# REINFORCEMENT ON EPOXY-BASED COMPOSITES BY DOPAMINE-COATED GRAPHENE PREPARED THROUGH HIGH ENERGY BALL-MILLING

Runting Wang, Shujie Ren, Rongrong Xie, Wengang Yang, Xiaolong Jia*, Xiaoping Yang

State Key Laboratory of Organic-Inorganic Composites, College of Materials Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, P. R. China

Email: jiaxl@mail.buct.edu.cn

**Keywords:** Graphene, Composites, Dopamine, Ball-millng

## ABSTRACT

Simultaneous preparation of edge-carboxylated (ECG) and dopamine-coated graphene (pDA-ECG) through high energy ball-milling was investigated in details. The graphene with carboxylated edge was successfully fabricated via high energy ball-milling method in the presence of dry ice to create a high pressure environment. Meanwhile, the induced dopamine in the ball-milling system self-assembled and subsequently reacted with carboxyl groups in the edge of the graphene at a alkalescence condition (pH=8.5). As a result, the dopamine-coated graphene (pDA-ECG) was obtained. Benefiting from the universal binding ability of polydopamine, good dispersion of pDA-ECG in epoxy matrix was able to be achieved as the content of pDA-ECG being below 0.2 wt.%. Curing kinetics of epoxy composites with pDA-ECG were systematically studied by non-isothermal differential scanning calorimetry (DSC). Compared to the systems of neat epoxy or epoxy composites containing GO, epoxy composites loaded with pDA-ECG showed lower activation energy ($E_\alpha$) over the range of cure ($\alpha$). It revealed that the amino-bearing pDA-ECG was able to react with epoxy matrix and enhance the curing reactions as an amine-type curing agent. The nature of the interactions at GO-epoxy interface was further evaluated by Raman spectroscopy, confirming the occurrence of chemical bonding. The strengthened interfacial adhesion between pDA-ECG and epoxy matrix thus enhanced the effective stress transfer in the composites. Accordingly, the tensile and flexural properties of EP/pDA-ECG composites were enhanced due to both the well dispersion and strong interfacial bonding of pDA-ECG in epoxy matrix.

## 1 INTRODUCTION

As a newly 2D carbon nanomaterials, graphene has attracted great attention in scientific and engineering because of the excellent mechanical, photological, thermal and electrical properties.[1] The special two-dimensional sp2 carbon atoms' honeycomb structure allows the extra electron moved freely,the size of nanoscale makes graphene can influence greatly in many properties with a low filler content in composite materials. The fabrication of high quality graphene has been achieved, but how to produce high quality graphene in a large-scale is still a difficult problem. The graphene can be produced by mechanical exfoliation, epitaxial growth on SiC, chemical vapor deposition (CVD), the Hummers method of oxidization-redution graphite oxide (GO). Although the mechanical exfoliation method can produce the high quality graphene, but it is impossible to achieve the large-scale preparation because of the technique difficulties. The epitaxial growth on SiC and chemical vapor deposition (CVD) need expensive instrument and equipment, the processes of CVD is also very complicated. The Hummers method of oxidization-redution graphite is widely used in large-scale and laboratory produce, though the strong oxidizing reagent destroy the layer-to-layer structure of graphite, generated the oxygen containing group on graphite basal plane. It is inevitable to cause a large number of structure defects in final graphene product. The complicate precesses and involves a lot of hazardous oxidization-redution reagents, but only capture the graphene with many defects finally.[2]

Here, we introduced a novel approach to achieve the simultaneous preparation of edge-carboxylated (ECG) and dopamine-coated graphene (pDA-ECG) through ball-milling. The ball-

milling can provide enormous energy through the rub and impact of stainless steel ball. The dry ice is put into the ball-milling capsule to create a high pressure environment that filled with carbon dioxide(CO2),[3] high pressure ball-milling provide more energy. Compared with Hummer method which using the strong oxidizing reagents provided uncontrollable reaction energy that destroy the integrity of graphene structure, the high pressure ball-milling's reaction energy can only react with edge of graphene, because of the edge is more active than the basal plane in graphene structure.[4-5] In ball-milling system, the graphite peeled off as same as the dopamine self-assembled. High energy and pressure environment broken the large area, thickness size graphite into small size, but the thickness would not change much, because the layer to layer energy is much higher, but in this procedure, the edge of graphite structure opened and captured carbon dioxide which volatilized through dry ice. Then buffer solution was induced, strong polarity groups of carboxyl tend to repel each other to effectively open up the edges of graphite, at the same time, dopamine could react with carboxyl groups and self-assembled uniformly around graphene. In our study, we found the grapheme, generated by high energy and pressure ball-milling, presented a special circular shape micro-structure, which can react with dopamine uniformly and controllable.

## 2 EXPERIMENTAL SECTION

### 2.1 Facility and Materials

The planetary ball-milling mechine was using from Droide instrument and equipment Co.Ltd of Shanghai, the stainless steel ball-milling capsule's volume of is 100mL. Graphite was purchased from Weisi Chemical Co.Ltd. Dry ice was obtained from The vigour dry ice company of Beijing. Dopamine hydrochloride and tri(hydroxymethyl) aminomethane (Tris) were purchased from Sigma. The T800 carbon fiber was using Toray T800H-12K, Japan. The resin matrix, diglycidyl ether of bisphenolA (DGEBA) type epoxy resin (EP value, 0.51), was supplied by ShellCo. The diluter, diglycidyl ether of butanediol (EP value, 0.65− 0.75) was synthesized by authors for the purpose to reduce the viscosity of DGEBA resin. The curing agent, DETDA (composed of 74− 80 wt % 3,5-diethyltoluene-2,4-diamine and 20− 26 wt.% 3,5-diethyltoluene-2,6-diamine, Ahew 44.3), was obtained from Lonza (Switzerland).All other chemicals and reagents were purchased from Beijing Chemical Works (China) and used directly.

### 2.2 Sample preparation


Fig.1 Schematic for the preparation of ECG

Referring to our previous works, the schematic preparation of ECG is shown in Fig.1. Firstly, 1g graphite and 0.25g, 0.5g, 1g dopamine were put into the ball-milling capsule, according to our past experience, the ratio of stainless steel balls to materials was controlled. Then, the dry ice was filled in residual space of ball-milling capsule with different weight to provide oxygen-containing carbon source and pressure, it's crucial to seal off the ball-milling capsule quickly and ensured tightness. During the ball-milling process, the rub and impact of ball-milling caused temperature and pressure rising. After 600rpm ball-milling treated for 48h continuous, we should open air valve carefully and

wait carbon dioxide released slowly, the temperature would rise to nearly 60℃ when speed of revolution was 600rpm, and the temperature decreased rapidly when released carbon dioxide.

In this procedure, the large area graphite was broken into pieces and the edge of pieces would react with carbon dioxide to generate carboxyl, but the thickness of graphite was not change much, the layer to layer force was stronger than the graphene part broke into pieces.

Then 15mL buffer solution (which pH is 8.5) and same weight of dry ice to ensure accordant pressure were added, another 24h ball-milling treated. The final products need to washed by DI water because the p-ECG is hydrophil and can disperse in water symmetrically, and through sonication and centrifugation to remove the large flakes graphene which was unpeeled, collect supernatant and dialysis of one day to remove unreacted dopamine molecules, followed by freeze-dry to obtain the p-ECG powders.

### 2.3 preparation

The ECG and p-ECG were dispersed into diluter partly for 24h at room temperature, followed by ultrasonication under ice bath to form a masterbatch. Then, epoxy mixtures were obtained by mixing epoxy resin, DETDA, diluter/ECG or p-ECG masterbatch and other agent. The EP/ECG or p-ECG composites were prepared by pouring epoxy mixtures into molds and curing at 80℃/1h+120℃/2h+150℃/3h as described in our previous works. To guarantee the uniformly of the obtained composites, the gelation time of epoxy matrix was adjusted to be around 0.5h by setting the weight ratio of epoxy resin, diluter, curing agent and accelerator as 70:30:30:3. The content of ECG and p-ECG in composites were adjusted to be 0, 0.1, 0.2, or 0.5wt% of the total weight of organic epoxy matrix.

Before preparation of the p-ECG coated fibers, the p-ECG powder was dispersed in de-ionized water by ultrasonication(bath sonicator, sonic power 100W, sonic frequency 80 kHz) for 3 h to obtain the stable suspension at a concentration of 0.05wt%. Then, the carbon fiber bundles were immersed in a bath containing the suspension for 20 min, and were dried at 70 C° for 2h, followed by drying at 120 C° for 2h. The procedure of production of the p-ECG coated fibers is illustrated in Fig. 1.

In order to increase the content of p-ECG in the aqueous suspension, another p-ECG-suspension was prepared, which contained a kind of non-ionic surfactant polyoxyethylene octyl phenyl ether (Triton X-100, supplied by Shantou Xilong Chemical Factory) with the weight ratio of 5:1 to p-ECG. This surfactant has been used to disperse p-ECG in epoxy resin, and the maximum content of p-ECG in de-ionized water containing Triton X-100 is 0.3 wt.% in our laboratory. The process of production of the CNT-coated fibers using Triton X-100 is the same as that without Triton X-100.

Like the sizing and the spraying methods mentioned, our route of depositing functionalized p-ECG is also undamaged for fiber and the process is not complex. Moreover, this method does not need to remove industrial sizing and the deposition process can be used for various types of carbon fiber reinforcements, such as yarn, fabric and preform.

### 2.4 Characterization

Chemical structure of ECG and p-ECG were studied by Fourier transform infrared(FTIR) spectroscopy. The edge-carboxylated and existence of pDA were identified by X-ray photoelectron spectroscopy(XPS) using a Theta Probe AR-XPS System (VG ESCALAB MKII spectrometer) equipped with a monochromatic Mg Kα (hv = 1486.6 eV) source at a power of 150W. Raman spectra were characterized by using a LabRAM HR microspectrometer (Horiba jobin Yvon) with 514 nm laser excitation. Micro-structure was investigated by scanning electron microscopy (SEM, JEOL JSM-5800) observation and transmission electron microscopy (TEM, JEOL JEM-1010) analyses. The thickness of paper structure was characterized by AFM.Thermal stability was measured by thermogravimetric analysis (TGA, Mettler Toledo TGA/DSC1).

## 3.RESULTS AND DISCUSSION

### 3.1 The analysis of p-ECG

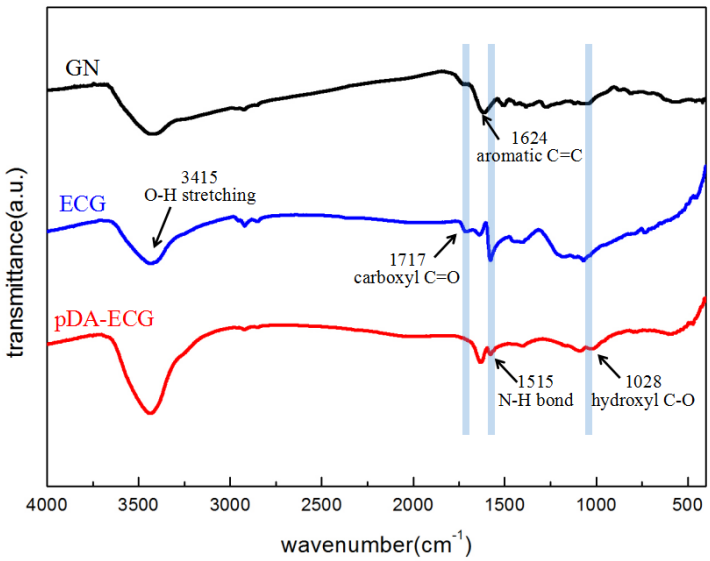


Fig.2 FTIR curves of GN, ECG, p-ECG

As shown in Fig.2, we observed in FTIR spectrum that GN has a strong 1624cm$^{-1}$ C=C stretching peak, the characteristic peaks of 1717cm$^{-1}$ carboxyl C=O stretching can be easily observed in ECG, it means carboxyl has produced in the edge of graphene, and there were no other oxygen groups peaks such as hydroxy groups or epoxy groups in the ECG. The 1515cm$^{-1}$ N-H stretching peak was appeared in p-ECG means the dopamine modified the ECG successfully through reacted with the carboxyl groups in the edge of graphene.

### 3.2 Formation mechanism of circular-like p-ECG

The pressure is critical factor which influenced the productivity and quality of circular graphene. With the weight of dry ice increased, the pressure magnified but limited by temperature, the rub and impact of ball-milling system would create much heat to raise the temperature in capsule. The pressure reached nearly 12Mpa when system temperature was 60℃. In conclusion, we need to increase the speed of revolution and continuity ball-milling time to preserve stable temperature and higher pressure.

Put enough dry ice into ball-milling system which can ensure the high pressure environment and there were still dry ice can adsorbed graphite powders, it avoided graphite powders adsorbing by the wall and floor of stainless steel capsule which can't be robbed uniformly.

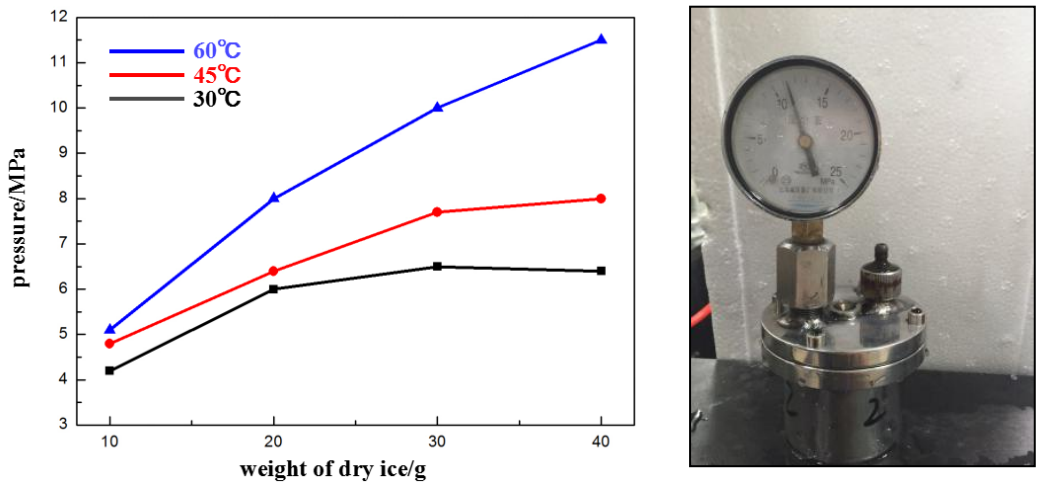


Fig.3 Weight-pressure curves in different temperature

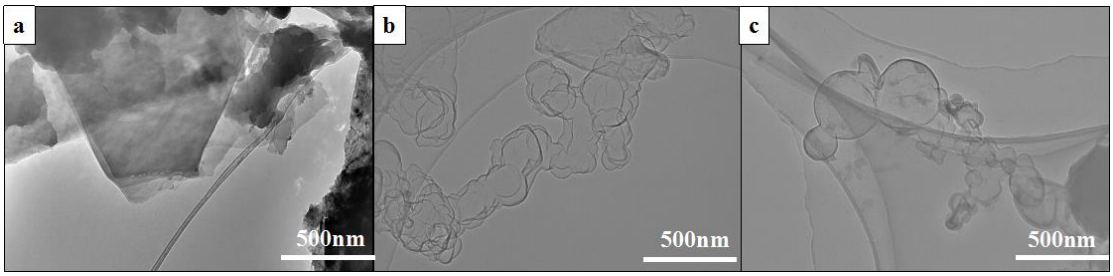


Fig.4 TEM Morphology of ECG in low pressure 0-5MPa(a), medium pressure 5-8MPa and high pressure 8-12MPa

With the pressure increased, the micro-structure of ECG edges tend to be smooth, when the rotation rate of ball-milling system was 600rpm, the rub heat made temperature of capsule to nearly 60℃ and through PV=nRT the pressure increased with temperature to 11.5MPa, the micro-structure of ECG with circular structure was obtained.

### 3.3 Reinforcement on epoxy composites

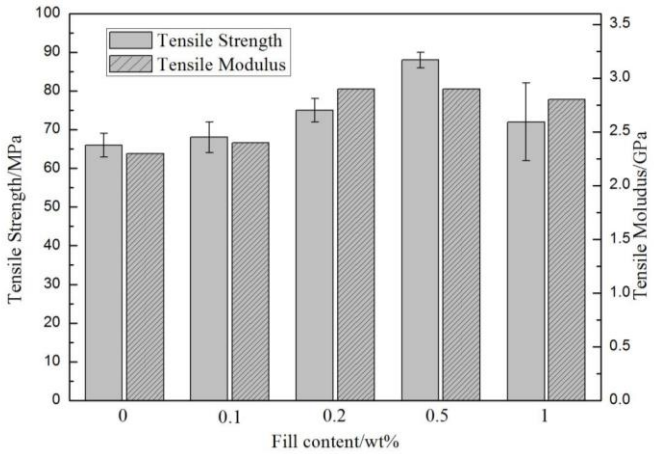


Fig.5 Tensile properties of epoxy composites with various contents of p-ECG

As shown in Fig.5, the p-ECG displayed reinforcement effect on epoxy composites in relating to its intrinsically remarkable mechanical strength. With the content of p-ECG increased, the mechanical properties improved when 0.5wt% get best. While the epoxy composites reinforced with p-ECG demonstrated significantly higher tensile properties than those composites. Similar to literature reports, these enhancements in mechanical properties with incorporation of pDA surface layer onto graphene sheets were ascribed to the strengthened interfacial adhesion between graphene and epoxy matrix. Deductively, the dispersion of p-ECG in epoxy composites should also be ameliorated. This was a common phenomenon in many publications relating to nanofillers. Even the interfacial adhesion being improved, p-ECG sheets might stack together due to their large specific surface area, which caused insufficient impregnation of epoxy resin into the p-ECG layers.

## 4 CONCLUSIONS

Through high pressure and energy ball-milling successfully fabricated the dopamine modified graphene with special circular shape, which made dopamine grafting uniformly to obtained structure in controlled materials. The p-ECG which grafted uniformly showed better thermal stability, dispersity and mechanical property in composite materials. The method for fabricating p-ECG is simple and eco-friendly at a low cost, by using the graphite powders and dry ice in ball-milling. The function of pressure and temperature made graphite robbed and impacted adequately to generate the circular

graphene structure, and carbon dioxide tended to react with the edge of graphene to generated carboxyl which could graft dopamine uniformly in ball-milling condition.

## ACKNOWLEDGEMENTS

The authors are very pleased to acknowledge financial support from the National Natural Science Foundation of China (Grant no. U1362205, 5157031049), Natural Science Foundation of Jiangsu Province (Grant No. BK20140271), National High Technology Research and Development Program of China (Grant no. 2012AA03A203), Beijing Youth Talent Plan (Grant no. YETP0492) and 2014 Open Project of State Key Laboratory of Organic-Inorganic Composites.

## REFERENCES

[1] Lee W, Lee J U, Jung B M, et al. Simultaneous enhancement of mechanical, electrical and thermal properties of graphene oxide paper by embedding dopamine[J]. *Carbon*, 2013, 65: 296-304.

[2] Jeon I Y, Shin Y R, Sohn G J, et al. Edge-carboxylated graphene nanosheets via ball milling[J]. *Proceedings of the National Academy of Sciences*, 2012, 109(15): 5588-5593.

[3] Shen A, Zou Y, Wang Q, et al. Oxygen reduction reaction in a droplet on graphite: Direct evidence that the edge is more active than the basal plane[J]. *Angewandte Chemie*, 2014, 126(40): 10980-10984.

[4] Xu J, Jeon I Y, Seo J M, et al. Edge-Selectively Halogenated Graphene Nanoplatelets (XGnPs, X= Cl, Br, or I) Prepared by Ball-Milling and Used as Anode Materials for Lithium-Ion Batteries[J]. *Advanced materials*, 2014, 26(43): 7317-7323.

[5] Zhao W, Fang M, Wu F, et al. Preparation of graphene by exfoliation of graphite using wet ball milling[J]. *J. Mater. Chem*., 2010, 20(28): 5817-5819.