ZnO material that emerged after the HEM method were in the frequency range of 9.8 GHz to 13 GHz.

To increase the absorbing performances of the MWCNT/ZnO, the return loss of MWCNT/ZnO was calculated based on equation (10). Figure 4 shows the effect of milling time variation in the return loss of MWCNT/ZnO (within a frequency range of 8 GHz to 13 GHz) with a thickness of 2.0 mm.

The microwave absorption peak increases with the increasing time of milling. The best result is MWCNT/ZnO in 5 h of the HEM method. The return loss reaches a minimum of $-26.4$ dB at frequency 11.2 GHz and the bandwidth correlative to the return loss is below $-10$ dB at a frequency greater than 1.5 GHz.

4. Conclusions

The microwave and electromagnetic absorbing properties based on the contents of MWCNT/ZnO with the HEM method were investigated. Dielectric tangent loss analysis indicated that MWCNT/ZnO was a dielectric material, so it is good when used as a radar-absorbent material. The cooperative effect of the HEM method on MWCNT/ZnO highly influenced the microwave absorption properties of MWCNT/ZnO composites. The results showed that 5 h of the HEM process yielded the optimum microwave absorption capacity with a material thickness of 2.0 mm.

The minimum return loss is $-26.4$ dB and the bandwidth correlative to the return loss is below $-10$ dB at a frequency greater than 1.5 GHz. The results show that the prepared MWCNT/ZnO composite has great potential in application to lightweight and strong absorption microwave absorbers.
The five-hour milling process has increased the dielectric properties of MWCNT/ZnO so that the absorption performance of MWCNT/ZnO is maximized. In addition to this, the reduced size of this particle could have increased the surface area of the particles, which increased the polarization mechanism occurring in the material. This mechanism was also a factor in the increased return loss in the material.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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