Anti-ultraviolet and microwave transmission property of ZnO coating on PLA plate

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Abstract: The ZnO coated on the PLA (Polylactic acid) plate with the anti-ultraviolet and high microwave transmission property was fabricated. The particle morphology was measured by the scanning electron microscopy (SEM). The UV-spectrum was measured by the UV Spectrometer. The complex permittivity was measured using a vector network analyzer in 2-18 GHz and the transmission rate (S12) was calculated for the two materials respectively. In order to get the high transmittance property, the genetic algorithm was used to optimize the thickness of the composite and the weight content of the ZnO absorbent. The results showed that the ZnO coating had the good UV protection property, UPF could be estimated 45~50 as the wavelength was 200~400 nm, and as the weight content increased, the transmittance value decreased. The composites with thickness 0.1 mm ZnO coating and 1 mm PLA plate had the high transmission rate (larger than 0.95).

1. Introduction

The absorbing effect of the plasma becomes an interesting field based on the fundamental theory of the radio wave propagation and scattering in the plasma [1-3]. Recently many works had been focusing on the related problem, simulation measurement on the aircraft model coating the plasma materials become a low time-waste way. Considering the complex fluid field on the object surface coated by the plasma, the measurement on the object coated the plasma in the chamber was effective to obtain the true simulation result. Meanwhile, the dielectric barrier discharge (DBD) plasma was a low-cost way to fabricate the plasma environment. After investigating the micro plasma molecular emission spectrometer based on an atmospheric pressure DBD, the result showed that traces of gas were detected at a molecular emission line of 100~900 nm. It indicated that the ultraviolet (UV) was formed according to the plasma simulation measurement, which was harmful to the measurement worker. In order to avoid the ultraviolet radiation, using the UV absorber could be effective. ZnO nanostuctures were often used in UV protective coatings because ZnO is not only biologically compatible but also more efficient than their bulk counterparts. However, as the ZnO coating was used on the plasma simulation model, the microwave might be attenuated in the ZnO coating due to the dielectric loss [4-6]. In order to maintain the microwave propagation characteristics in the plasma, the coating should be of good transmission property simultaneously.
This paper proposed a double layer composite with the PLA plate and the ZnO film. Firstly the ZnO coating was fabricated using the spraying process with variable weight content and thickness. Secondly, the UV protection property and the microwave attenuation property were tested. Finally, a genetic method was applied to optimize the two-layer structure to keep the good UV protection property and the microwave transmission property.

2. Material and methods

2.1 Materials measurement and preparation

The morphology of the composites was observed by scanning electron microscopy (HITACHI SU-70 SEM) to evaluate the dispersion state and microstructure of the ZnO. UV–spectrum was recorded on Perkin Elmer Lambda 750 UV spectrometer. Ultraviolet protection factor (UPF) was measured using Perkin Elmer Lambda 750 UV spectrometer. The effective complex permittivity and permeability were measured using the E8386C vector network analyzer in the frequency range of 2-18 GHz.

In order to get the standard testing sample, the silicone rubber and the ZnO were mixed in a mixer for mechanical stirring 15-30 minutes. The testing samples for EM parameters measurement were modeled to a toroidal shape with outer diameter 7.0 mm, inner diameter 3.04 mm and thickness 2 mm. All the samples were vulcanized into pieces at the room temperature for 5 hours.

The epoxy resin and the hardener were added into the thinner (acetone), and the weight ratio of the three parts was 10:1:10. Then the ZnO particles were added to the compound liquid, the weight content of the epoxy resin to the ZnO was 80:20 and 90:10 respectively. The compound was stirred using the high speeding mixture with the velocity 670 r/min for 20 min. Finally, the coating was made using the spraying gun, the spraying coating thickness was from 0.08 mm to 0.5 mm, after 8 hours the coating was harden in the air.

2.2 Calculation on the transmission ratio

For the multi-layer absorbing plate, as shown in figure 1, the transmission ratio (S12) and the reflection ratio (S11) of the n-th layer is expressed as follows [7].

\[
\begin{bmatrix}
S_{11} \\
1
\end{bmatrix} = \frac{1}{(1+r_0)(1+r_1)\cdots(1+r_{N-1})} \begin{bmatrix}
1 & r_0 & r_1 & \cdots & r_{N-1} \\
0 & e^{-j\pi d_1} & e^{-j\pi d_2} & \cdots & e^{-j\pi d_N} \\
r_{N-1} & e^{-j\pi d_N} & e^{-j\pi d_{N-1}} & \cdots & 0 \\
e^{-j\pi d_N} & e^{-j\pi d_{N-1}} & e^{-j\pi d_{N-2}} & \cdots & 0
\end{bmatrix} \begin{bmatrix}
S_0 \\
S_1 \\
S_2 \\
\vdots \\
S_{N-1} \end{bmatrix}
\]

(1)

Where \( r_i \) is the reflective coefficient between the \( i \)th layer and the \((i+1)\)th layer, as the layer area is infinite.

\[
\begin{align*}
\frac{Z_{i+1} - Z_i}{Z_{i+1} + Z_i}
\end{align*}
\]

(2)
where \( Z_n = \sqrt{\mu_n / \varepsilon_n} \) is the characteristic impedance of the \( n \)th layer. \( \gamma_i \) was the propagation constant, \( \gamma_i = \gamma_i' - j \gamma_i'' = k_0 \sqrt{\varepsilon_i \mu_i} = k_0 n_i \). \( k_0 = \omega / c \) was the wave number of the vacuum, \( n_i \) was the index of refraction of the \( i \)th layer. The above equation could be simplified as:

\[
\begin{bmatrix}
S_{11} \\
1
\end{bmatrix} = \frac{1}{D} \begin{bmatrix}
0 & b \\
0 & h
\end{bmatrix} \begin{bmatrix}
0 \\
S_{12}
\end{bmatrix}
\]

(3)

Then the two parameters could be obtained, \( S_{11} = b / h \), \( S_{12} = b / h \).

3. Results and discussion

3.1 Characteristics of the particles

Figure 2. shows the morphology of the ZnO. It could be obtained that the commercial ZnO was of the needle-like shape. The particle size of the samples was analyzed using the microscopic statistical method, the average length of ZnO was 400 nm and the diameter was about 40 nm. As the particle was added to the resin with the high speeding mixture, the obtained ZnO was of uniform dispersion.

![Morphology of the particle and surface](image)

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Figure 3. shows that the intensity of UV absorbance and transmittance of ZnO coating with variable weight content. ZnO exhibited a strong absorption below 400 nm with four absorbance peaks at around 205 nm, 232 nm, 278 nm and 286 nm respectively, which meant that the ZnO could be used as an anti-ultraviolet material. As 10% ZnO was added, the number of absorbance peaks was four, while as 20% ZnO was added it could be observed the two peaks at 205 nm and 232 nm also existed, the other two peaks was not obvious. From the transmittance curve, the UV protection property was very obvious, the 10% ZnO coating had the better property on the ultraviolet C (200-280 nm), while the protection property was weak on ultraviolet A (UV-A, 315–400 nm) and ultraviolet B (UV-B, 280–315 nm). As the content increased to 20%, the protection property was excellent, and the transmittance ratio could be less than 0.02% for the three ultraviolet bands. According to the relationship of the transmittance and the UV protection factors (UPF), UPF could be estimated from 40 to 50 for the two ZnO coatings. So, the two coatings were both suitable to avoid the radiations led by the plasma reactions effectively.
3.2 Electromagnetic parameters of the ZnO particle

Figure 4. shows the the complex permittivity ($\varepsilon$) of the ZnO/resin composites as a function of the frequency. The smoothing fitting process was used to get the smooth parameter curves, the abnormal peaks could be neglected and the testing precision could be increased. As the particles were added from weight content 0% to 20%, both the real part of the permittivity ($\varepsilon'$) and the imaginary part of permittivity ($\varepsilon''$) increased. The composites added 20% ZnO had the largest $\varepsilon'$ (the average $\varepsilon'$ value was 6.1). $\varepsilon''$ of all the three composite was fluctuated as the frequency increased. The maximum value could be obtained at 13 GHz, 0.62 of the 20% ZnO/resin composite. Although the changing tendency of $\varepsilon''$ was irregular, the changing magnitude was much lower (less than 0.65) than $\varepsilon'$, it meant that the dielectric loss of the ZnO coating was weak. Both the increasing tendency of $\varepsilon'$ and $\varepsilon''$ was attributed to the weight content, the detailed mechanism could be explained as follows.

3.3 Optimizing on the transmission ratio of the two-layer structure

The genetic algorithm was used to optimizing the layer characteristics and the thickness of the transmission materials according to the calculated $S_{12}$. Firstly, the composites filled with the single absorbent with the different weight content ZnO and the thickness were used as the input data. Then the electromagnetic parameters and the thickness of the two layers were chosen. The chromosome of the genetic algorithm includes a sequence of bits, which contains information on each layer with its material number, weight content and thickness. So, the chromosome can be operated in the program. In the optimized process, the random population containing chromosomes was created, then the number of material choice was decoded, the electromagnetic parameters could be used to calculate the
fitness of each individual, then the select operation, cross operation and mutate operation was done. Finally, the optimized result could be obtained.

The $S_{12}$ of the three optimized samples was shown in figure 5 as a function of the frequency in 2-18 GHz using the previous formulas. Two thicknesses including 1.1 mm and 1.2 mm were optimized as the thickness of the ZnO coating was 0.1 mm or 0.2 mm in table 1, the least thickness of the PLA was 1 mm in order to maintain the strength of the anti-ultraviolet materials. By comparing the transmittance ratio of the three samples, it was obviously obtained that as the 10% ZnO coating thickness increased from 0.1 mm to 0.2 mm, the $S_{12}$ value decreased in nearly the total frequency 2-18 GHz. It indicated that as the ZnO coating thickness could weaken the microwave transmittance property, and as the frequency increased the transmittance property could be lower. In addition, as the weight content of the ZnO increased, the composite had the poorer transmittance property although the thickness of the coating was the same 0.1 mm and the anti-ultraviolet property could better, the smallest transmittance ratio could be found 92.25% at 18 GHz. So in order to maintain the good anti-ultraviolet property and the microwave transmittance property, the ZnO coating thickness and weight content should be smaller, however the two content of the coating in this work might be much higher than the threshold value of anti-ultraviolet property. Above all, the optimized No.1 sample could be the best choice for the microwave transmission and ultraviolet protection.

![Figure 5. Transmission property of composite with various thickness in 2-18 GHz](image)

**Figure 5. Transmission property of composite with various thickness in 2-18 GHz**

**Table 1. TR of composite using the optimized algorithm**

| No. | first layer | second layer | minimum $S_{12}$ |
|-----|-------------|--------------|------------------|
|     | type        | Thickness (mm) | content | type | Thickness (mm) |          |
| 1   | ZnO         | 0.1           | 10%     | PLA  | 1             | 0.95     |
| 2   | ZnO         | 0.2           | 10%     | PLA  | 1             | 0.94     |
| 3   | ZnO         | 0.1           | 20%     | PLA  | 1             | 0.92     |

Usually, the excellent transmission material should satisfy the important conditions called the matching characteristics. In order to achieve the good transmission property, the composite could satisfy the requirements as far as possible, the thickness, the particle dispersion density and structure could improve the transmission property of the composite. In this paper, only the two-layer transmission composite was studied, the internal structure of the composite using the better ZnO coating could be considered in the further research.

**4. Conclusion**

A multi-layer including the ZnO coating on the PLA plate was designed to avoid the ultraviolet and achieve the high microwave transmittance. The coating added 10% or 20% ZnO had the larger UPF for UV protection, UPF could be estimated as 45~50, and as the weight content increased, the property was also improved. Using the optimized process, the composite of 0.1 mm ZnO coating and 1 mm
PLA plate had the good transmission rate, the value could be much larger than 0.95. The designed two-layer structure was effective for the ultraviolet protection and the microwave transmission.

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