Graphene-polymer Composites for Enhancing the Mechanical Properties

Xiao Zhang1*, Jian Zheng1 and Zilong Ma2
1Shijiazhuang Campus, Army Engineering University, Shijiazhuang, 050003, China
2Huayin Ordnance Test Ctr., Huayin, 714200, China

*Corresponding author: zxleo@foxmail.com

Abstract. Graphene is widely used in the improvement of mechanical properties of composite materials due to its excellent mechanical properties. In order to more fully utilize the enhanced performance of graphene, many preparation methods have been developed and gradually improved. In this paper, the research status of graphene to improve the mechanical properties of polymer composites is reviewed. The preparation process of materials and the effects of different processes on the mechanical properties of the materials are studied.

1. Introduction
Graphene is currently the strongest material, 200 times higher than the best performing steel. The defect-free graphene has a Young's modulus of 1.0TPa and a breaking strength of 130GPa. Due to its excellent mechanical properties, graphene is widely used to enhance the mechanical properties of materials. Graphene is currently mainly used in polymer matrix composites and metal matrix composites. In this paper, the application status of graphene in improving the mechanical properties of polymer composites is reviewed. The main preparation methods and processes for improving the mechanical properties of polymer composites are summarized. The main problems are pointed out.

2. Methods
In polymer/graphene nanocomposites, the key to improving the mechanical reinforcement of graphene is improving the surface compatibility between graphene and polymer and promoting stress transfer. The covalent bond and non-covalent bond modification have improved the interface properties to a certain extent, so it has become the main research direction to improve the mechanical reinforcement of graphene. Lu [1] used molecular mechanics and molecular dynamics simulation to study the effect of chemical functional groups on the surface of graphene on the interfacial bonding properties between graphene and polymer. The results show that both energy and shear stress between graphene and polymer increase with increasing chemical modification, and it has been found that some special functional groups modified on the surface of graphene play an important role in enhancing the shear stress between graphene and polymer interface. Therefore, chemical modification of graphene surface is an effective method to enhance stress transfer between interfaces when preparing graphene/polymer composites. Wu [2] proposed an effective way to synthesize hyperbranched aromatic polyamine functionalized graphene sheets (GS-HBA) with 3,5-diaminobenzoic acid as monomer. The obtained GS-HB exhibits stable solution-like dispersibility and good compatibility with thermoplastic polyurethane. By controlling the content of GS-HBA, the mechanical properties of the composite can
be adjusted. Zhang [3] synthesized an epoxy group-containing hyperbranched polysiloxane-grafted graphene oxide (HPE-GO) by hydrolysis condensation method, and prepared HPE-GO by melt blending into DCPDCE resin. The HPE-GO/DCPDCE nanocomposite system, the addition of HPE-GO increases the impact and bending strength of the resin. Wu et al. [4] first synthesized a high fluorine content fluorinated graphene, and then used the nucleophilic substitution reaction activity of the secondary amine group on the aramid III (PA) imidazole ring to replace the fluorine in the fluorinated graphene. The atom forms a chemical bond with the graphene sheet layer, thereby achieving the purpose of fluorinated graphene grafting to enhance the mechanical properties of the PA film. Li et al. [5] prepared ethylene diamine (EDA) covalently functionalized modified graphene oxide sheets (GS-EDA)/acidified multi-walled carbon nanotubes (MWNT-COOH)/polystyrene grafting by solution-composite method. The surface structure of the filler was characterized by infrared spectroscopy and X-ray diffraction. The mechanical properties of the material were tested by tensile, impact and melt flow rate tests. It is shown that the EDA is successfully grafted onto the surface of graphene oxide, and the mechanical properties of the composite are obviously improved. Su et al. [6] prepared a thermotropic liquid crystal polymer/graphene oxide (TLCP/GO) hybrid material by solution mixing of oxidized graphene oxide with a thermotropic liquid crystal polymer, and through roll milling and extrusion. Thermotropic liquid crystal polymer/graphene oxide/phenolic resin (TLCP/GO/PF) composites were prepared by compression molding process. The effects of TLCP/GO hybrid filler content on the mechanical properties of phenolic resin composites were investigated. When the amount is low, the bending strength and flexural modulus of the composite material are significantly improved. Cano et al. [7] grafted PVA molecules onto the surface of graphene oxide by covalent modification and used to improve the mechanical properties of the composite.

3. Mechanical Properties
The improvement of mechanical properties of graphene is divided into two aspects: static mechanical properties and dynamic mechanical properties. The research on the mechanical properties of graphene/polymers mainly focuses on these two aspects. On the other hand, the creep property has also been studied.
3.1. Static and Dynamic Mechanical Properties
Numerous studies have shown that the addition of a small amount of graphene or graphene oxide can significantly improve the strength, fracture toughness and fatigue properties of polymer materials. Bao [10] selected polylactic acid (PLA), polyvinyl alcohol (PVA) and polystyrene (PS) as polymers, and studied the different interfacial interactions between graphene and these polymers. Based on GO, graphene and the different polymeric matrices, the essential relationship between the microstructure and properties of GPNC has been revealed. It is proposed that graphene can enhance the mechanical properties of polymer composites on the one hand, but at the same time block the mutual interaction between polymer chains, resulting in the reducing of the mechanical properties of the composite material. The mutual competition between the two leads to the repetition and inflection point of the polymer composite when the graphene content reaches a certain value. Zhang [11] studied the mechanism of mechanical reinforcement of graphene-carbon nanotube hybrid composites. A graphene-carbon nanotube hybrid structure reinforcement model was proposed. The molecular structure simulation method was used to study the hybrid structure/polymer. The mechanical response of composite materials under axial load and the mechanism of interface mechanics enhancement are analyzed. The mechanism of mechanical response of hybrid structures is analyzed. The effects of different structural parameters on the strength and mechanical behavior of the composites are studied. Huang et al. [12] obtained a boron cross-linked graphene oxide-polyvinyl alcohol (B-GO/PVA) film by incorporating a boron cross-linked structure into a graphene oxide-polyethylene structure, and examined it with a dynamic analyzer. Compton et al. [13] studied the stiffness characteristics of graphene oxide film and PVA/graphene oxide composite film by combining experimental, theoretical and numerical calculation methods. The effect of water molecules between interfaces was investigated. The results showed that water between molecular layers can act as a network of hydrogen bonds to enhance the stiffness of the film. Li et al. [14] established a sandwich structure model of single-layer graphene and ultra-thin polymer layer in order to study the enhancement of interface mechanical properties. The results of this model show that the significantly enhancing effect of graphene occurs in the small strain range and the interfacial shear strength of the structure is given by this method.

![Schematic of the method to create the graphene nano-sandwiches](image)

Shen et al. [15] analyzed the mechanical properties of graphene reinforced epoxy resin and epoxy resin/carbon fiber composite laminates, analyzed the ultimate tensile strength and toughness of graphene/epoxy resin, and studied the tensile fatigue strength of epoxy resin/carbon fiber composite laminate at the graphene filling mass fraction of 0.25%. Yan et al. [16] coated a thin layer of polymer
on the surface of CVD-grown graphene to form a polymer/graphene composite film, and analyzed the mechanical properties of the material. The results show that both the frictional strength and friction coefficient of the composite have been improved. Biswas et al. [17] prepared a graphene/liquid crystal polymer nanocomposite. By improving the preparation process and improving the dispersibility of graphene, the modulus is increased by 25% and 55% when the volume fraction of graphene was 1% and 5%, respectively. Gouda et al. [18] studied the effects of the synergistic effect of graphene and carbon nanotubes on the mechanical properties such as tensile strength, toughness and hardness of polymer nanocomposites.

3.2. Creep properties
At the same time, graphene can also be used to improve the inherent defects of creep deformation of polymer materials, and also has an important impact on the service life (creep recovery behavior) of polymer materials. Wang [19] systematically carried out research on creep resistance and recovery behavior of graphene modified polymer nanocomposites, on the basis of not affecting the static mechanical properties of materials and other important functional properties. Targeting two different polymer systems (thermoplastic polystyrene and elastomeric silicone rubber), graphene/polymer nanocomposites were prepared by different processes, and different nanocomposites were systematically studied, in order to improve the mechanical properties such as creep resistance and recovery of polymer materials. The creep recovery behavior under stress and temperature conditions was explored. The mechanism of interaction between graphene and polymer segments was explored. Combined with relevant theoretical models, the structure-activity relationship between viscoelastic behavior and microstructure of the composites was analyzed.

4. Conclusion
Graphene has been widely used in improving the mechanical properties of polymers, and has achieved remarkable results. The literature has shown that graphene can significantly improve the static mechanical properties, dynamic mechanical properties and creep properties of polymer composites. At the same time, the preparation process and the distribution state of graphene have an important influence on the improvement of mechanical properties.

References
[1] Lv Cheng, MD Smilation of Effects of Chemisorption on the Interfacial Bonding and Characteristics of Graphene/ploymer Composites, Master Degree Thesis, China University of Petroleum, 2011.
[2] Wu Chao, Controlled Preparation and Properties of Polymer-Based Graphene Composites, Doctor Degree Thesis, Shanghai Jiao Tong University, 2014.
[3] Zhang Mengmeng, Graphene Oxide Grafted with Hyperbranched Polymers and Its Application in Modification of Cyanate Ester Resin, Doctor Degree Thesis, Northwestern Polytechnical University, 2015.
[4] Wu Peng, Wang Huina, Li Baoyin, Wang Xu, Liu Xiangyang, Characterization of Fluorinated Graphene and Its Reinforced Aromatic Polyamide Film, Polymer Materials Science and Engineering, 2016, 32(9): 59-64.
[5] Li Jiamei, Wang Gang, Chen Lixing, Xu Yuming, Bian Jun, Lu Yun, Preparation and Mechanical Properties of Polystyrene Nanocomposites Modified Collaboratively by Functionalized Graphene Sheets and Carbon Nanotubes, China Plastics Industry, 2015, 43(4): 74-78.
[6] Su Le, Wei Chun, Fu Jun, Wang Wu, Wei Jingliang, Huang Xiaohua, Lv Jian, Study on Mechanical and Tribological Properties of TLCP/GO/PF Hybrid Composites, New Chemical Materials, 2015, 43(2): 108-110.
[7] Cano M, Khan U, Sainsbury T, O’Neill A, Wang Z M, McGovern I T, Master W K, Benito A M, Coleman J N, Improving the Mechanical Properties of Graphene Oxide Based Materials
by Covalent Attachment of Polymer Chains, Carbon, 2013, 52: 363-371.

[8] Kuila T, Kharra P, Mishra A K, Kim N H, Lee J H, Functionalized-graphene/ethylene vinyl acetate co-polymer composites for improved mechanical and thermal properties, Polymer Testing, 2012, 31: 282-289.

[9] Fang M, Wang K G, Lu H B, Yang Y L, Nutt S, Covalent polymer functionalization of graphene nanosheets and mechanical properties of composites, J. Mater. Chem., 2009, 19: 7098-7105.

[10] Bao Chenlu, Preparation, Structure and Mechanism Research of Graphene and Typical Polymer-based Nanocomposites, Doctor Degree Thesis, University of Science and Technology of China, 2012.

[11] Zhang Yong, Study on Mechanical Enhancement Mechanism of Carbon Nanotube-graphene Hybrid Reinforced Composites, Master Degree Thesis, Harbin Institute of Technology, 2016.

[12] Huang Yifu, Ruan Wenhong, Zhang Mingqiu, Rong Minzhi, Studies on the Dynamic Mechanical Properties of Boron Cross-linked Graphene Oxide-Polyvinyl Alcohol Composite, 29th Annual Academic Conference of China Chemical Society, 2014.

[13] Compton O C, Cranford S W, Putz K W, An Z, Brinson L C, Buehler M J, Nguyen S B T, Tuning the Mechanical Properties of Graphene Oxide Paper and Its Associated Polymer Nanocomposites by Controlling Cooperative Intersheet Hydrogen Bonding, ACS Nano, 2012, 6(3): 2008-2019.

[14] Li X G, Warzywoda J, McKenna G B, Mechanical Responses of a Polymer Graphene-sheet Nanosandwich, Polymer, 2014, 55: 4976-4982.

[15] Shen M Y, Chang T Y, Hsieh T H, Li Y L, Chiang C L, Yang H, Yip M C, Mechanical Properties and Tensile Fatigue of Graphene Nanoplatelets Reinforced Polymer Nanocomposites, Journal of Nanomaterials, 2013, 2013(4): 7758-7765.

[16] Yan C, Kim K S, Lee S K, Bae S H, Hong B H, Kim J H, Lee H J, Ahn J H, Mechanical and Environmental Stability of Polymer Thin-Film-Coated Graphene, ACS Nano, 2012, 6(3): 2096-2103.

[17] Biswas S, Fukushima H, Drzal L T, Mechanical and electrical property enhancement in exfoliated graphene nanoplatelet/liquid crystalline polymer nanocomposites, Composites: Part A, 2011, 42: 371-375.

[18] Gouda P S S, Kulkarni R, Kurbet S N, Jawali D, Effects of multi walled carbon nanotubes and graphene on the mechanical properties of hybrid polymer composites, Adv. Mat. Lett., 2013, 4(4): 261-270.

[19] Wang Xu, The Preparation, Creep and Recovery Behavior of Graphene-filled-polymer Nanocomposites, Master Degree Thesis, Hangzhou Normal University, 2015.