

## Tensile, Compressive and Thermal Properties of Epoxy / Hollow Glass Beads/ Graphene Ternary Foamed Composites

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**Abstract:** Hollow glass beads and graphene were used to improve the performances of the epoxy resin. The density, tensile, compressive properties and thermal behaviors of the as-prepared samples were discussed. Experiment results showed that hollow glass beads could effectively reduce the density of the epoxy resin matrix. When the hollow glass beads loading was 30 wt%, the density of the composites was  $0.81 \text{ g}\cdot\text{cm}^{-3}$ . Moreover, graphene could enhance the mechanical performances of the foamed composites. When the graphene loading was 0.75 wt%, the tensile strength, Young's modulus and strain break of the epoxy/hollow glass beads/graphene ternary samples were 85.2 %, 53.4 % and 11.0 % more than the control binary sample, respectively. Moreover, the compressive strength and modulus were 10.8 % and 68.6 % more than the control binary sample, respectively. In addition, DSC and TG results showed that graphene could accelerate the curing and improve the thermal stability of the foamed composites.

Keywords: Epoxy resin; Hollow glass beads; Graphene; Foamed composites.

### Introduction

Because of light weight and moderate strength, foamed composites are used in lots of fields such as marine, aerospace and automotive. In recent years, many attempts have been taken to improve the properties of the foamed composites, such as changing the resin matrix [1], adjusting the micro-balloon size and volume fraction [2-5], using glass fibers [6-7], carbon fibers [8-9], nanoclay [10-11] and carbon nanotubes [12] as reinforcing agents. As far as we know, epoxy resin has been the most commonly-used polymer matrix for the foamed composites [2-6]. Moreover, hollow glass beads (HGB) were frequently-used filler for the production of epoxy based foamed composites [13-14]. Though the epoxy/HGB foamed composites were light, their mechanical and thermal properties still needed to be improved.

Recently, graphene has attracted much attention for its unique two-dimensional structure, large specific surface area, excellent mechanical and thermal properties [15-17]. It has been expected to be the most promising filler for improving the properties of the resin matrix [18-20]. However, there are no related papers focusing on the epoxy/HGB/graphene ternary foamed composites.

In this work, epoxy resin, HGB and graphene were used to prepare ternary foamed composites. Experiment results showed that HGB could act as good filler to decrease the density of the matrix. Moreover, graphene could improve the

tensile, compressive properties and thermal stability of the composites. In addition, graphene was beneficial to accelerate the curing and enhance the thermal stability of the foamed composites.

### Experimental

#### Materials

Graphene (as shown as in Fig. 1) was provided in our laboratory [21]. The density of HGB (brand: VS5500) was  $0.38 \text{ g}\cdot\text{cm}^{-3}$  and it was purchased from 3M Corp., USA.  $\gamma$ -aminopropyltriethoxysilane (brand: KH550) was purchased from Nanjing Chengong Organic Silicone Material Corp., China. Both bisphenol-A epoxy resin (brand: Airstone 760E) and curing agent (brand: Airstone 766H) were bought from Dow Corp., USA.

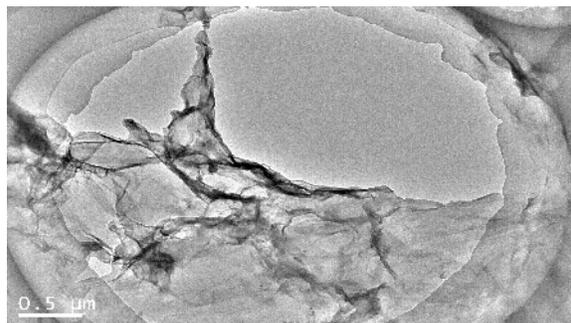


Fig. 1: TEM image of graphene.

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### Surface Treatment of HGB

HGB were mixed with alcohol/water/KH550 solution for 2 h (the volume ratio of the alcohol to the water was 9:1 and the KH550 concentration was 1 vol./vol.%). Subsequently, they were collected and dried at 120 °C for 4 h. Then, The amino-functionalized HGB were obtained.

### Preparation of Epoxy/HGB Binary Foamed Composites

Typically, 50.0 g epoxy resin and 25.0 g curing agent were mixed together under stirring for 5 min. Then, the as-treated HGB (0, 10, 20, 30, 40 and 50 wt%, based on the weight of the epoxy resin) were added into the mixture system and continued to fast stir for another 10 min. Subsequently, the as-prepared epoxy/HGB binary foamed composites were degassed in a vacuum oven at 55 °C. Then, the mixture was poured into a mould for curing 2 h at 80 °C and post-curing 2 h at 110 °C.

### Preparation of epoxy/HGB/graphene ternary foamed composites

50.0 g epoxy resin and 15.0 g the as-treated HGB (the HGB loading was 30 wt% based on the weight of the epoxy resin) were fully mixed. Graphene (0.25, 0.50, 0.75, 1.00 or 1.25 wt%, based on the weight of the epoxy resin) was well dispersed in 25.0 g curing agent through ultrasonic wave. Subsequently, the as-prepared epoxy/HGB/graphene ternary foamed composites were fabricated via a similar process of preparing the epoxy/HGB binary composite, which was regarded as the control sample.

### Characterization

The density of the binary foamed composites with different HGB loadings was calculated by the following equation:

$$\rho = \frac{m}{v}$$

where  $\rho$  ( $\text{g}\cdot\text{cm}^{-3}$ ) is the density,  $m$  (g) is the weight and  $v$  ( $\text{cm}^3$ ) is the volume of the samples.

The tensile and compressive properties of the as-prepared epoxy/HGB/graphene ternary foamed samples were characterized by using a universal testing machine (Model: M350-20KN, XIN SAN SI Corp., China). At least five specimens were tested and the average value was adopted for each sample. The curing behavior of the as-prepared ternary foamed composites (the graphene loading was 0.75 wt%) and the control binary sample (without using graphene) were performed by differential scanning calorimetry (DSC, Model: DSC822<sup>e</sup>, METTLER

TOLEDO Corp., Switzerland) at a rate of 20 °C·min<sup>-1</sup> under the protection of argon gas. Moreover, the thermal stability of the as-prepared ternary foamed composite and the control binary sample were performed via thermo-gravimetric analysis (TGA, Model: TGA/SDTA 851<sup>e</sup>, METTLER TOLEDO Corp., Switzerland) via at a scanning rate of 20 °C·min<sup>-1</sup> under the protection of argon gas.

## Results and Discussion

### Density

Fig. 2 shows the density of the epoxy/HGB binary foamed composites with different HGB loadings (i.e. 0, 10, 20, 30, 40 and 50 wt%). It is clear that HGB could effectively reduce the density of the epoxy resin matrix. The density of the as-prepared samples was 1.13  $\text{g}\cdot\text{cm}^{-3}$  when the HGB loading was 0 wt%. Moreover, it turned to 0.81  $\text{g}\cdot\text{cm}^{-3}$  as the HGB loading increased to 30 wt%. However, it reduced only a little as the HGB loading continually increased to 50 wt%. This could be explained by that the density of HGB was 0.38  $\text{g}\cdot\text{cm}^{-3}$ , and they could not endlessly reduce the density of the resin matrix. Moreover, the mechanical properties of the samples would be very likely worse if it continually increased in the loading of HGB. Therefore, 30 wt% of the HGB loading was chosen.

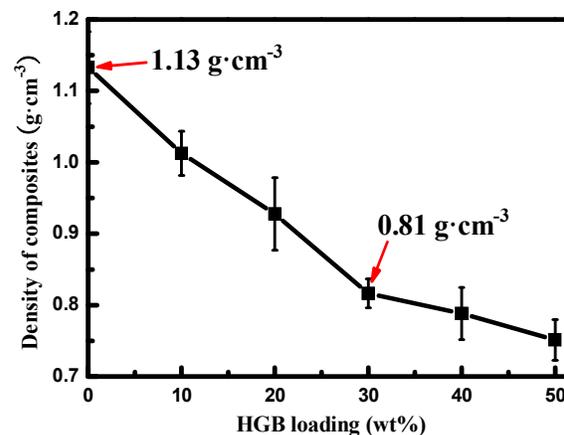


Fig. 2: Density of the epoxy/HGB binary foamed composites.

### Mechanical Properties

#### Tensile Properties

Fig. 3 shows the tensile strength, Young's modulus and elongation at break of the epoxy/HGB/graphene ternary foamed composites. It is clear that all of them were increased first and then decreased with the increasing in the loading of graphene. When the graphene loading was 0.75 wt%, they reached to the maximum values which were 85.2

%, 53.4 % and 11.0 % more than the control binary sample, respectively. It could be explained by that: 1) Graphene was a kind of ideal reinforcing filler; for example, it possessed large specific surface area (TEM image of the as-used graphene was shown in Fig. 1), which was in favor of enhancing the mechanical properties of the matrix [22]; thus, only a small amount of graphene could show obviously reinforcing effect; 2) Like other fillers, if the loading of graphene was excessive, the mechanical performances of the samples would be deteriorated.

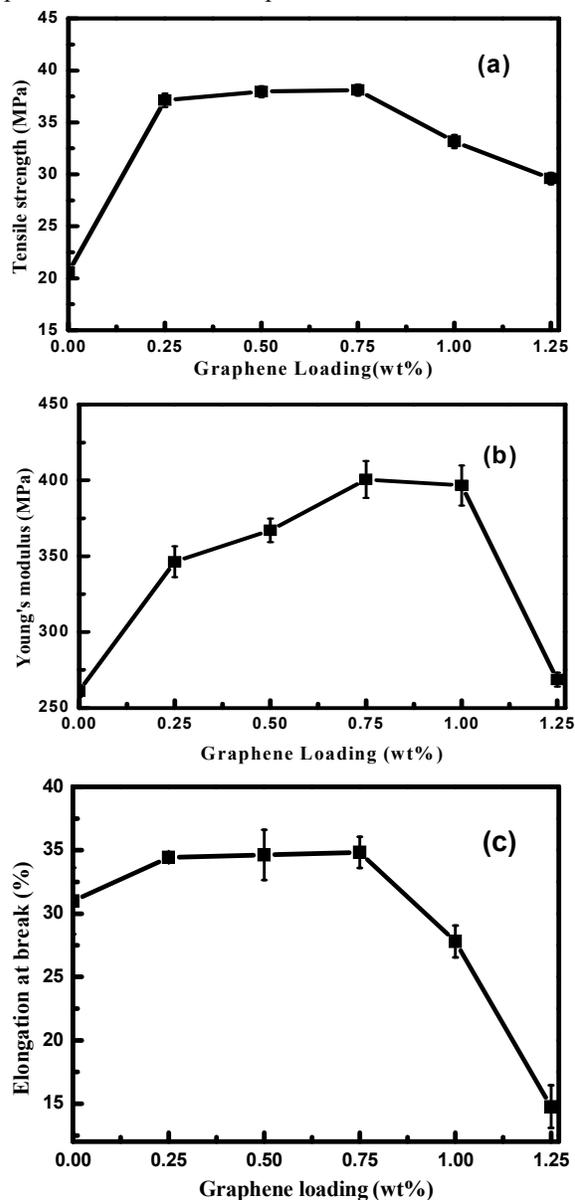


Fig. 3: Tensile strength (a), Young's modulus (b) and elongation at break (c) of the epoxy/HGB/graphene ternary foamed composites.

### Compressive Properties

Fig. 4 shows the compressive strength and modulus of the ternary foamed composites. Both of them increased first and then fast decreased with the increasing in the loading of graphene. This result was similar with the tensile properties. When graphene loading was 0.75 wt%, the compressive strength and modulus of the samples reached to the maximum which were 10.8 % and 68.6 % more than the control binary sample, respectively. As a consequence, graphene could not only enhance the strength, but also improve the toughness of the resin matrix.

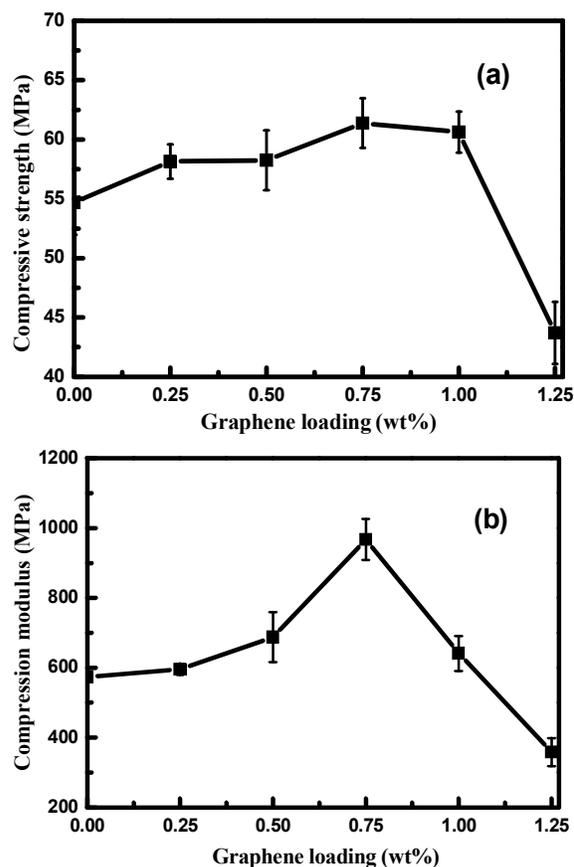


Fig. 4: Compressive strength (a) and modulus (b) of the epoxy/HGB/graphene ternary foamed composites.

### Thermal Properties

Fig. 5 shows the thermal behaviors of the ternary foamed composites. In Fig. 5 (a), DSC results showed that the peak temperature, which means that the curing rate was the fastest, was moved to 140.6 °C from 141.5 °C. This indicated that graphene was in favor of accelerating the curing of the composites.

The possible reason was that the graphene possessed good thermal conductivity [23]. Moreover, in Fig. 5 (b), TG results showed that the thermal decomposition temperature moved to 293.6 °C from 235.0 °C. This might be explained by that the graphene had high decomposition temperature and could improve the thermal stability of the matrix [24].

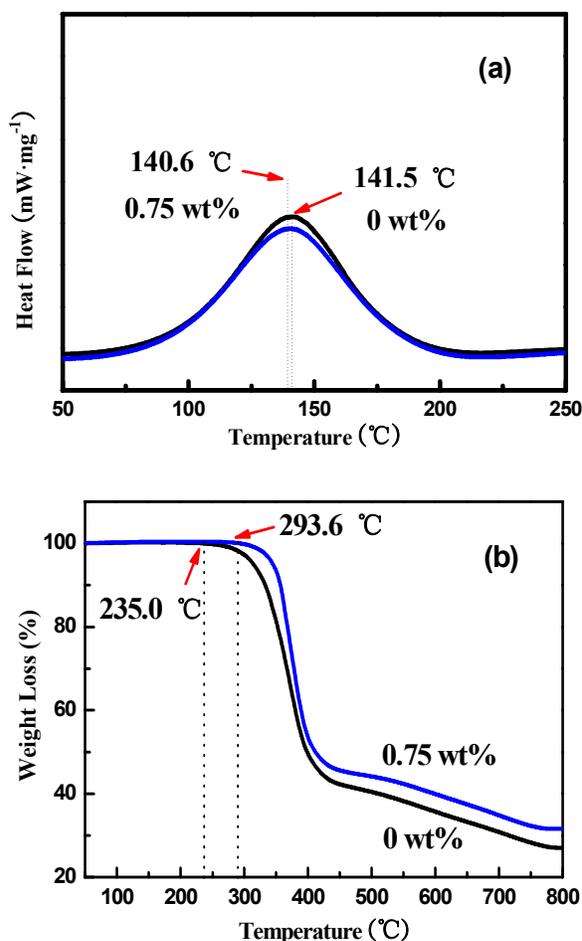


Fig. 5: DSC (a) and TG (b) spectrums of the epoxy/HGB/graphene ternary foamed composites.

### Conclusion

Epoxy/HGB/graphene ternary foamed composites were prepared, and the tensile properties, compressive properties and thermal behaviors of the as-prepared samples were discussed. Density results showed that HGB could act as good light-weight fillers to reduce the density of the epoxy resin matrix. Moreover, mechanical, DSC, TG results showed that only a small amount of graphene, typically 0.75 wt%,

could improve the tensile, compressive and thermal properties of the foamed composites.

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### References

1. K. A. Devi, B. John, C. P. R. Nair and K. N. Ninan, Syntactic Foam Composites of Epoxy-Allyl Phenol-Bismaleimide Ternary Blend-Processing and Properties, *J. Appl. Polym. Sci.*, **105**, 3715 (2007).
2. Kishore, R. Shankar and S. Sankaran, Effects of microballoons' Size and Content in Epoxy on Compressive Strength and Modulus, *J. Mater. Sci.*, **41**, 7459 (2006).
3. N. Gupta, E. Woldeesenbet and P. Mensah, Compression Properties of Syntactic Foams: Effect of Cenosphere Radius Ratio and Specimen Aspect Ratio, *Compos. Part A*, **35**, 103 (2004).
4. N. Gupta and W. Ricci, Comparison of Compressive Properties of Layered Syntactic Foams Having Gradient in Microballoons Volume Fraction and Wall Thickness, *Mater. Sci. Eng. A*, **427**, 331 (2006).
5. M. Porfiri and N. Gupta, Effect of Volume Fraction and Wall Thickness on The Elastic Properties of Hollow particle Filled Composites, *Compos. Part B*, **40**, 166 (2008).
6. C. S. Karthikeyan, S. Sankaran and Kishore, Investigation of Bending Modulus of Fiber-Reinforced Syntactic Foams for Sandwich and Structural Applications, *Polym. Adv. Technol.*, **18**, 254 (2007).
7. B. John, C. P. R. Nair and K. N. Ninan, Tensile and Flexural Properties of Glass-Fiber-Reinforced Cyanate Ester Syntactic Foams, *Polym. Polym. Compos.*, **16**, 431 (2008).
8. R. L. Poveda, G. Dorogokupets and N. Gupta, Carbon Nanofiber Reinforced Syntactic Foams: Degradation Mechanism for Long Term Moisture Exposure and Residual Compressive Properties, *Polym. Degrad. Stab.*, **98**, 2041 (2013).
9. R. L. Poveda and N. Gupta, Carbon-Nanofiber-Reinforced Syntactic Foams:

- Compressive Properties and Strain Rate Sensitivity, *JOM*, **66**, 66 (2014).
10. M. C. Saha and S. Nilufar, Nanoclay-Reinforced Syntactic Foams: Flexure and Thermal Behavior, *Polym. Compos.*, **31**, 1332 (2010).
  11. A. Asif, V. L. Rao and K. N. Ninan, Nanoclay Reinforced Thermoplastic Toughened Epoxy Hybrid Syntactic Foam: Surface Morphology, Mechanical and Thermo Mechanical Properties, *Mater. Sci. Eng., A*, **527**, 6184 (2010).
  12. M. E. Guzman, A. J. Rodriguez, B. Minaie and M. Violette, Processing and Properties of Syntactic Foams Reinforced with Carbon Nanotubes, *J. Appl. Polym. Sci.*, **124**, 2383 (2012).
  13. C. Swetha and R. Kumar, Quasi-Static Uni-Axial Compression Behaviour of Hollow Glass Microspheres/Epoxy Based Syntactic Foams, *Mater. Des.*, **32**, 4152 (2011).
  14. M. Colloca, N. Gupta and M. Porfiri, Tensile Properties of Carbon Nanofiber Reinforced Multiscale Syntactic Foams, *Compos. Part B*, **44**, 584 (2013).
  15. K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva and A. A. Firsov, Electric Field Effect in Atomically Thin Carbon Films, *Science*, **306**, 666 (2004).
  16. C. Lee, X. D. Wei, J. W. Kysar and J. Hone, Measurement of The Elastic Properties and Intrinsic Strength of Monolayer Graphene, *Science*, **321**, 385 (2008).
  17. K. S. Novoselov, D. Jiang, F. Schedin, T. J. Booth, V. V. Khotkevich, S. V. Morozov and A. K. Geim, Two-Dimensional Atomic Crystals, *Proc. Natl. Acad. Sci. USA.*, **102**, 10451 (2005).
  18. J. T. Yang, L. Q. Huang, L. L. Li, Y. F. Zhang, F. Chen and M. Q. Zhong, Preparation of Polystyrene/Graphene Oxide Composites and Their Supercritical Carbon Dioxide Foaming, *J. Polym. Res.*, **20**, 1 (2013).
  19. A. S. Patole, S. P. Patole, H. Kang, J. B. Yoo, T. H. Kim and J. H. Ahn, A Facile Approach to The Fabrication of Graphene/Polystyrene Nanocomposite by *in situ* Microemulsion Polymerization, *J. Colloid Interface Sci.*, **350**, 530 (2010).
  20. M. A. Rafiee, J. Rafiee, Z. Wang, H. Song, Z. Z. Yu and N. Koratkar, Enhanced Mechanical Properties of Nanocomposites at Low Graphene Content, *Acs Nano*, **3**, 3884 (2009).
  21. X. F. Wu, J. Zhang, Y. F. Zhuang, J. Li, L. C. Han and F. J. Xiao, Template-Free Preparation of A Few-Layer Graphene Nanomesh Via A One-Step Hydrothermal Process, *J. Mater. Sci.*, **50**, 1317 (2015).
  22. T. Ramanathan, A. A. Abdala, S. Stankovich, D. A. Dikin, M. Herrera-Alonso, R. D. Piner, D. H. Adamson, H. C. Schniepp, X. Chen, R. S. Ruoff, S. T. Nguyen, I. A. Aksay, R. K. Prud'Homme and L. C. Brinson, Functionalized Graphene Sheets for Polymer Nanocomposites. *Nat. Nanotechnol.*, **3**, 327 (2008).
  23. A. A. Balandin, S. Ghosh, W. Z. Bao, I. Calizo, D. Teweldebrhan, F. Miao and C. N. Lau, Superior Thermal Conductivity of Single-Layer Graphene, *Nano Lett.*, **8**, 902 (2008).
  24. R. Verdejo, F. Barroso-Bujans, M. A. Rodriguez-Perez, J. A. de Saja and M. A. Lopez-Manchado, Functionalized Graphene Sheet Filled Silicone Foam Nanocomposites, *J. Mater. Chem.*, **18**, 2221 (2008).