

Effects of Surface Functionalization on Interface Bonding of Graphite/Epoxy Composites

Dongmei Yao, Junsheng Zheng *, Pingwen Ming

1 Clean Energy Automotive Engineering Center and School of Automotive Studies, Tongji University, 4800 Caoan Road, Shanghai, 201804, China Affiliation of author A

(*Corresponding Author: jszheng@tongji.edu.cn)

ABSTRACT

Epoxy resin-reinforced graphite composite materials have found significant applications in the construction of fuel cell bipolar plates under stable power supply, owing to their lightweight and high durability characteristics. These composite materials are formulated by blending graphite with thermosetting resin and curing agent. The interfacial bonding between graphite and epoxy resin plays a pivotal role in determining the performance of these composites. Typically, the bonding between graphite and resin is governed by van der Waals forces, which possess relatively lower binding energy, rendering the interface susceptible to failure under external forces. To address this limitation, this study endeavors to modify the graphite surface with functional groups and adjust the process to facilitate a chemical bonding interface between graphite and resin. Characterization techniques reveal the formation of new chemical bonds between graphite and resin. Molecular dynamics simulations further validate the detailed mechanism through which this enhanced interface bonding elevates the mechanical performance of the composite material. This

investigation offers valuable insights for the advancement of graphite-resin composite materials.

Keywords: G/EP interface bonding, composite bipolar plate, molecular dynamic simulation, fuel cell

1. INTRODUCTION

Epoxy resin-reinforced graphite composite materials have emerged as crucial components in the construction of fuel cell bipolar plates, particularly in applications demanding stable power supply, due to their exceptional lightweight and high durability characteristics[1-3]. These composite materials are meticulously prepared by blending graphite with a thermosetting resin and a curing agent[4]. The adhesive strength at the interface between the graphite and epoxy resin is of paramount importance, profoundly influencing the overall performance of these composites[5, 6]. Conventionally, the interaction between graphite and resin relies on van der Waals forces, which, though fundamental, inherently exhibit relatively low binding energy[7, 8]. This inherent

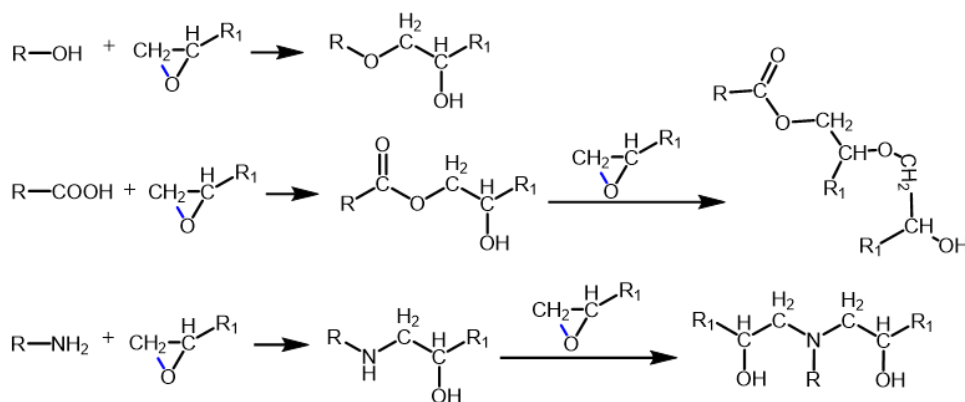


Fig. 1. The cross-linking reaction between epoxy resin and curing agent.

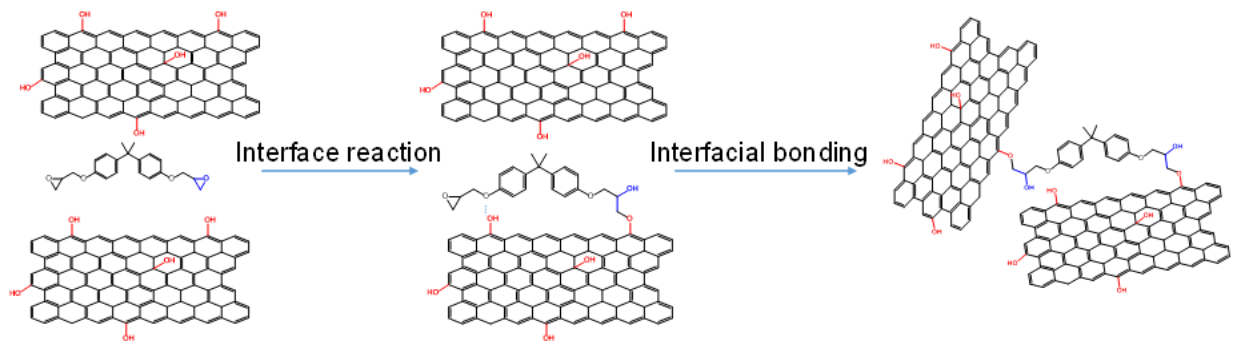


Fig. 2. Schematic of the interface bonding process.

weakness renders the interface vulnerable to failure when subjected to external forces, thus limiting the practical utility of such composite materials[9, 10].

In light of these limitations, this study embarks on a mission to enhance the adhesive strength between graphite and epoxy resin. The curing process[4] of epoxy resin involves cross-linking reactions between the epoxy groups at the ends of epoxy resin molecules and functional groups, such as amino, hydroxyl (or carboxyl) groups, present in the curing agent (Fig.1). Therefore, we hypothesize that the introduction of functional groups on the graphite surface can facilitate chemical reactions with the epoxy resin, thereby achieving the purpose of forming interfacial bonds (Fig.2). The primary focus of this investigation is twofold: first, to modify the graphite surface by introducing functional groups, and second, to optimize the fabrication process to create a chemical bonding interface between graphite and resin. The implications of these modifications are far-reaching, as they aim to address the shortcomings of the existing van der Waals interactions[11-13]. Characterization techniques have been employed to scrutinize the molecular-level changes that transpire during the modification process[14-16]. These techniques reveal the formation of new and robust chemical bonds between graphite and epoxy resin, thereby bolstering the interfacial adhesion[10, 17].

To elucidate and substantiate the mechanisms underlying this enhanced interface bonding, molecular dynamics (MD) simulations are leveraged[18, 19]. These simulations serve to validate and provide a detailed insight into the complex interactions occurring at the atomic level, reinforcing the mechanical performance of the composite material[20, 21]. By elucidating the interplay between modified graphite surfaces and epoxy resin, this investigation contributes to a deeper understanding of composite material design, offering valuable insights for the continued development and optimization of graphite-resin composites. Consequently, the outcomes of this research are

expected to pave the way for advancements in the field, ushering in more robust and durable composite materials for critical applications, such as fuel cell bipolar plates..

2. EXPERIMENT

Natural graphite (G) was sourced from the Nanshu graphite mine in Shandong Province. The graphite surface underwent treatment using a 3:1 (weight ratio) mixture of concentrated H_2SO_4 and HNO_3 for approximately one week. Potassium permanganate and diethylenetriamine were introduced to the surface as functional groups. Following this treatment, the treated graphite was subjected to multiple washes with deionized (DI) water to facilitate filtration. Subsequently,

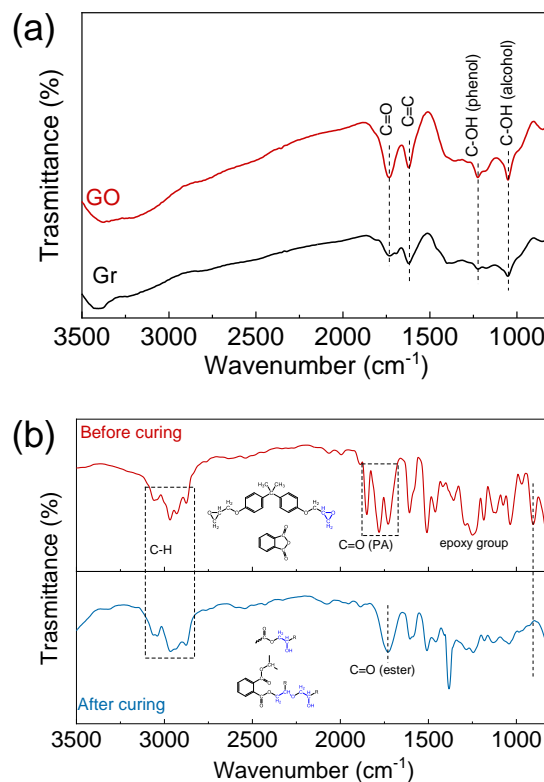


Fig. 3. FT-IR Spectroscopy: (a) Graphite and graphite oxide; (b) resin before and after curing.

desulphurization was carried out in an oven at 50 ° C for a duration of 5-7 hours, followed by high-temperature expansion at 300 ° C. These steps were conducted to ultimately yield graphite oxide (GO). The curing of the epoxy resin is accomplished by heating it at 100 ° C in oven for one day. The characterization of graphite and resin were determined using Fourier transform infrared spectroscopy (FT-IR, IRAffinity-1S, Japan).

3. RESULTS AND DISCUSSION

3.1 chemical analysis

From the Fig.3a, it can be observed that, following surface treatment, there is minimal change in the C=C peak at 1623 cm⁻¹ in the graphite. However, significant increases in the peaks at 1726 cm⁻¹, 1223 cm⁻¹, and 1046 cm⁻¹, corresponding to C=O, C-OH (alcohol), and C-OH (phenol)[22, 23], respectively, indicate an elevated presence of these functional groups on the graphite surface. These functional groups have the capacity to react with the epoxy groups at the terminus of epoxy resin molecules.

Furthermore, we conducted a characterization of the resin both before and after curing (Fig. 3b). It is evident that, following curing, the epoxy functional group peak at 1224 cm⁻¹ disappears, transitioning into the ester peak at 1728 cm⁻¹.

3.2 MD simulation

In the MD simulation process, the molecular models of graphite and graphite oxide were constructed using the 3D atomistic document module in Materials Studio, and the models were geometrically optimized and energy minimized using the Forcite module. The optimized spatial structures of the monomers are shown in Fig. 4.

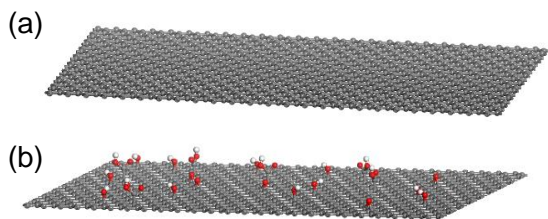


Fig. 4. The molecular structures of graphite (a) and graphite oxide (b).

From Table 1, it is evident that the introduction of carboxyl and carbonyl groups in GO results in an increased charge energy compared to pure graphene, by 21 kcal/mol. Furthermore, the incorporation of these functional groups significantly elevates the model's bond

energy, increasing it from 649 kcal/mol to 1450 kcal/mol. Consequently, the total energy of oxidized graphene rises to 4380 oxidized graphene, which is notably higher than that of pure graphene. This enhancement allows it to exhibit heightened reactivity in chemical reactions, providing favorable conditions for chemical bonding between graphene and resin.

Table 1. Energy of the different carbon substrate models after reaching the equilibrium state

Type	E _{total} (kcal/mol)	E _{valence} (kcal/mol)	E _{non-bond} (kcal/mol)	E _e (kcal/mol)
G	3.65×10 ³	649	3.00×10 ³	0
GO	4.38×10 ³	1.45×10 ³	2.93×10 ³	-21

4. CONCLUSION

This paper introduces a novel method for directly bonding graphite to resin, successfully preparing oxidized graphene for interface bonding. MD simulations have further validated the significantly enhanced chemical reactivity of oxidized graphene compared to pristine graphite, offering favorable conditions for interface bonding. This innovative approach to interface connection promotes a stronger bond between graphite and resin, providing valuable insights for enhancing the interfaces in graphite/resin composite materials.

ACKNOWLEDGEMENT

The authors would like to acknowledge the financial supports from the National Key R&D Program of China (2020YFB1505904).

DECLARATION OF INTEREST STATEMENT

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. All authors read and approved the final manuscript.

REFERENCE

- [1] K.I. Jeong, J. Oh, S.A. Song, D. Lee, D.G. Lee, S.S. Kim, A review of composite bipolar plates in proton exchange membrane fuel cells: Electrical properties and gas permeability, *Composite Structures*, 262 (2021).
- [2] Q. Kang, G. Zhang, Y. Liu, Z. Zhang, *Research Progress in Graphite/Resin Composite Bipolar Plate for PEMFC*, *Battery Bimonthly*, 49 (2019) 346-349.
- [3] I.A. Kinloch, J. Suhr, J. Lou, R.J. Young, P.M. Ajayan, *Composites with carbon nanotubes and graphene: An outlook*, *Science*, 362 (2018) 547-553.
- [4] L. Chunyu, R.B. Andrea, C. Stephen, S. Alejandro, *Atomistic simulations on multilayer graphene reinforced*

epoxy composites, *Composites Part A: Applied Science and Manufacturing*, 43 (2012) 1293-1300.

[5] B. Lv, Z. Shao, L. He, Y. Gou, S. Sun, A novel graphite/phenolic resin bipolar plate modified by doping carbon fibers for the application of proton exchange membrane fuel cells, *Progress in Natural Science-Materials International*, 30 (2020) 876-881.

[6] Z. Wenqing, D. Xi, S. Gang, Y. Xiaoping, Improving interfacial and mechanical properties of carbon nanotube-sized carbon fiber/epoxy composites, *Carbon*, (2019).

[7] Y. Zhang, P. Yang, Y. Sun, G. Li, X. Yang, Optimization of interfacial properties of different high modulus carbon fiber composites by tailored interphase stiffness with MWNT-EP/epoxy sizing, *Surfaces and Interfaces*, 39 (2023).

[8] H. Wang, K. Jin, C. Wang, X. Guo, Z. Chen, J. Tao, Effect of fiber surface functionalization on shear behavior at carbon fiber/epoxy interface through molecular dynamics analysis, *Composites Part A: Applied Science and Manufacturing*, 126 (2019) 105611.

[9] N. Iqbal, Y. Ali, S. Lee, Analysis of mechanical failure at the interface between graphite particles and polyvinylidene fluoride binder in lithium-ion batteries, *Journal of Power Sources*, 457 (2020) 228019.

[10] Z. Li, R.J. Young, I.A. Kinloch, Interfacial stress transfer in graphene oxide nanocomposites, *ACS Appl Mater Interfaces*, 5 (2013) 456-463.

[11] C. Yan, Y. Zhu, D. Liu, H. Xu, G. Chen, M. Chen, G. Cai, Improving interfacial adhesion and mechanical properties of carbon fiber reinforced polyamide 6 composites with environment-friendly water-based sizing agent, *Composites Part B: Engineering*, 258 (2023) 110675.

[12] J. He, L. Li, J. Zhou, J. Tian, Y. Chen, H. Zou, M. Liang, Ultra-high modulus epoxy resin reinforced by intensive hydrogen bond network: from design, synthesis, mechanism to applications, *Composites Science and Technology*, 231 (2022) 109815.

[13] D. Lu, X. Shi, J. Zhong, Interfacial bonding between graphene oxide coated carbon nanotube fiber and cement paste matrix, *Cement and Concrete Composites*, 134 (2022) 104802.

[14] X. Zhang, J. Zheng, H. Fang, Y. Zhang, S. Bai, Surface modified graphene oxide cross-linking with hydroxyl-terminated polybutadiene polyurethane: Effects on structure and properties, *Composites Part A: Applied Science and Manufacturing*, 103 (2017) 208-218.

[15] K. Şahin, N.A. Fasanella, I. Chasiotis, K.M. Lyons, B.A. Newcomb, M.G. Kamath, H.G. Chae, S. Kumar, High strength micron size carbon fibers from

polyacrylonitrile-carbon nanotube precursors, *Carbon*, 77 (2014) 442-453.

[16] A.S.K. Mohammed, R. Rateick, H. Sehitoglu, Deformation-induced microstructural evolution of fiber-matrix interface in pyrolytic carbon-carbon composites, *Acta Materialia*, 242 (2022) 118498.

[17] P. Yuan, P. Zhang, T. Liang, S. Zhai, Effects of surface functionalization on thermal and mechanical properties of graphene/polyethylene glycol composite phase change materials, *Applied Surface Science*, 485 (2019) 402-412.

[18] Y. Wang, W. Nie, L. Wang, D. Zhang, K. Niu, W. Xia, Understanding the graphene-polymer interfacial mechanical behavior via coarse-grained modeling, *Computational Materials Science*, 222 (2023).

[19] N.B. Shenogina, M. Tsige, S.S. Patnaik, S.M. Mukhopadhyay, Molecular Modeling Approach to Prediction of Thermo-Mechanical Behavior of Thermoset Polymer Networks, *Macromolecules*, 45 (2012) 5307-5315.

[20] H. Tang, J. Liu, M. Zhang, Z. Zhai, Microscale investigation on the carbon fiber surface physical properties and interfacial behavior of carbon fiber/polypropylene composites fabricated by self-resistance electric heating technique, *Polymer Composites*, (2022).

[21] L.-h. Tam, M.A. Ntjam Minkeng, D. Lau, W. Mansour, C. Wu, Molecular interfacial shearing creep behavior of carbon fiber/epoxy matrix interface under moisture condition, *Engineering Fracture Mechanics*, 282 (2023) 109177.

[22] M. Fan, J. Liu, X. Li, J. Cheng, J. Zhang, Curing behaviors and properties of an extrinsic toughened epoxy/anhydride system and an intrinsic toughened epoxy/anhydride system, *Thermochimica Acta*, 554 (2013) 39-47.

[23] M. Ochi, D. Nii, M. Harada, Preparation of epoxy/zirconia hybrid materials via in situ polymerization using zirconium alkoxide coordinated with acid anhydride, *Materials Chemistry and Physics*, 129 (2011) 424-432.