

# 使用六方氮化硼片材與氧化鋅奈米粒子混合而成的抗阻燃和抗電磁建築塗料

吳旻緯 (Min-Wei Wu)

元智大學化學工程與材料科學學系碩士生

\*謝建德 (Chien-Te Hsieh)

元智大學化學工程與材料科學學系教授

朱展驛 (Chang-Yi Chu)

元智大學化學工程與材料科學學系學士生

蔡宗濱 (Tsung-Pin Tasi)

奕通工程顧問公司

## 摘要

此研究使用均質化法製備了由六方氮化硼 (h-BN) 和氧化鋅 (ZnO) 奈米顆粒組合而成的複合材料，將二維和零維奈米材料結合在一起，形成了三維結構。將此複合材料與亞矽酸鈉和石膏結合後，表現出卓越的阻燃性能，同時也有效地屏蔽電磁干擾。實驗結果顯示，此複合材料在減緩火勢蔓延和碳化方面發揮重要作用。此外，還顯著地減少了電磁和電場的影響。這種改進性能歸功於 h-BN + ZnO 複合材料的設計，它調節了電阻和介質損耗，ZnO 奈米顆粒並促進了的電磁吸收。  
**關鍵字：**六方氮化硼；氧化鋅奈米顆粒；阻燃性；電磁干擾屏蔽；建築塗料

## Fire Retardant and Anti-electromagnetic Construction Coatings Using Hexagonal Boron Nitride Sheets Mixed with Zinc Oxide Nanoparticles

### Abstract

This study employs an efficient homogenizing method to create composites consisting of hexagonal boron nitride (h-BN) sheets and zinc oxide (ZnO) nanoparticles, resulting in a three-dimensional architecture. These 2D + 0D composites, when integrated with a sodium metasilicate + gypsum matrix, demonstrate not only outstanding flame retardancy but also effective electromagnetic interference (EMI) shielding properties. The experimental results from fire injection at 1050°C highlight the significant role played by the well-designed h-BN + ZnO composites in mitigating flame propagation and charring, ultimately leading to reduced carbonization areas. Additionally, thermal analysis of the h-BN + ZnO composite coating, indicating enhanced thermal insulating performance through the optimal architectural design of the composites. Furthermore, these composite coatings exhibit a substantial reduction in both electromagnetic and electric fields, demonstrating their effectiveness in EMI shielding.

**Keywords:** Hexagonal boron nitride; Zinc oxide nanoparticles; Fire retardancy; Electromagnetic interference shielding; Construction coating

## 1. Introduction

Wood is generally considered as a fundamental material, particularly in the realm of construction, due to its commendable mechanical attributes, including an exceptional strength-to-weight ratio [1]. However, wood does harbor inherent risks, most notably its susceptibility to fire, which can markedly jeopardize both its structural integrity and overall performance. Given that wood plays an extensive role in our daily lives, fires involving wood can pose significant threats to human safety and well-being.

To determine an optimal fire retardancy, the weight ratio of h-BN to ZnO was chosen as a crucial factor in determining the fireproof performance of the composite films coated on wooden substrates. Furthermore, a comprehensive exploration into the influence of h-BN/ZnO ratio in functional coatings on EMI shielding performance was undertaken.

## 2. Experimental

### 2.1 Synthesis of h-BN + ZnO composites

The synthesis of h-BN + ZnO composites employed in this work could be described as follows. First, hydroxylated h-BN sheets were modified using a milling method, where h-BN nanosheets (Sigma-Aldrich, purity: > 98 %) and glycine (Sigma-Aldrich, purity: > 99 %) were uniformly mixed with distilled water inside a stainless steel container in 3D ball mills for 15 min under the air atmosphere. The presence of the glycine protects the h-BN sheets along with preventing the formation of lattice defects. Upon completing the 3D ball-milling step, the h-BN samples were mixed at room temperature for 2 h. Finally, the h-BN samples were dehydrated at 80 °C in vacuum oven overnight, to finalize the hydroxylated h-BN sheets.

Second, the deposition of ZnO nanoparticles was performed by pulse microwave deposition using a microwave oven. The pulse microwave-assisted synthesis was carried out at 80 °C under 720W microwave power, and the deposition and rest periods were set at 2 and 3 s, respectively. The pulse microwave synthesis thus took a total of 8 min, and the as-prepared ZnO nanoparticles were dried in an oven at 105 °C overnight.

The mixture of h-BN + ZnO composites were homogeneously dispersed in ethanol solution through an ultrasonic bathing technique. Herein five combinations of h-BN/ZnO weight ratio were set at 1:3, 1:2, 1:1, 2:1, and 3:1 in w/w. The mixture was placed into a high-performance homogenizer (IKA, Model T25, Germany). The homogenizing dispersion process was carried out at ambient temperature for 15 min, ensuring the formation of homogeneous hybrids. After that, the h-BN + ZnO composites were separated from filtering apparatus and then dried at 105 °C in an oven overnight.

### 2.2 Fireproof performance of carbon composite coatings

To examine the fire-retardant performance, the fireproof coating (including sodium metasilicate + gypsum) mixed with five types of the h-BN + ZnO composites were prepared to coat over wooden plate. Herein each fireproof coating was composed of 20 mL of sodium metasilicate, 0.408 g of gypsum, and 1.8 g of h-BN + ZnO composite. The fireproof slurries were then well dispersed and then stirred by a magnetic bar at 160 rpm overnight. The as-prepared slurries were pasted on the wooden substrates with a doctor blade and then dried at 60 °C in an oven overnight. The thickness of each carbon composite coating was well controlled within 0.3 mm.

The anti-flammability of the construction coatings on wooden plates was evaluated by using a high-performance flamethrower. The distance between the coating and the top of flame was set at 2 cm, where the surface temperature on the wooden plates was kept at 1050 °C.

### 2.3 EMI shielding performance of carbon composite coatings

To evaluate the efficiency of EMI shielding, we uniformly applied h-BN + ZnO composite coatings onto wallpaper substrates. To establish a reference point, we activated an electrical appliance (operating at a utility frequency of 60 Hz) emitting an electric field of 350 V/m and a magnetic field of  $43 \times 10^{-6}$  T. This appliance served as our baseline reference. This procedure was repeated for a total of 10 runs, and subsequently, the collected data from each run were averaged to obtain the final measurement results.

### 2.4 Materials characterization

The morphology and structural characteristics of h-BN sheets and ZnO nanoparticles were assessed. To delve into the thermal stability and calorimetric changes exhibited by the carbon coatings, a thermogravimetric analyzer (TGA, Perkin Elmer TA7) was employed. During the TGA analysis, which took place under an air atmosphere, the samples were subjected to a heating rate of 5 °C/min, with the temperature ramping from 50 °C to 800 °C.

## 3. Results and discussion

We employed TGA, a technique that provides quantitative insights into material decomposition, allowing us to investigate degradation kinetics and char formation [2,3]. Throughout the chemical decomposition process, we closely monitored the weight loss in an air environment, as illustrated in Figure 1. The TGA curves for all the samples consistently revealed three distinctive weight-loss stages:

(i) Dehydration (100–200 °C): This initial stage primarily involves the release of water vapor from the gypsum and sodium metasilicate mixture.

(ii) Ignition and Decomposition (200–350 °C): During this phase, the materials

undergo ignition followed by subsequent decomposition.

(iii) Pyrolysis and Degradation (450–800 °C): This stage encompasses further pyrolysis and degradation of the materials.

It is widely recognized that the effectiveness of flame retardant materials can be assessed by analyzing the volatiles and the resulting residue as the temperature increases. After subjecting the materials to thermal oxidation at 800 °C, the residual weight ratios follow this order: B: Z (3:1) (83.5 wt.%) > B: Z (2:1) (81.5 wt.%) > B: Z (1:1) (77.5 wt.%) > B: Z (1:2) (72.1 wt.%) > B: Z (1:3) (72.1 wt.%). Based on these experimental findings, it is evident that an optimal combination of h-BN + ZnO composite coating significantly enhances the fire resistance of the construction coating.

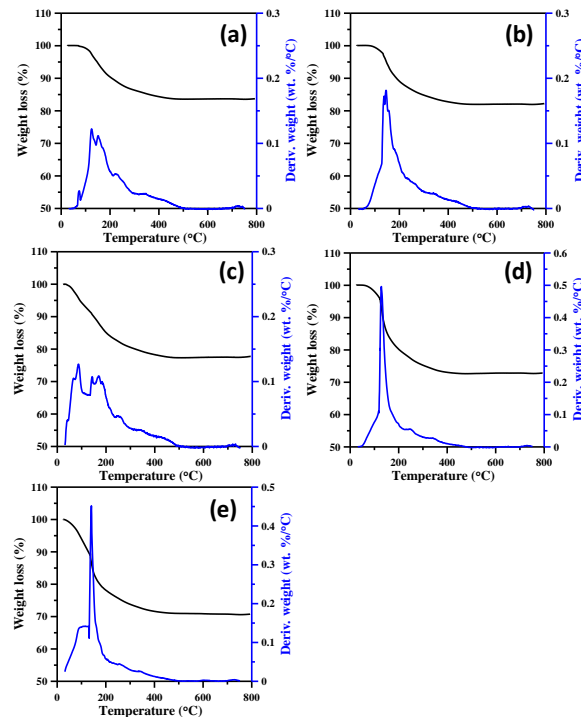


Figure 1. TGA curves of h-BN + ZnO composite coatings with various h-BN: ZnO weight ratios: (a) 3:1, (b) 2:1, (c) 1:1, (d) 1:2, and (e) 1:3.

Figure 2 depicts the variation of carbonization fractions with flame injection time for all fireproof coatings applied to wooden substrates. We observe that the h-BN/ZnO weight ratio plays a crucial role in determining the carbonization fraction of the wooden substrates. Accordingly, this resulting composite film serves as a robust physical barrier that curtails mass and heat exchange between the condensed and gas phases while inhibiting the escape of volatile substances, leading to a significant enhancement in flame retardancy and smoke suppression [4].

Figure 2(a) illustrates the shielding effect on electromagnetic and electric fields by blank (i.e., gypsum + sodium metasilicate mixture) and various h-BN + BN composite coatings. In this experiment, an electrical appliance operating at a utility frequency of 60 Hz emitted an electric field of 350 V/m and a magnetic field of  $43 \times 10^{-6}$  T, serving as

the reference background. Initially, upon covering with the blank coating, both the magnetic and electric fields show a slight reduction to  $34 \times 10^{-6}$  T and 225 V/m, respectively. Relative to the original magnetic source, the EMI shielding effectiveness has an order as B: Z (3:1) (57.0 %) < B: Z (2:1) (57.7 %) < B: Z (1:1) (58.1 %) < B: Z (1:2) (65.1 wt.%) < B: Z (1:3) (82.6 wt.%). Furthermore, when assessed in decibels (dB), the sequence can be expressed as follows: B: Z (3:1) (-3.66 dB) < B: Z (2:1) (-3.73 dB) < B: Z (1:1) (-3.78 dB) < B: Z (1:2) (-4.57 dB) < B: Z (1:3) (-7.58 dB). The EMI shielding performance also showed a similar sequence with the reduction in electrical field, as depicted in Figure 2(a).

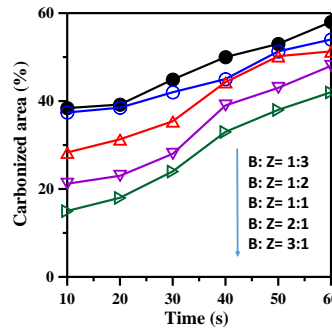


Figure 2. Variation of carbonized area of the composite coatings with the fire injection time.

Notably, the higher ZnO content is beneficial for the EMI shielding effect, as shown in Figure 2(a). The strong magnetic wave loss occurs due to the presence of ZnO nanoparticles, the resonant behaviors induced by the ZnO interface and skin effect effectively broaden the reflection loss [5]. With increasing the ZnO content, the absorption bandwidth thus increases. The enhanced EMI shielding performance achieved through the utilization of the h-BN + ZnO composite coating can be attributed to a synergistic effect that involves both reflection-loss phenomena within the 0D + 2D composites. This effect can be categorized into two main types: the first type is a result of resonant behaviors arising from the presence of the h-BN + ZnO interface, while the other type stems from wavelength attenuation [5]. The results indicate that the 0D + 2D composites can be promising candidates for new generation EMI shielding and magnetic wave-absorption materials. Hence, the inclusion of h-BN + ZnO fillers composites plays a pivotal role in tuning the resistance and dielectric loss, thereby facilitating electromagnetic absorption by carbon composites. Figure 3(b) showcases the influence of layer thickness on the EMI shielding performance of the h-BN + ZnO composite coating (1:3 in w/w). Notably, an increase in layer thickness exhibits no significant effect on improving EMI shielding performance.

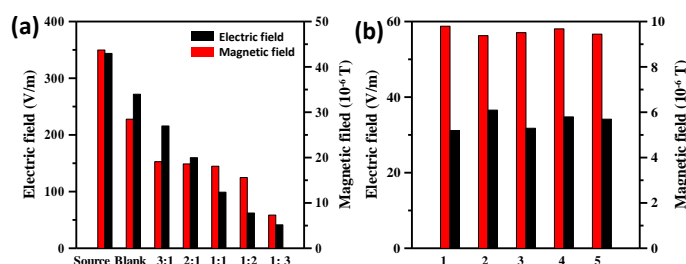


Figure 3. (a) Magnetic and electric field as a decreasing function of h-BN + ZnO composite coatings, and (b) the variation of magnetic and electric acid with layer number at the fixed h-BN: ZnO ratio (=1:3 in w/w).

#### 4. Conclusions

This study adopted an efficient homogenizing method to fabricate the composites of h-BN sheets + ZnO nanoparticles, producing a stereo architecture. The h-BN + ZnO composites incorporated with sodium metasilicate + gypsum matrix displayed not only excellent flame retardancy but also satisfactory EMI shielding effect, applied for construction coatings on wooden and wallpaper substrates. The TGA analysis of h-BN + ZnO composite coating revealed that high mass of char residue can be obtained at 800 °C, indicating the enhanced thermal insulating performance through the optimal design of composite architectures. Such a significant improvement in flame retardancy and EMI shielding demonstrated that the h-BN + ZnO composites are excellent additives to flame-retardant and EMI-adsorbing construction coating, considering their high efficiency, pollutant reduction, non-toxicity, low cost, and environmental friendliness.

#### References

- [1] de la Roche, I.; Dangerfield, J. A.; Karacabeyli, E. Wood products and sustainable construction. *New Zel. Timber Des. J.* 12 (2003) 9-13.
- [2] Lowden, L.A., and Hull, T.R. (2013) Flammability behaviour of wood and a review of the methods for its reduction. *Fire Sci. Rev.* 2 (2013) 1-19.
- [3] H.-C. Yang, T.-P. Tsai, C.-T. Hsieh, Enhancement on fireproof performance of construction coatings using calcium sulfate whiskers prepared from wastewater. *Chem. Pap.* 71 (2017) 1343-1350.
- [4] Y. Feng et al., Superior flame retardancy and smoke suppression of epoxy-based composites with phosphorus/nitrogen co-doped graphene, *J. Hazard Mater* 346 (2018) 140-151.
- [5] W.-L. Song et al., Synthesis of zinc oxide particles coated multiwalled carbon nanotubes: Dielectric properties, electromagnetic interference shielding and microwave absorption, *Mater. Res. Bull.* 47 (2012) 1747-1754.