Supporting Information

Ionic Liquid-Graphene Oxide for Strengthening Microwave Curing Epoxy Composites

Ke Shi^{a,‡}, Jintao Luo^{a,‡}, Xianhua Huan^a, Song Lin^d, Xin Liu^a, Xiaolong Jia^{a,b,*}, Lei Zu^{c,*}, Oing Cai^a, Xiaoping Yang^{a,b}

* Corresponding author

^aState Key Laboratory of Organic-Inorganic Composites, Beijing University of Chemical Technology, Beijing 100029, P. R. China

^bKey Laboratory of Carbon Fiber and Functional Polymer, Ministry of Education, Beijing University of Chemical Technology, Beijing 100029, P. R. China

^cSchool of Mechanical Engineering, Hefei University of Technology, Hefei 230009, P. R. China

^dNorth China Institute of Aerospace Engineering, Hebei 065000, P. R. China

[‡] contributed equally to the work

Corresponding Authors

*Tel/Fax: +86-10-6442-7698.

* E-mail: jiaxl@mail.buct.edu.cn (Xiaolong Jia), zulei@hfut.edu.cn (Lei Zu)

Chemical structure of synthesized BIL was characterized by FT-IR and MS (Figure

S1). As shown in the FT-IR spectra of Figure S1(a), two new absorption peaks appeared at 3450 and 1112 cm⁻¹ for BIL compared with IL, which were corresponded to the -OH bending vibration and -O- stretching vibration, respectively. The new -OH group was resulted from the reaction between IL and BGE, while the additional -O- bond came from the chemical structure of BGE. Meanwhile, two absorption peaks were observed at 3114 and 3154 cm⁻¹ in the spectra of both BIL and IL, which were ascribed to the peaks of the H-C-C-H antisymmetric stretching vibration and N=C-N stretching vibration in the imidazolium ring, respectively [1]. These results strongly proved that the BGE was successfully introduced into IL structure. Furthermore, the structural features of anion and cation contained in BIL were identified using MS. Normally, the molecular structures of anion and cation were regularly distributed in the opposite and forward directions of MS spectrum, accordingly. It was found that the mass-to-charge ratio (m/z) of anion was mainly concentrated at the value of 87.07 as shown in the opposite direction of MS spectrum in the upper inset of Figure S1(b). Judging from this molecular weight value, the main structure of anion in BIL was still BF₄-, indicating no change in the anion structure after the modification on IL using BGE. Differently, it was detected that the molecular weight of cation distributed in various values as shown in Figure S1(b), due to the complexity of the organic reaction. As listed in the table of Figure S1(c), the homologues with similar chemical structures were generated on the side chain of the imidazolium five-membered ring in BIL, and a binary or even multicomponent association between BILs probably existed. It was reasonable that these homologues should have similar physicochemical reactivity, since similar functional groups and five-membered ring structures were possessed by them. Combined with the data of FT-IR, the calculation on the molecular weight distributions of these homologues were carried out. Thus, one of homologues, which occupied the abundance close to 100 %, was selected as the typical structure of cation in BIL in the present study. The typical structural formula of synthesized BIL was shown in Figure S1(b).



Figure S1. (a) FT-IR spectra of BGE, IL and BIL, (b) MS spectra for the mass-to-charge ratio (m/z) distribution of cation in BIL and (c) the table for possible chemical structures of anion and cation in BIL obtained from MS spectra. In panel (b), the upper inset is

the m/z distribution of anion and the lower inset is typical chemical structural formula of synthesized BIL.



Figure S2. (a1-a3) N atom percentage and average particle size of BIL-GO with processing time at different MW powers of 300, 400 and 500 W, as well as. (b1-b3) SEM images of BIL-GO obtained with best processing time at each power.

The conditions of MW power and time were critical factors to affect the preparation and subsequent dispersion of BIL-GO in our present study. By selecting the MW powers of 300, 400 and 500W, the atomic percentage of N in BIL-GO and the average particle size of BIL-GO were measured at different processing times as presented in Figure S2. As the power increasing, the time to reach the maximum value of N atomic% decreased, while this value range were close at different power conditions. Meanwhile, the average particle size and size distribution of BIL-GO was detected to be different when changing MW powers. Although the average particle size of BIL-GO obtained at 300 W and at 400W was close, a large amount of tiny GO was still observed in the obtained morphology at 300 W. This indicated that the combination of BIL and GO lag behind the peeling of GO under MW, which resulted in a small amount of GO microchips that were not combined with BIL. Moreover, the average particle size of BIL-GO obtained at 500 W for 50 s was very small. This might be due to the violent exfoliation of GO by BIL under MW, which weakened the combination of BIL and GO through conjugation, so that the morphology of BIL-GO appeared to be a lot of fragments. Comprehensively, by examining the highest N Atom% in BIL-GO and the average particle size of BIL-GO, the best power and time of MW could be determined. BIL-GO obtained at 400 W for 60 s was considered to be an optimum sample that balanced the peeling of GO by BIL and the combination of BIL and GO.



Figure S3. The O element content curves at microwave powers of 300, 400 and 500 W with processing time.

At the same time, the content of O element under different processing time and power has also got our attention. It can be found that the oxygen content does not change significantly under different power and treatment time, because GO is not further oxidized in BIL. At the same time, the oxygen content in GO is relatively large, and the introduction of oxygen in BIL will not cause a large change in oxygen content.



Figure S4. Optical images of GO (sample A) and BIL-GO (sample B) in EP resin after standing for (a) 0, (b) 2, (c) 10 and (d) 20 h.

The dispersion states of GO (sample A) and BIL-GO (sample B) in EP after the irradiation treatment of MW were investigated by sedimentation tests. Both sample A and sample B were under magnetic stirring for 0.5 h at room temperature. Both sample A and sample B were treated under MW irradiation at 400 W for 1 min during the stirring process. The optical images of both sample A and sample B standing for different time periods were shown in Figure S4. As shown in Figure S4(b-d), the phase separation was observed in sample A within 10 h, and GO could be clearly seen subsiding to the bottle bottom after 20 h, showing their poor dispersion stability in EP. Differently, BIL-GO possessed perfect and stable dispersion in EP without any optical phase separation over time. This phenomenon obviously proved that the

functionalization with BIL was effective in enhancing the dispersibility and dispersion stability of GO by restraining the formation of big-sized aggregations.

Particle spacing probability density theory

Particle spacing probability density could be used to quantitatively evaluate the microscale dispersion of particles (GO and BIL-GO in this case). As shown in Model S1(a), in a solid sample with various irregular inclusions (in black color) in a matrix, a random line was used to intercept the particles to obtain the spacing between these particles, x_1 , $x_2, \ldots, x_i, \ldots, x_n$. The spacings were divided into several groups of intervals Δx and the frequency density f_i was the ratio of n_i to n, where n_i was the number of data falling into this group and n was the total number of the measurements. Therefore, the histogram could be made to display the spacing data distribution, as shown in Model S1(b). If the interval Δx was small enough and the number of data n was sufficiently large, a smooth curve of the frequency function could be obtained as shown in Model S1(c). For instance, the dispersion quantities of D0.1 was the shadowed areas below the f (x) curve, corresponding to the possibilities of the spacing data falling into the range of $\mu \pm 0.1 \mu$. The probability of the particle dispersion coefficient D was defined as the probability that the average particle spacing was within a certain range. The dispersion coefficient D was a monotonically increasing function of μ/σ , where μ and σ referred to the average particle spacing and standard deviation of the particles, respectively. In the actual statistical calculation, the average particle spacing was \bar{x} ,

which could be calculated from Equation (1). Also, the standard deviation s could be calculated using Equation (2).

$$\overline{\mathbf{x}} = \frac{\sum_{i} \mathbf{x}_{i}}{\mathbf{N}} \tag{1}$$

$$s = \sqrt{\frac{\sum_{i}(x_{i} - x)^{2}}{N - 1}}$$
(2)

where \bar{x} was the average particle spacing and N was the number of particles. When the number of particles N was sufficiently large, it was feasible that $\mu = \bar{x}$ and $\sigma = s$. The measurement obeyed a normal or lognormal distribution. The larger the \bar{x}/s value, the more uniform the dispersion of particles.



Model S1. (a) A section from the solid sample where free-path spacing of the particles were measured, (b) the histogram construction of particle spacing distribution and (c) the definition of dispersion D0.1 quantity from the frequency function f(x).

Table S1. The average particle distance and \overline{x}/s value for GO and BIL-GO dispersed in EP before and after curing.

Sample		x (um)	s(um)	x/s
GO/EP	before	49.0	39.5	1.24
00/11	after	39.3	35.8	1.11
BIL-GO/EP	before	64.6	34.4	1.88
	after	57.3	32.9	1.74



Figure S5. Temperature-time curves of GO/EP and BIL-GO/EP during the curing process under MW irradiation (400 W).

Figure S5 shows temperature-time curves of GO/EP and BIL-GO/EP during the curing process under MW irradiation. It could be seen that the system temperature of BIL-GO/EP was distinctively higher than that of GO/EP with time going. This result proved that BIL-GO was rapidly heated prior to GO, because BIL-GO hybrid acted as a more efficient MW absorber than GO due to the positive synergistic effect of both GO and BIL in absorbing MW. The exfoliated interlayer structure of BIL-GO became the trap center of MW, which intensified the in-situ activation effect of MW and thus led to a faster temperature rising in BIL-GO/EP than GO/EP.

Figure S6 shows effect of different curing temperatures on the gel time of GO/EP and BIL-GO/EP under MW irradiation. It could be seen that the gel time of BIL-GO/EP decreased significantly with curing temperature, while such decreasing trend was rather mild with GO/EP. This result indicated that BIL-GO/EP was heated quickly prior to GO/EP by MW, also due to their stronger absorbing capability to MW energy than GO/EP. This caused the rapid temperature increasing in the whole system, resulting in a much shorter gel time. The phenomenon further confirmed the positive synergistic effect of both GO and BIL in absorbing MW.



Figure S6. Effect of different curing temperatures on the gel time of GO/EP and BIL-GO/EP under MW irradiation (400 W).

Table S2. Fitting parameters for curing kinetics of GO/EP and BIL-GO/EP using Kamal model.

Temperature/°C		80	90	100	110
GO/EP	\mathbf{k}_1	0.110	0.195	0.290	0.448
	k_2	0.123	0.196	0.310	0.518
BIL-GO/EP	\mathbf{k}_1	0.170	0.263	0.399	0.580
	k_2	0.185	0.279	0.420	0.604

Table S3. The calculated activation energy of GO/EP and BIL-GO/EP composites via MW irradiation.

E_{a1} (KJ/mol)

E_{a2} (KJ/mol)

GO/EP	51.7	53.7
BIL-GO/EP	45.9	44.4
$\frac{[E_a(GO/EP) - E_a(BIL - GO/EP)]}{E_a(GO/EP)} \times 100\%$	11.2 %	17.3 %



Figure S7. DSC curves before and after curing of (a) GO/EP and (b) BIL-GO/EP.

The fitting parameters for curing kinetics of both GO/EP and BIL-GO/EP using the Kamal model were listed in Table S1. Obviously, as the temperature increased, the rate constants of k_1 and k_2 showed an increasing trend. Comparing k_1 and k_2 at each temperature, the values of k_2 were always higher than those of k_1 , indicating that the curing behaviors of both GO/EP and BIL-GO/EP systems exhibited the autocatalytic reaction characteristics according to the literatures [2-3]. In particular, all k_1 and k_2 values were distinctively higher for BIL-GO/EP than GO/EP at each temperature. At the same time, BIL-GO/EP and GO/EP were tested by DSC in order to confirm that the composite material under the curing process was completely cured. The disappearance

of the curing peak after the curing process could prove that BIL-GO/EP and GO/EP have been completely cured.



Figure S8. (a1, b1) SEM and (a2-a3, b2-b3) TEM images of fractured surfaces for GO/EP (Left column) and BIL-GO/EP (Right column) composites. The graphs in panel a3 and b3 are the high-magnification TEM images. The yellow and red arrows in panel a1-a3 and b1-b3 denote the GO and BIL-GO in EP composites, respectively.

The practical reinforcing effect closely related to the dispersion state of nanoparticles in composites. The fractured surfaces of GO/EP and BIL-GO/EP composites were presented in Figure S8. Apparently, GO aggregates were partly observed. And the interfacial area between GO and EP in the sample was loose and irregular as shown in Figure S8(a1-a3), so that their adverse effect on mechanical properties of composites could not be ignored. The structural defects, which were resulted from the insufficient impregnation of EP resin into GO aggregates, would generate stress concentration during mechanical property evaluation. In contrast, a uniform dispersion of BIL-GO in EP matrix was clearly found (Figure S8(b1)). The BIL-GO in fractured surface of EP composites appeared to be sheet-like arrangement with fluffy structure and riveted to each other (Figure S8(b2, b3)). The interfacial area between BIL-GO and EP was in full contact, indicating a much better interfacial impregnation of EP into BIL-GO. This result further verified that the interfacial bonding between BIL-GO and EP matrix was efficiently strengthened.

Figure S9 shows SEM images of fractured surfaces for TFBT samples of GO/EP and BIL-GO/EP. As shown in Figure S9(a1, a2), an amount of voids and defects were found at the fractured interface of GO/EP. The "separation" between GO film segment and EP matrix as well as less residual GO at the interface after stretching was clearly visible, suggesting a poor GO/EP adhesion. In contrast, the fractured surface of BIL-GO/EP appeared to be dense (Figure S9(b1, b2)), also indicating a much better interfacial impregnation of EP into BIL-GO. This much contributed to the enhancement in TFBT strength and cumulative AE energy at the fracture point.



Figure S9. SEM images of fractured surfaces for TFBT samples of (a1, a2) GO film/EP and (b1, b2) BIL-GO film/EP. The images in panel a2 and b2 are the corresponding high-magnification of the yellow and red rectangle areas in panel a1 and b1. The yellow and red arrows denote the GO and BIL-GO in the fractured interfaces, respectively.

The dielectric constants (ϵ') of GO/EP and BIL-GO/EP composites before and after curing were shown in Figure S10. For both composites before or after curing, the dielectric constants (ϵ') showed the decreasing trend with the frequency. This was because the contribution of polar structure to dielectric constant was gradually reducing and the micro-structural relaxation became the determining factor to dielectric constant little by little, as the frequency was increasing. In the case before curing, the dielectric constant was apparently higher for BIL-GO/EP than GO/EP composites, which was definitely due to the high polarization nature of BIL contained in BIL-GO. In contrast, the dielectric constants for both composites after curing jumped to much lower values. This phenomenon should be originated from the consumption of polar groups during the curing reaction and the subsequent formation of crosslinked network structure with weak polarity in the final cured samples. Interestingly, the dielectric constant of BIL-GO/EP composites was lower than that of GO/EP composites over the whole testing frequency. The total polarization of the system was mainly attributed to the interfacial polarization, since the dipole was less affected by adjacent nanoparticles in the external electric field when the nanoparticles were dispersed uniformly in the system. And the strong interfacial bonding would restrict the motion of polymer chains and thus suppress the interfacial polarization. BIL-GO showed a more uniform dispersion state along with strengthened interfacial bonding in cured EP matrix, which would suppress the interfacial polarization in BIL-GO/EP composites. Additionally, with more chemical reaction sites in comparison with GO, the rotation of dipoles in BIL-GO was relatively slower in an electric field, resulting in longer relaxation time of microstructure in cured BIL-GO/EP composites. Hence, the lower dielectric constant demonstrated that the obvious suppression of interfacial polarization and prolonging of relaxation time existed in cured BIL-GO/EP composites, which further identified the excellent interfacial bonding between BIL-GO and EP matrix.



Figure S10. Dielectric constant-frequency curves of GO/EP and BIL-GO/EP composites (a) before and (b) after curing.



Figure S11. X-ray diffraction of GO and BIL-GO.

The x-ray diffraction (XRD) of GO and BIL-GO were provided as shown in Figure S11. For GO, the peak of the (001) crystal plane was the characteristic peak of 2D planar structure. When BIL was successfully introduced into GO, the 2D structure of GO was affected by the 3D structure of BIL, so that the peak intensity at the (001) crystal plane was reduced. Therefore, the hybridization of BIL and GO destroyed the crystal order of GO.

The data comparison of thermomechanical properties and curing time of GO-filled EP composites in the literatures and our present study was listed in Table S4. It could be found that the increasing percentages in the glass transition temperature T_g and elastic modulus E of BIL-GO/EP composites in our present study were generally enhanced compared with the data reported in the literatures. More importantly, the MW curing time of BIL-GO/EP composites was far shorter than reported values of various GO-filled EP composites in the literatures, manifesting the accelerating effect of BIL-GO on the curing reaction of EP composites due to the combining function of the strong "non-thermal effect" and the normal "thermal effect".

f-GO/GO content	Increase in T _g [°C]	Gain in E [%]	Time of curing	References
[wt.%]	(matrix T _g [°C])	(matrix E [GPa])		
0.25 Pristine GO	0.6	~5	21 h	[4]
0.50 Pristine GO	3.0 (126.3)	~5 (~3.0)	21 h	
0.10 Pristine GO	-2.7 (197.1)	7 (1.36)	6 h	[5]
0.10 Pristine GO	-1	-		[6]
0.50 Pristine GO	-2 (150)	-		
0.10 Pristine GO	-	~7		[7]
0.50 Pristine GO	-	~20 (2.30)		
0.10 Pristine GO	-	8	28 h	[8]
0.50 Pristine GO	-	24 (2.5)	28 h	

Table S4. Mechanical and thermal properties of neat epoxy and its composites.

0.10 Pristine GO	-	16		[8]
0.50 Pristine GO		20 (2.5)		
0.10 Pristine GO	-	16		
0.50 Pristine GO	-	16 (2.5)		
0.10 Pristine GO	-	~8		[9]
0.20 Pristine GO	-	~20 (~2.5)		
0.10 Large-sized GO	~5.5	~8	6 h	[10]
0.30 Large-sized GO	~6.5 (~167.5)	~8 (~1.53)	6 h	
0.10 Small-sized GO	~6.5	~8	5 h	[10]
0.30 Small-sized GO	~7.0(~167.5)	~10 (~1.53)	5 h	
0.50 Pristine GO	1.0 (62.0)	~8 (~0.47)	24 h	[11]
0.50	6.0 (120.0)	8.6 (~3.0)	0.6 h	This work

REFERENCES

(1) Fan, X.; Wang, L. Highly Conductive ionic liquids toward high-performance spacelubricating greases. *ACS Applied Materials & Interfaces* **2014**, 6 (16), 14660-14671.

(2) Johnston, K.; Pavuluri, S. K.; Leonard, M. T.; Desmulliez, M. P. Y.; Arrighi, V. Microwave and thermal curing of an epoxy resin for microelectronic applications. *Thermochimica Acta* **2015**, 616, 100-109.

(3) Ren, R.; Xiong, X.; Ma, X.; Liu, S.; Wang, J.; Chen, P.; Zeng, Y. Isothermal curing

kinetics and mechanism of DGEBA epoxy resin with phthalide-containing aromatic diamine. *Thermochimica Acta* **2016**, 623, 15-21.

(4) Bortz, D. R.; Heras, E. G.; Martin-Gullon, I. Impressive fatigue life and Fracture Toughness Improvements in graphene oxide/epoxy composites. *Macromolecules* 2012, 45 (1), 238-245, DOI: 10.1021/ma201563k.

(5) Chen, L.; Chai, S.; Liu, K.; Ning, N.; Gao, J.; Liu, Q.; Chen, F.; Fu, Q. Enhanced epoxy/silica Composites mechanical properties by introducing graphene oxide to the interface. *ACS Applied Materials & Interfaces* **2012**, 4 (8), 4398-4404, DOI: 10.1021/am3010576.

(6) Li, Z.; Wang, R.; Young, R. J.; Deng, L.; Yang, F.; Hao, L.; Jiao, W.; Liu, W.
Control of the functionality of graphene oxide for its application in epoxy nanocomposites. *Polymer* 2013, 54 (23), 6437-6446, DOI: https://doi.org/10.1016/j.polymer.2013.09.054.

(7) Liu, Q.; Zhou, X.; Fan, X.; Zhu, C.; Yao, X.; Liu, Z. Mechanical and thermal properties of epoxy resin nanocomposites reinforced with graphene oxide. *Polymer-Plastics Technology and Engineering* **2012**, 51 (3), 251-256, DOI: 10.1080/03602559.2011.625381.

(8) Paiva, M. C.; Covas, J. A. Carbon nanofibres and nanotubes for composite applications. In Fibrous and Textile Materials for Composite Applications; Rana, S.;

Fangueiro, R., Eds.; Springer Singapore: Singapore, 2016; pp 231-260.

(9) Wang, R.; Li, Z.; Liu, W.; Jiao, W.; Hao, L.; Yang, F. Attapulgite-graphene oxide hybrids as thermal and mechanical reinforcements for epoxy composites. *Composites Science and Technology* 2013, 87, 29-35, DOI: https://doi.org/10.1016/j.compscitech.2013.08.002.

(10) Wang, X.; Jin, J.; Song, M. An investigation of the mechanism of graphene toughening epoxy. *Carbon* 2013, 65, 324-333, DOI: https://doi.org/10.1016/j.carbon.2013.08.032.

(11) Yousefi, N.; Lin, X.; Zheng, Q.; Shen, X.; Pothnis, J. R.; Jia, J.; Zussman, E.; Kim,
J..K. Simultaneous in situ reduction, self-alignment and covalent bonding in graphene oxide/epoxy composites. *Carbon* 2013, 59, 406-417, DOI: https://doi.org/10.1016/j.carbon.2013.03.034.