

The Comparison of Mechanical and Thermal Properties of Carbon Nanotubes and Graphene Nanosheets Enhanced Phenol-formaldehyde Resin

Xiang-Feng Wu*, Yong-Ke Zhao, Yun Zhang, Yu Zhu Wu, Yi Jin Wang, Hui Li
Chen Xu Zhang and Xin-Yue Yang

*School of Materials Science and Engineering, Hebei Provincial Key Laboratory of Traffic Engineering
Materials, Shijiazhuang Tiedao University, Shijiazhuang 050043, China.*

wuxiangfeng@stdu.edu.cn*

(Received on 3rd August 2016, accepted in revised form 11th April 2017)

Summary: Graphene nanosheets were prepared via one-pot hydrothermal process in a Teflon-lined autoclave. Moreover, the mechanical and thermal degradation behaviors of the phenol formaldehyde/carbon nanotubes and phenol formaldehyde/graphene nanosheets composites were discussed. Experimental results showed that the graphene nanosheets possessed better performances than that of carbon nanotubes. When the filler loading was 0.6wt%, tensile strength, Young's modulus, compressive strength and modulus of the as-prepared composites reached their maximum values, which were increased by 77.0, 141.3, 109.1 and 114.8% for graphene nanosheets and 54.7, 85.9, 61.7 and 45.2% for carbon nanotubes than those of pure sample, respectively. In addition, both of these two carbon materials could increase the thermo-stability of the matrix. When their usage amount was 0.6wt%, the thermal degradation temperature (at 10% weight loss) was increased to 255.6°C for phenol formaldehyde/graphene nanosheets composites and 253.5°C for phenol formaldehyde/carbon nanotubes composites from 233.6°C for pure sample.

Key words: Phenol formaldehyde; Carbon nanotubes; Graphene nanosheets; Mechanical properties; Thermal degradation

Introduction

In recent years, carbon materials, such as carbon nanotubes (CNT) and graphene nanosheets (GNS), have attracted much attention due to their high specific surface, excellent mechanical, thermal and electrical performances [1, 2]. Polymer/carbon composites have potential applications in the fields of emission displays, chemical sensors, semi-conductor devices, interconnects and structural materials [3, 4]. However, because of the quantum size and aggregation effects, the dispersion of the nanosized fillers has great influences in their enhancing roles [5]. Scientists begin to pay close attention to the "dimension effect" of the nano-meter materials [6, 7]. Starkova [8] fabricated the epoxy composites filled with thermally reduced graphene oxide (RGO) and multi-wall carbon nanotubes (MWCNT). Experimental results showed that the improvement of thermo-mechanical properties of neat epoxy from the addition of RGO is higher than those achieved by incorporating MWCNT. Despite the high interests to investigations of the basic physical/chemical properties of polymer composites reinforced with CNT and GNS [9, 10], the different enhancing mechanism of carbon fillers still cannot be explained clearly.

Phenol formaldehyde (PF) resin is a typical polymer, which can be divided as thermoplastic and thermosetting resins according to different synthesis conditions. It is widely used in the fields of aerospace,

cars, electronics, national defense industry and so on. Because it possesses some obvious advantages, such as low cost, simple production technologies and equipment, excellent heat resistance, cold resistance, dimensional stability and smoke resistance [11, 12]. However, the poor toughness and weak strength limit its further development in industry [13]. Hence, the PF composites with excellent integrated properties have become a hot research topic [14, 15].

GNS would be fabricated via one-pot strategy in a Teflon-lined autoclave in this work. In order to improve the mechanical and thermo-stability of the PF matrix, the CNT and the as-prepared GNS were adopted to fabricate polymer composites, and the related properties of the as-prepared polymer composites were discussed. Moreover, the mechanism of the CNT and the as-prepared GNS enhancing the properties of the matrix were also investigated.

Experimental

Materials

The multi-walled CNT (CNT, diameter: 10~20nm, length: 10~30 μ m, ρ : 0.22g cm⁻³), containing 2wt% carboxyl groups, were purchased from Chengdu Organic Chemicals Co., Ltd, China. PF resin and alkaline hardener were supplied by Jinan Sheng Quan Co., Ltd., China. Graphite flakes

*To whom all correspondence should be addressed.

(325 mesh) were purchased from Alfa Aesar Co., Ltd, Tianjin, China. Potassium permanganate (KMnO_4), concentrated sulfuric acid (H_2SO_4 , 98wt%), hydrogen peroxide (H_2O_2 , 30wt%), ethanol and acetone were obtained from Sinopharm Chemical Reagent Co., Ltd, China. All of these reagents were of analytical grade.

Preparation of the GNS

Typically, 0.5g graphite flake was mixed with 40ml concentrated H_2SO_4 in a 100ml Teflon-lined autoclave. The mixture was then subjected to stirring for 30min under ice bath, with a speed of 300rpm. Then 2.5g KMnO_4 was added within 30min. The autoclave was sealed and placed in an oven for 2h, in which the temperature was set at 155°C . The as-obtained intermediates were poured into 300ml deionized water under mild stirring, followed by addition of 30ml H_2O_2 . In order to remove the impurities in these samples, these mixtures were repeatedly rinsed with deionized water until the $\text{pH}\approx 7$. The neutralized intermediates were subjected to ultra-sonication (325W) for 30min and filtered by through $0.22\mu\text{m}$ Poly Tetra Fluoro Ethylene (PTFE) membrane. Finally, the filter cakes were dried in the vacuum oven at 60°C for 48h.

Preparation of the PF/CNT and PF/GNS Composites

The fabrication procedure of the PF/CNT and PF/GNS composites was shown in Fig. 1. A certain amount of CNT and the as-prepared GNS were scattered in 100mL acetone by through sonication (500W), respectively. Then a total weight of 50g PF resin was added into the above solution. Full stirring was adopted and the temperature was kept at 80°C until the acetone was completely evaporated. The fillers loading of the PF/CNT or PF/GNS composites was 0, 0.3, 0.6 or 0.9wt% based on the weight of the PF resin. Subsequently, 5g

hardener (the weight ratio of the hardening to PF resin was 1:5), was added into the mixture. Then, the intermediate product was poured into a metal mould at 30°C for pre-curing 15min and at 100°C for post-curing 2h. A control sample (pure PF) was fabricated via the same method without using carbon materials.

Characterization

For morphological observation, the CNT and the as-prepared GNS were dispersed into ethyl alcohol by through sonication, loaded on a micro-grid and then observed by transmission electrical microscopy (TEM, Model: JEM-2100, JEOL Co., Japan) with an accelerating voltage of 200KV. The crystal structures of the CNT and the as-prepared GNS were characterized by using X-ray diffraction (XRD, Model: D8ADVANCE, Bruker Co., Germany) with $\text{Cu-K}\alpha$ radiation at a scanning rate of $4^\circ \cdot \text{min}^{-1}$ in a 2θ range from 10 to 80° . The functional groups analysis of the CNT and the as-prepared GNS were carried out by using Fourier transform infrared spectroscopy (FTIR, Model: Nicolet Avatar 330, Thermo Electron Co., USA). The scanning range was selected from 500 to 4000cm^{-1} .

The tensile and the compressive properties of the samples were characterized on a universal testing machine (Model: M350-20KN, Xin San Si Co., China) according to the standards of GB/T2568-1995 and GB/T2569-1995, respectively.

The thermal stability of the as-prepared composites was characterized via thermo-gravimetric analysis (TGA, Model: TGA/SDTA 8H $^\circ$, Mettler Toledo Co., Switzerland) at a scanning rate of $20^\circ\text{C} \cdot \text{min}^{-1}$ from 50 to 800°C under the protection of argon.

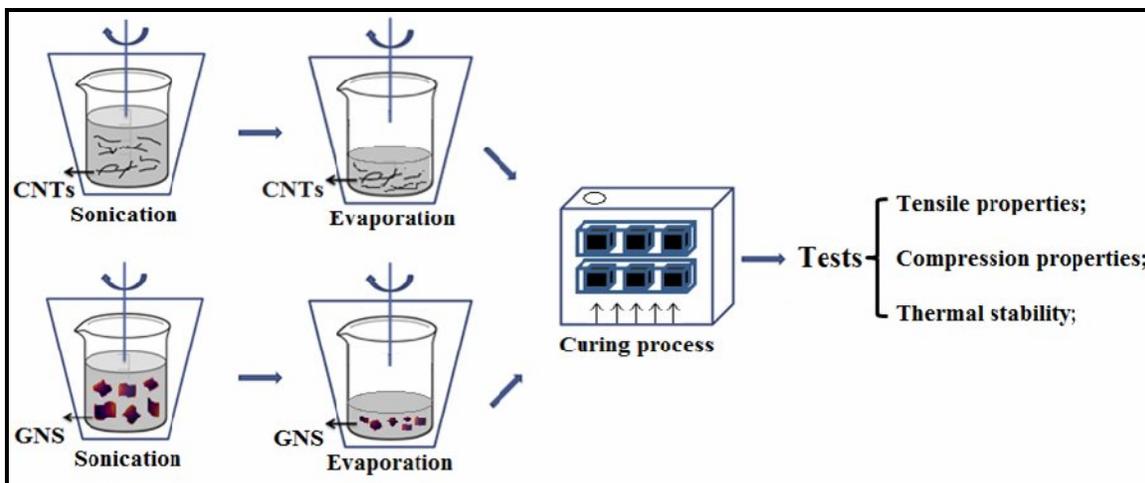


Fig. 1: Fabrication and characterization of the PF/CNT and PF/GNS composites.

Results and Discussion

TEM

Fig. 2 shows the micrographs of CNT (a) and the as-prepared GNS (b). It can be clearly seen that the CNT presented a typical tubular structure and had a narrow diameter ranging from 10 to 20nm. Moreover, the as-prepared GNS possessed 2-dimension structure with several micrometers scale, wrinkled and fluctuant edges. According to previous report [16], this meant that both of them possessed large specific surface area. It would be beneficial to improve the mechanical and thermal properties of the PF matrix.

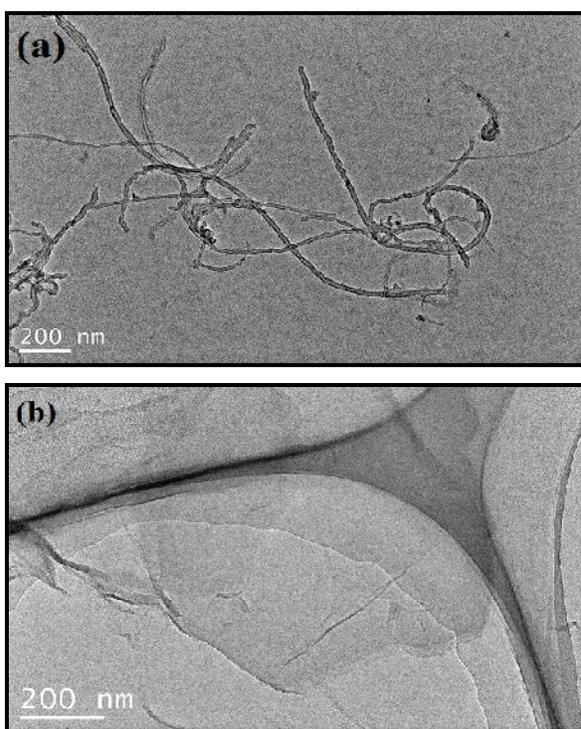


Fig. 2: TEM images of the CNT (a) and the as-prepared GNS (b).

XRD

XRD was used to evaluate the structure of CNT and the as-prepared GNS, and the results are shown in Fig. 3. It can be seen in Fig. 3(a) that there were two characteristic diffraction peaks at 25.6° and 42.8° , which were in accord with the CNT. The result also indicated that CNT exhibited high graphitization degree [17]. Moreover, in Fig. 3(b), the as-prepared GNS exhibited one broad diffraction peak at 23.5° and a weak peak at 42.8° , indicating that the layers of the as-prepared GNS were looser than that of the pristine graphite [18, 19].

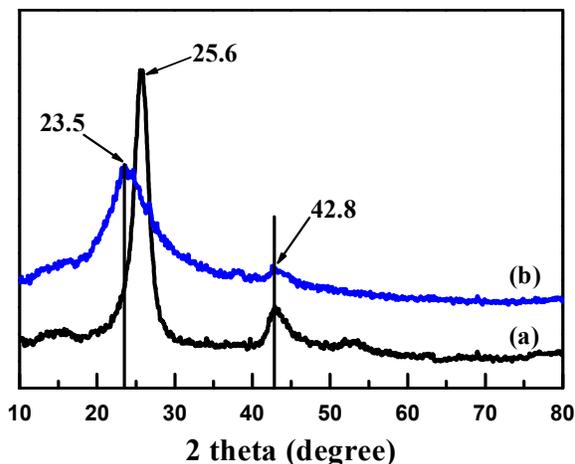


Fig. 3: XRD spectra of the CNT (a) and the as-prepared GNS (b).

FTIR

Fig. 4 shows the FTIR spectra of CNT (a) and the as-prepared GNS (b). In Fig. 4(a), there were two peaks at about 1743 and 1667cm^{-1} , corresponding to the stretching vibration of C=O. Moreover, a peak at 1184cm^{-1} was found. This peak could be ascribed the stretching vibration of C-O [20, 21]. In Fig. 4(b), two peaks at 1717 and 1215cm^{-1} were found. They were attributed to the stretching vibration of C=O and C-O-C. In addition, a visible peak was found at 1571cm^{-1} , which was assigned to the C=C of GNS layer. Few hydroxyl groups were found at about 3400cm^{-1} . This indicated that the conjugated structure was partly recovered during high temperature treatment. These functional groups would be helpful to improve the interface bonding between the inorganic fillers and PF matrix.

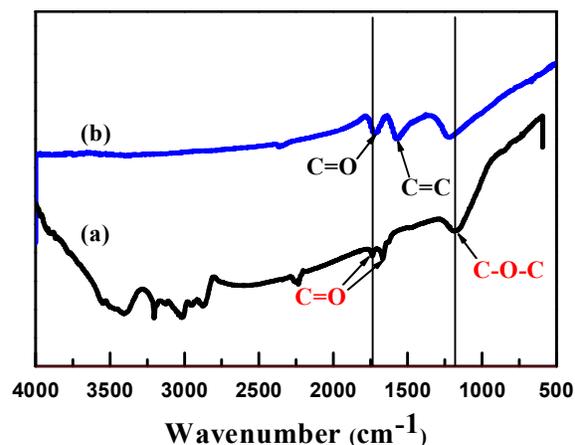


Fig. 4: FTIR spectra of the CNT (a) and the as-prepared GNS (b).

Tensile Properties

Fig. 5 shows the tensile properties for the PF/CNT (a) and PF/GNS (b) composites. It can be seen that the as-prepared GNS possessed better performance than that of the CNT. Moreover, the tensile strength and Young's modulus of all the samples increased first and then decreased with increasing of the filler loading. When the filler loading was 0.6wt%, tensile strength and Young's modulus of all the as-prepared composites reached their maximum values, which were increased by 77.0 and 141.3% for the as-prepared GNS and 54.7 and 85.9% for CNT than that of pure sample, respectively.

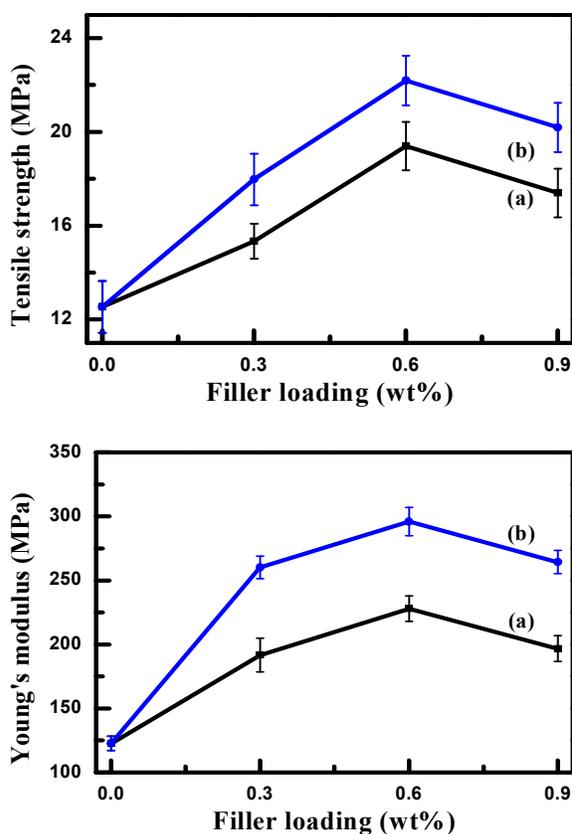


Fig. 5: Tensile strength and Young's modulus of the PF/CNT (a) PF/GNS (b) composites.

These results suggested that both of CNT and GNS could improve tensile properties of the PF matrix. It could be explained by that the carbon nanomaterials possess excellent specific surface area and mechanical strength [22]. Moreover, the as-prepared GNS possessed better enhancement effects and consumed more energy than that of CNT due to the 2-dimensional structure. It possessed larger contact area than that of CNT. In addition, the planar

geometry for the as-prepared GNS could result in better mechanical interlocking between the GNS and the polymer chains [23]. In addition, fillers aggregation might occur if the usage amount of fillers were excessive. The tensile properties of the as-prepared composites would also be affected adversely.

Compression Properties

Fig. 6 shows the compression properties of the PF/CNT (a) and PF/GNS (b) composites. It can be observed that the compressive strength and modulus of the as-prepared samples showed similar patterns as in Fig. 5. That was because that the as-prepared GNS possessed better performances than that of the CNT. When the usage amount of the filler was 0.6wt%, the compressive strength and modulus of all the as-prepared composites reached their maximum values. They were increased by 109.1 and 114.8% for the as-prepared GNS and 61.7 and 45.2% for CNT than that of pure sample, respectively.

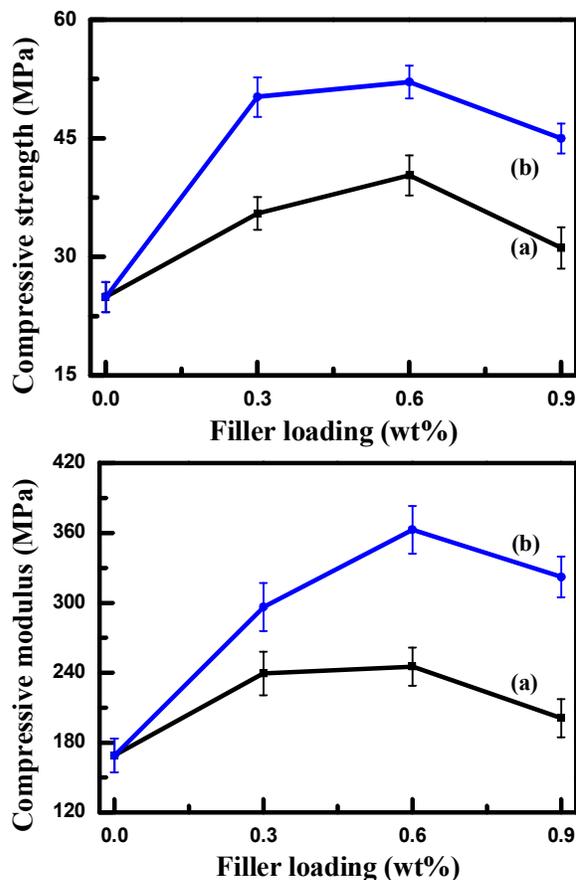


Fig. 6: Compressive strength and modulus of the PF/CNT (a) and PF/GNS (b) composites.

This phenomenon could be explained by two points: (1) the as-prepared GNS, with 2-dimensional structure, possessed larger specific surface area than that of CNT, with 1-dimensional structure. It was in favor of increasing the contact surface between the GNS and the matrix; (2) the as-prepared GNS possessed wrinkled and fluctuant edges (as shown in Fig. 2), which would result in better mechanical interlocking between the fillers and polymer phase [23]. However, aggregations might occur and the compressive properties of the composites would be adversely affected if the filler loading was excessive.

Thermal Properties

Fig. 7 shows the thermal decomposition behaviors of the pure PF (a), PF/CNT (b) and PF/GNS (c) composites. In Fig. 7, there are three stages. The first stage (before 200°C) could be ascribed to volatilization of the remaining H₂O, acetone and unreacted oligomers. The second stage (around from ~200 to 500°C) was attributed to the broken of the polymer network. The third stage (from 500 to 800°C) was due to the degradation of forming carbon layers. According to the illustration, it can be observed that, when the filler loading was 0.6wt%, the thermal degradation temperature (at 10% weight loss) was increased to 255.6°C for PF/GNS composites and 253.5°C for PF/CNT from 233.6°C for pure PF. It can also be seen that the residual carbon content of the as-prepared PF/GNS composites were higher than that of the PF/CNT composites and pure PF.

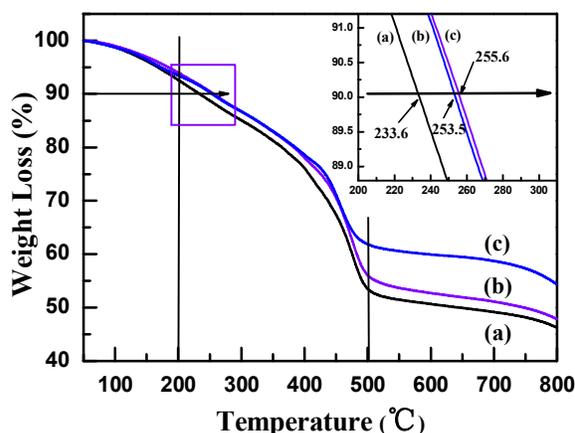


Fig. 7 TGA spectra of the pure PF (a), PF/CNT (b) and PF/GNS (c) composites (The filler loading was 0.6wt%).

These results indicated that both of the CNT and the as-prepared GNS could improve the thermal

stability of the PF matrix. It might be caused by their large specific surface area, so-called “free radical trapping” and “tortuous path” effects [24, 25]. Moreover, these two carbon fillers, especially in the as-prepared GNS, possessed high heat resistance. Hence, they would limit the degradation of the products.

Conclusion

In summary, GNS were prepared via one-pot hydrothermal process in a Teflon-lined autoclave. The comparison of mechanical and thermal properties of the PF/CNT and PF/GNS composites was also discussed. Experimental results indicated that appropriate usage amount of the CNT or the as-prepared GNS could improve the tensile and compressive properties of the PF. When the filler loading was 0.6wt%, the tensile strength, Young’s modulus, compressive strength and modulus reached their maximum values, which were increased by 77.0, 141.3, 109.1 and 114.8% for PF/GNS and 54.7, 85.9, 61.7 and 45.2% for PF/CNT than those for pure PF, respectively. Moreover, the thermal degradation temperature (at 10% weight loss) and the residual carbon content of the as-prepared composites were higher than that of pure PF, and the as-prepared GNS showed better enhancing effects than that of the CNT.

Acknowledgements

The authors gratefully acknowledge the financial support from Youth Science and Technology Foundation of Higher Education Institutions of Hebei Province, China (Grant No: Q2012111), Natural Science Foundation of Hebei Province, China (Grant No: E2013210011).

References

1. Z. Spitalsky, D. Tasis, K. Papagelis and C. Galiotis. Carbon Nanotube-Polymer Composites: Chemistry, Processing, Mechanical and Electrical Properties. *Prog. Polym. Sci.*, **35**, 357 (2010).
2. Y. Q. Sun and G. Q. Shi. Graphene/Polymer Composites for Energy Applications. *J. Polym. Sci. Pol. Phys.*, **51**, 231 (2013).
3. Q. B. Zheng, Z. G. Li, J. H. Yang and J. K. Kim. Graphene Oxide-Based Transparent Conductive Films. *Prog. Mater. Sci.*, **64**, 200 (2014).
4. L. X. He and S. C. Tjong. Carbon Nanotube/Epoxy Resin Composite: Correlation between State of Nanotube Dispersion and Zener Tunneling Parameters. *Synthetic Met.*, **162**, 2277

- (2012).
- S. K. Yadav and J. W. Cho. Functionalized Graphene Nanoplatelets for Enhanced Mechanical and Thermal Properties of Polyurethane Nanocomposites. *Appl. Surf. Sci.*, **266**, 360 (2013).
 - J. H. Du, L. Zhao, Y. Zeng, L. L. Zhang, F. Li, P. F. Liu and C. Liu. Comparison of Electrical Properties Between Multi-walled Carbon Nanotube and Graphene Nanosheet/High Density Polyethylene Composites with a Segregated Network Structure. *Carbon*, **49**, 1094 (2011).
 - M. E. Achaby and A. Qaiss. Processing and Properties of Polyethylene Reinforced by Graphene Nanosheets and Carbon Nanotubes. *Mater. Design*, **44**, 81 (2013).
 - O. Starkova, S. Chandrasekaran, L. A. S. A. Prado, F. Tölle, R. Mülhaupt and K. Schulte. Hydrothermally Resistant Thermally Reduced Graphene Oxide and Multi-wall Carbon Nanotube Based Epoxy Nanocomposites. *Polym. Degrad. Stabil.*, **98**, 519 (2013).
 - A. G. D'Aloia, F. Marra, A. Tamburrano, G. D. Bellis and M. S. Sarto. Electromagnetic Absorbing Properties of Graphene-Polymer Composite Shields. *Carbon*, **73**, 175 (2014).
 - M. Martin-Gallego, M. M. Bernal, M. Hernandez, R. Verdejo and M. A. Lopez-Manchado. Comparison of Filler Percolation and Mechanical Properties in Graphene and Carbon Nanotubes Filled Epoxy Nanocomposites. *Eur. Polym. J.*, **49**, 1347 (2013).
 - A. Zmihorska-Gotfryd. Coating Compositions Based on Modified Phenol-Formaldehyde Resin and Urethane Prepolymers. *Prog. Org. Coat.*, **49**, 109 (2004).
 - A. S. Hussein, K. I. Ibrahim and K. M. Abdulla. Tannin-Phenol Formaldehyde Resins as Binders for Cellulosic Fibers: Mechanical Properties. *Nat. Resour.*, **2**, 98 (2011).
 - H. Ku, D. Rogers, R. Davey, F. Cardona and M. Trada. Fracture Toughness of Phenol Formaldehyde Composites: Pilot Study. *J. Mater. Eng. Perfor.*, **17**, 85 (2008).
 - Q. Fang, H. W. Cui and G. B. Du. Montmorillonite Reinforced Phenol Formaldehyde Resin: Preparation, Characterization, and Application in Wood Bonding. *Int. J. Adhes. Adhes.*, **49**, 33 (2014).
 - D. Yan, X. F. Li, Y. Jiang, H. B. Zhang, B. B. Jia, H. L. Ma and Z. Z. Yu. Thermally Conductive Phenol Formaldehyde Composites Filled with Carbon Fillers. *Mater. Lett.*, **118**, 212 (2014).
 - 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).
 - D. Eder and A. H. Windle. Morphology Control of CNT-TiO₂ Hybrid Materials and Rutile Nanotubes. *J. Mater. Chem.*, **18**, 2036 (2008).
 - C. L. Zhang, Y. X. Yuan, S. M. Zhang, Y. H. Wang and Z. H. Liu. Biosensing Platform Based on Fluorescence Resonance Energy Transfer from Upconverting Nanocrystals to Graphene Oxide. *Angew. Chem. Int. Edit.*, **50**, 6851 (2011).
 - D. I. Son, B. W. Kwon, H. H. Kim, D. H. Park, B. Angadi and W. K. Choi. Chemical Exfoliation of Pure Graphene Sheets from Synthesized ZnO-Graphene Quasi Core-Shell Quantum Dots. *Carbon*, **59**, 289 (2013).
 - P. C. Ma, S. Y. Mo, B. Z. Tang and J. K. Kim. Dispersion, Interfacial Interaction and Re-Agglomeration of Functionalized Carbon Nanotubes in Epoxy Composites. *Carbon*, **48**, 1824 (2010).
 - L. J. Cui, H. Z. Geng, W. Y. Wang, L. T. Chen and J. Gao. Functionalization of Multi-wall Carbon Nanotubes to Reduce the Coefficient of the Friction and Improve the Wear Resistance of Multi-wall Carbon Nanotube/Epoxy Composites. *Carbon*, **54**, 277 (2013).
 - A. Rahaman and A. Mohanty. Effect of Carbon Nanotubes on the Curing and Thermomechanical Behavior of Epoxy/Carbon Nanotubes Composites. *Polym. Composite.*, **25**, 441 (2014).
 - M. Martin-Gallego, M. Hernandez, V. Lorenzo, R. Verdejo and M. A. Lopez-Manchado. Cationic Photocured Epoxy Nanocomposites Filled with Different Carbon Fillers. *Polymer*, **53**, 1831 (2012).
 - Y. Q. Guo, C. L. Bao, L. Song, B. H. Yuan and Y. Hu. *In situ* Polymerization of Graphene, Graphite Oxide, and Functionalized Graphite Oxide into Epoxy Resin and Comparison Study of No-The-Flame Behavior. *Ind. Eng. Chem. Res.*, **50**, 7772 (2011).
 - Y. W. Cao, J. C. Feng and P. Y. Wu. Preparation of Organically Dispersible Graphene Nanosheet Powders Through A Lyophilization Method and Their Poly(lactic acid) Composites. *Carbon*, **48**, 3834 (2010).