Supporting Information For

Reinforced Magnetic Epoxy Nanocomposites with Conductive Polypyrrole Nanocoating on Nanomagnetite as a Coupling Agent

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Surface functionalization of Fe_3O_4 nanoparticles

Fe_3O_4 nanoparticles were functionalized with PPy via a facile SIP method. Briefly, Fe_3O_4 nanoparticles (4.9510 g), PTSA (15 mmol) and APS (9 mmol) were added into 100 mL deionized water in an ice-water bath for one-hour mechanical stirring (SCILO-GEX OS 20-Pro LCD Digital Overhead stirrer, 300 rpm) combined with sonication (Branson 8510). Then the pyrrole solution (18 mmol in 25 ml deionized water) was mixed with the above Fe_3O_4 nanoparticles suspension and mechanically and ultransonically stirred continuously for an additional 1.5 hours in an ice-water bath for further polymerization. The product was vacuum filtered and washed with deionized water. The final product was dried at 50 °C overnight. Pure PPy was also fabricated following the aforementioned procedures without adding nanoparticles for comparison.

Characterization of Fe_3O_4 nanoparticles

Fig. S1(a&b) shows the SEM images of the u-Fe_3O_4 and f-Fe_3O_4 nanoparticles. The u-Fe_3O_4 nanoparticles appear as ball-like shape, and the surface of the u-Fe_3O_4 nanoparticles is relatively smooth, Fig. S1(a). However, the surface of the f-Fe_3O_4 nanoparticles becomes much rougher. Fig. S1(c,d,e&f) shows the HRTEM images of the u-Fe_3O_4 and f-Fe_3O_4 nanoparticles. For the u-Fe_3O_4 and f-Fe_3O_4 nanoparticles, the lattice fringes are observed, indicating the highly crystalline structure of the nanoparticles. Compared with u-Fe_3O_4 nanoparticles, the surface of the f-Fe_3O_4 nanoparticles is much rougher, and after functionalization, a thin PPy layer was observed surrounding the nanoparticles and was marked by red cycles. All the results indicate the polymerization of pyrrole occurred on the surface of f-Fe_3O_4 nanoparticles.

The FT-IR analysis is used to verify the surface functional groups. Fig. S1(g) shows the FT-IR spectra of the u-Fe_3O_4 nanoparticles, pure PPy, and f-Fe_3O_4 nanoparticles. In the spectrum of u-

Fe_3O_4 nanoparticles, the only peak at 531 cm^{-1} is due to the vibration of Fe-O band.[1] For the f-Fe_3O_4 nanoparticles, the peaks at 1536 and 1446 cm^{-1} are contributed to the C=C and C-N stretching vibration, respectively.[2] The peaks located at 1288 and 1022 cm^{-1} are due to the C-H in-plane and out-of-plane deformation vibration, respectively.[3] The peak at 1150 cm^{-1} reflects the vibration of C-C bond.[3] The small peak at 957 cm^{-1} is attributed to the C-C out-of-plane deformation vibration.[2] All these peaks are the characteristic peaks of PPy in the f-Fe_3O_4 nanoparticles. However, compared with the characteristic peaks of pure PPy, these peaks have some shifts, indicating the interaction between Fe_3O_4 nanoparticles and PPy. All these results show that the Fe_3O_4 nanoparticles have been successful functionalized with PPy.

Fig. S1(h) shows the TGA curves of pure PPy, u-Fe_3O_4 nanoparticles, and f-Fe_3O_4 nanoparticles. For the u-Fe_3O_4 nanoparticles, the weight has only a slight change within the measured temperature. Two weight loss stages are observed in the TGA curves of pure PPy and f-Fe_3O_4 nanoparticles. The weight loss from 30 to 240 ^oC is attributed to the elimination of the moisture and dopant anions (PTSA).[2] The major weight loss is due to the decomposition of PPy from 240 to 650 ^oC.[2] At high temperature, the Fe_3O_4 nanoparticles are oxidized to form hematite (α-Fe_2O_3). The weight residue of α-Fe_2O_3 is 80.93 % in the f-Fe_3O_4 nanoparticles, then the weight percentage of Fe_3O_4 in the f-Fe_3O_4 nanoparticles is calculated to be 78.23%, which is consistent with the initial 80.0 wt% Fe_3O_4 nanoparticles in the f-Fe_3O_4.

Dispesion quality of epoxy nanosuspensions

Fig. S2 shows the SEM images of the dispersion quality of the f-Fe_3O_4 nanoparticles in the epoxy nanosuspensions. For epoxy nanosuspension with 5.0 wt% of f-Fe_3O_4 nanoparticles, Fig. S2(a), the f-Fe_3O_4 nanoparticles are well dispersed in the epoxy resin. However, when the

particle loading increases to 20.0 wt%, Fig. S2(b), the agglomeration of nanoparticles is obviously observed, which is due to the high particle loading and the magnetic dipole-dipole interactions between the f-Fe_3O_4 nanoparticles.[2]

Curing degree studied by FT-IR

The curing process of pure epoxy and epoxy PNCs with 10 wt% f-Fe_3O_4 was studied by the FT-IR spectra, Fig. S3. Because the intensity of peak at 913 cm^{-1} is decreases with increasing the curing extent, therefore, the variation of the epoxy groups can be reflected by this peak. And the absorption peak at 1616 cm^{-1} of a benzene ring is considered as the internal standard. According to the Beer-Lambert law, the extent of curing (α) is calculated by eqn S1:[4]

$$\alpha = \frac{A_{cured}^{1610} A_{uncured}^{913} - A_{cured}^{913} A_{uncured}^{1610}}{A_{cured}^{1610} A_{uncured}^{913}} \quad \text{(S1)}$$

where $A_{uncured}$ is the original absorbance of pure epoxy resin without curing, A_{cured} is the absorbance of cured epoxy and its PNCs. Table S1 shows the curing extent values of pure epoxy and its PNCs with 10.0 wt% Fe_3O_4 nanoparticles. The 0 hour represents the liquid phase samples containing the curing agent, which were heated at 70 ^oC for about 1-2 hours and were further heated at 120 ^oC for 5 hours. For the pure epoxy and its PNCs with 10.0 wt% f-Fe_3O_4 nanoparticles, the curing extent increases with increasing the curing time. The curing extent value of the 10.0 wt% f-Fe_3O_4/epoxy PNCs is almost the same as that of pure epoxy, which is due to the reaction between PPy on the f-Fe_3O_4 nanoparticles and epoxide groups. For the 10.0 wt% u-Fe_3O_4/epoxy PNCs, at 0 hour, the curing extent value is even a little higher than that of pure epoxy. However, with increasing the curing time, the curing extent of the 10.0 wt% u-Fe_3O_4/epoxy PNCs becomes much lower, which is induced by the obstructive effect of the nanoparticles.[4]

Differential scanning calorimetry of cured epoxy and its PNCs.

Fig S4. shows the DCS curves of the cured pure epoxy and its PNC with different loadings of Fe_3O_4 nanoparticles. The exothermal peak is observed in all the samples at the temperature range from 150 to 290 ^oC, indicating that the polymer network in the PNCs is not completely formed during the curing process. As the temperature is above glass transition temperature, the polymer segments can freely move and accomplish the curing process. Therefore, the exothermal peaks are observed. The value of the residual heat during this curing can be used to calculate the curing extent (α) of the PNCs based on eqn S2:[5]

$$\alpha = 1 - \frac{\Delta H}{(1 - W_p)\Delta H_{uc}} \qquad \text{(S2)}$$

where ΔH is the residual heat during the curing reaction in the PNCs (J/g), W_p is the particle weight percentage in the composites and ΔH_{uc} is the heat of the uncured pure resin (J/g). The ΔH_{uc} value of the uncured pure epoxy is 239.4 J/g. The curing extent (α) are summarized in Table S2. Compared with cured pure epoxy, the α value of the epoxy PNC with u-Fe_3O_4 nanoparticles is a little lower than that of pure epoxy, indicating that the u-Fe_3O_4 nanoparticles can slightly reduce the curing process. However, for the epoxy PNC with f-Fe_3O_4 nanoparticles, the α value is quite different from that of cured pure epoxy, which is induced by the interaction between the PPy on the f-Fe_3O_4 nanoparticles and the epoxide groups. For the epoxy PNC with 5 wt% f-Fe_3O_4 nanoparticles, as the f-Fe_3O_4 nanoparticles is well dispersed in the epoxy matrix, the PPy on the f-Fe_3O_4 nanoparticles can react with the epoxy matrix completely. Therefore the ΔH is increased to 31.11 J/g and the α is decreased to 0.86 as compared with that of the epoxy PNC with 5.0 wt% u-Fe_3O_4 nanoparticles. However, when the f-Fe_3O_4 nanoparticle loading is increased to 10.0 wt%, the agglomeration of nanoparticles occurred which would prevent the

direct interaction between PPy and epoxy matrix, therefore the ΔH is decreased to 20.68 J/g and α is increased to 0.92. With further increasing the particle loading to 20.0 wt%, the agglomeration of the f-Fe_3O_4 nanoparticle is much severe. But there are more PPy reacting with epoxy matrix as compared with the PNC with 5.0 wt% f-Fe_3O_4 nanoparticles. Therefore, the ΔH of the epoxy PNC with 20.0 wt% f-Fe_3O_4 nanoparticles is larger than that of the epoxy PNC with 5.0 wt% f-Fe_3O_4 nanoparticles.

Dielectric property

The dielectric property of the cured epoxy PNCs with different loadings of u-Fe_3O_4 nanoparticles, Fig. S6, is different from that of the cured epoxy PNCs with different loadings of f-Fe_3O_4 nanoparticles. The ε' of the cured epoxy PNCs with u-Fe_3O_4 nanoparticles is much lower than that of the cured epoxy PNCs with f-Fe_3O_4 nanoparticles, indicating almost no interfacial polarization occurred. In Fig. S6(a), the ε' of the cured epoxy PNCs with 5.0, 10.0 wt% u-Fe_3O_4 nanoparticles has the same trend as that of the cured pure epoxy, and the ε' values of the cured pure epoxy and epoxy PNCs with 5.0 and 10.0 wt% u-Fe_3O_4 nanoparticles is almost the same. The ε' of the cured epoxy PNCs with 20.0, 30.0 wt% u-Fe_3O_4 nanoparticles decreases with increasing the frequency. At low frequency, the cured epoxy PNCs with 20.0 wt% u-Fe_3O_4 nanoparticles show a higher ε' than the cured epoxy PNCs with 30.0 wt% u-Fe_3O_4 nanoparticles. In Fig. S6(b), the ε'' of the cured epoxy PNCs with 5.0 and 10.0 wt% u-Fe_3O_4 nanoparticles is almost the same as that of the cured pure epoxy. The cured epoxy PNCs with 20.0 and 30.0 wt% show a higher ε'' value. The tan δ, Fig. S6(c), of the cured epoxy PNCs with 10.0, 20.0 and 30.0 wt% u-Fe_3O_4 nanoparticles is lower than that of the cured epoxy PNCs with 10.0, 20.0 and 30.0 wt% f-Fe_3O_4 nanoparticles, indicating that the cured epoxy PNCs with 10.0, 20.0 and 30.0 wt% u-Fe_3O_4 nanoparticles show a lower dissipation energy.

Table S1. Curing extent value of pure epoxy and 10.0 wt% Fe_3O_4/epoxy PNCs at different curing time.

Curing time	0 hour	4 hour	5 hour
Pure epoxy	0.48	0.73	0.74
10.0 wt% f-Fe_3O_4/epoxy PNCs	0.47	0.68	0.71
10.0 wt% u-Fe_3O_4/epoxy PNCs	0.54	0.56	0.63

Table S2. Residual heat of curing, and curing extent of the cured pure epoxy and its PNC with different loadings of Fe_3O_4 nanoparticles.

Samples	ΔH (J/g)	α
cured pure epoxy	14.45	0.94
5.0 wt% f-Fe_3O_4/epoxy PNCs	31.11	0.86
5.0 wt% u-Fe_3O_4/epoxy PNCs	20.27	0.91
10.0 wt% f-Fe_3O_4/epoxy PNCs	19.71	0.90
10.0 wt% u-Fe_3O_4/epoxy PNCs	16.57	0.92
20.0 wt% f-Fe_3O_4/epoxy PNCs	41.16	0.79
20.0 wt% u-Fe_3O_4/epoxy PNCs	14.99	0.92

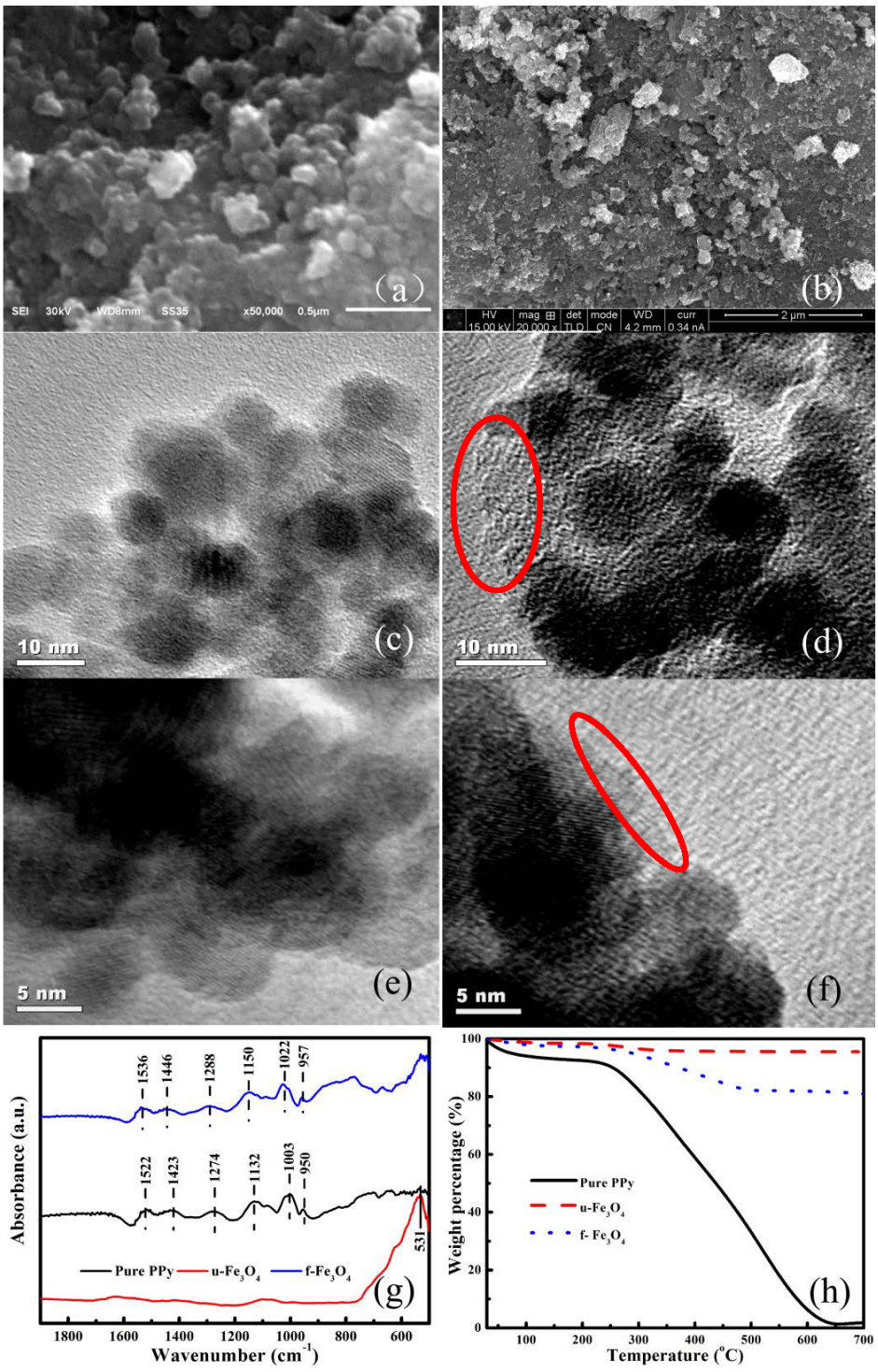

Fig S1. SEM images of **(a)** u-Fe_3O_4 and **(b)** f-Fe_3O_4 nanoparticles; HRTEM images of **(c,e)** u-Fe_3O_4 and **(d,f)** f-Fe_3O_4 nanoparticles; **(g)** FT-IR spectra of pure PPy, u-Fe_3O_4 nanoparticles, and f-Fe_3O_4 nanoparticles; and **(h)** TGA curves of pure PPy, u-Fe_3O_4 nanoparticles, and f-Fe_3O_4 nanoparticles.

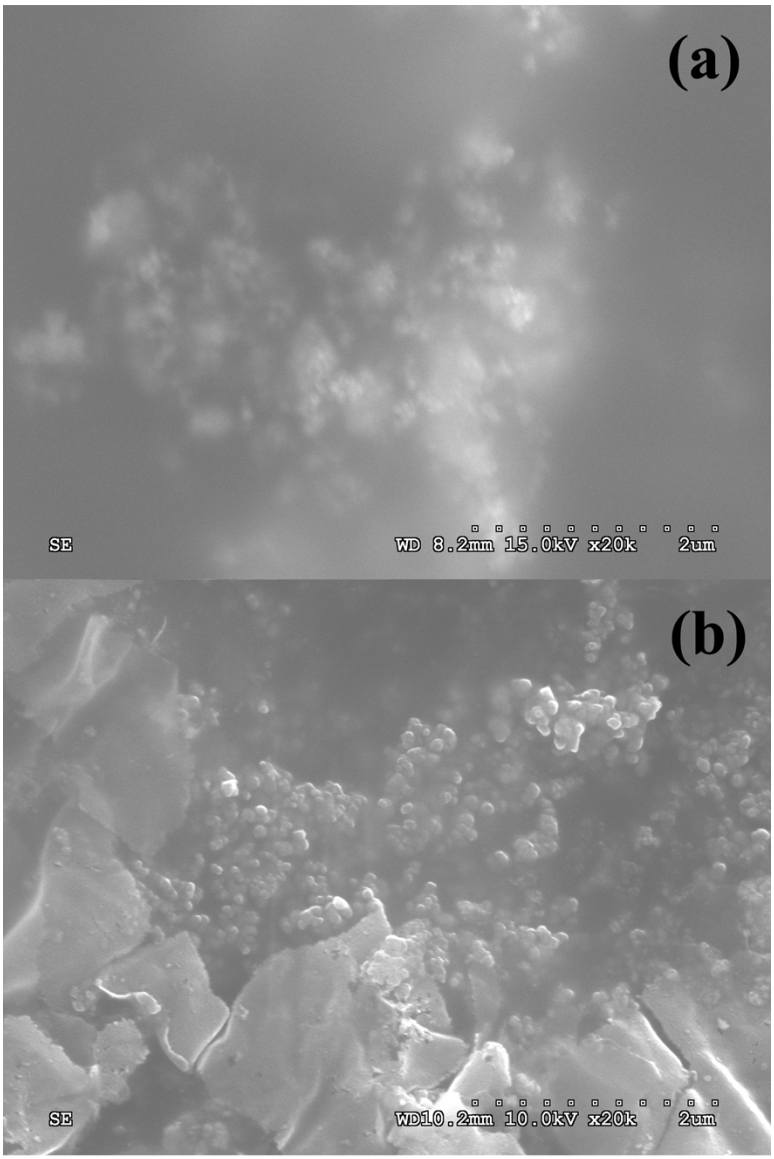

Fig S2. SEM images of the epoxy nanosuspensions with (a) 5.0 and (b) 20.0 wt% of f-Fe_3O_4 nanoparticles.

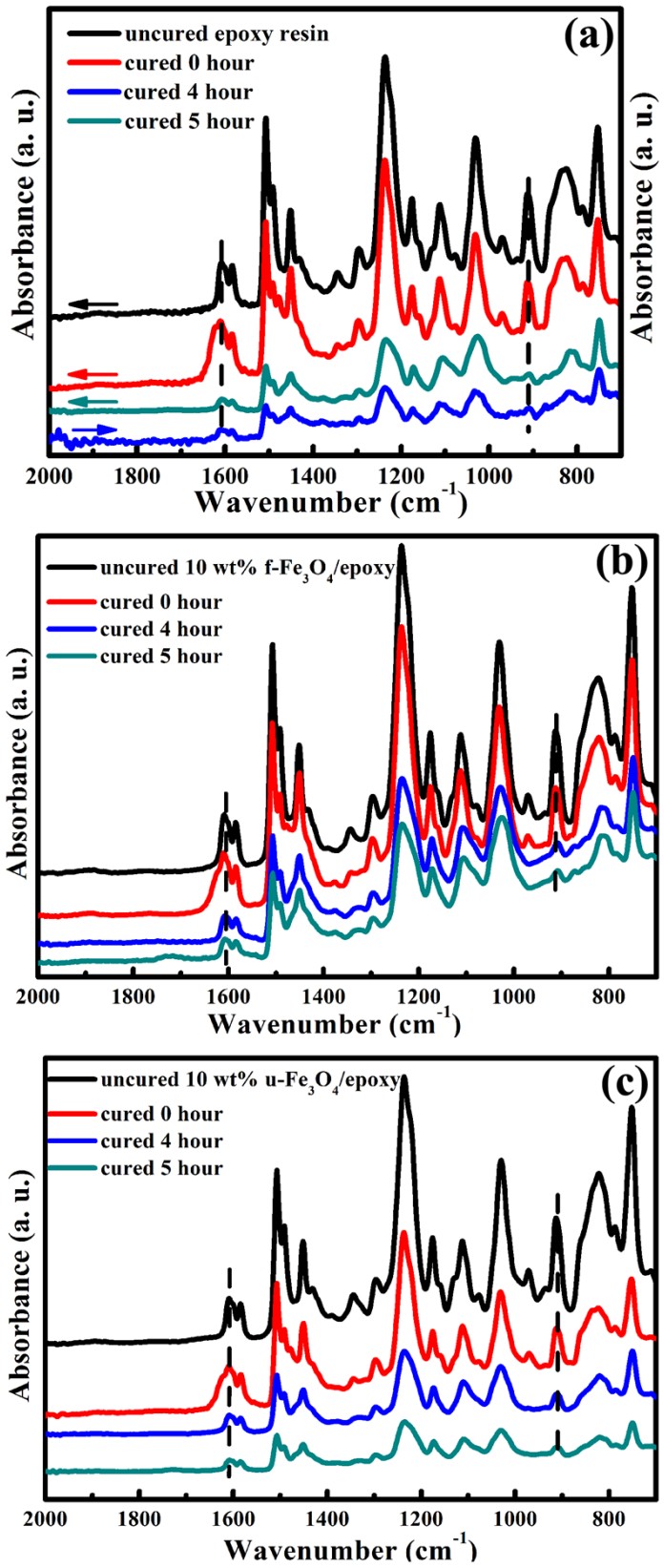

Fig S3. FT-IR spectra of pure epoxy and 10.0 wt% Fe_3O_4/epoxy PNCs.

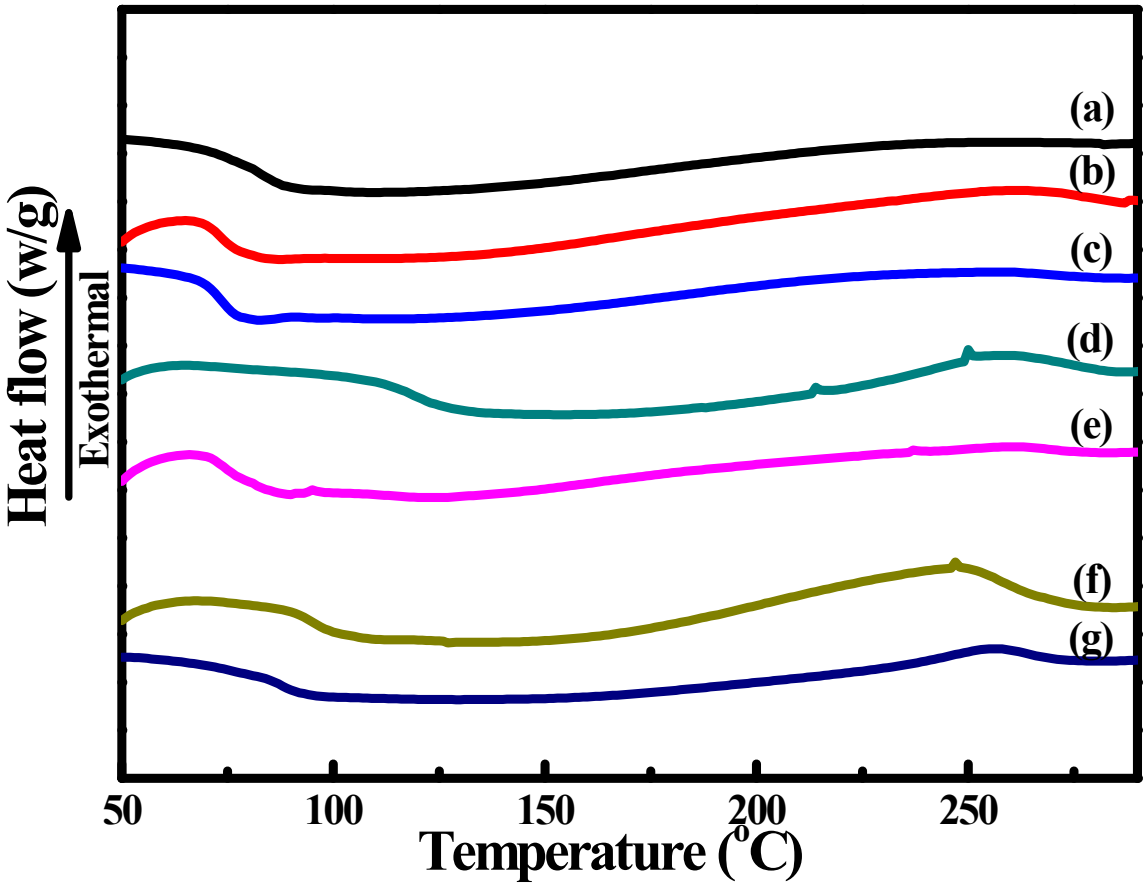

Fig S4. DSC curves of **(a)** cured pure epoxy and epoxy PNCs with **(b)** 5.0, **(d)** 10.0 and **(f)** 20.0 wt% f-Fe_3O_4 nanoparticles; epoxy PNCs with **(c)** 5.0, **(e)** 10.0 and **(g)** 20.0 wt% u-Fe_3O_4 nanoparticles.

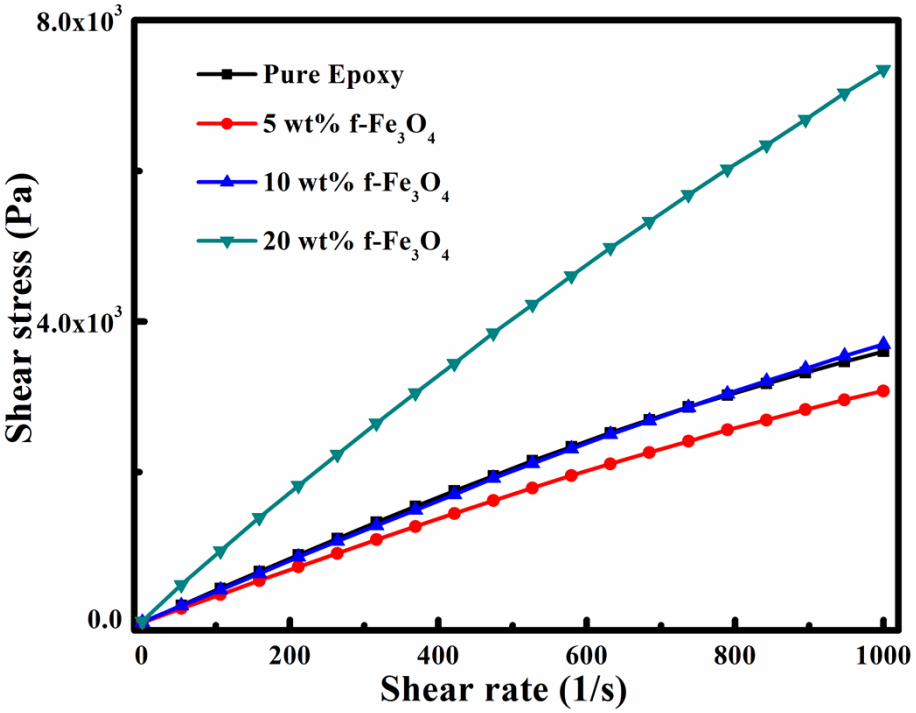

Fig S5. Shear stress *vs* shear rate of pure epoxy suspension and its nanosuspensions with 5.0, 10.0 and 20.0 wt% f-Fe_3O_4 nanoparticles.

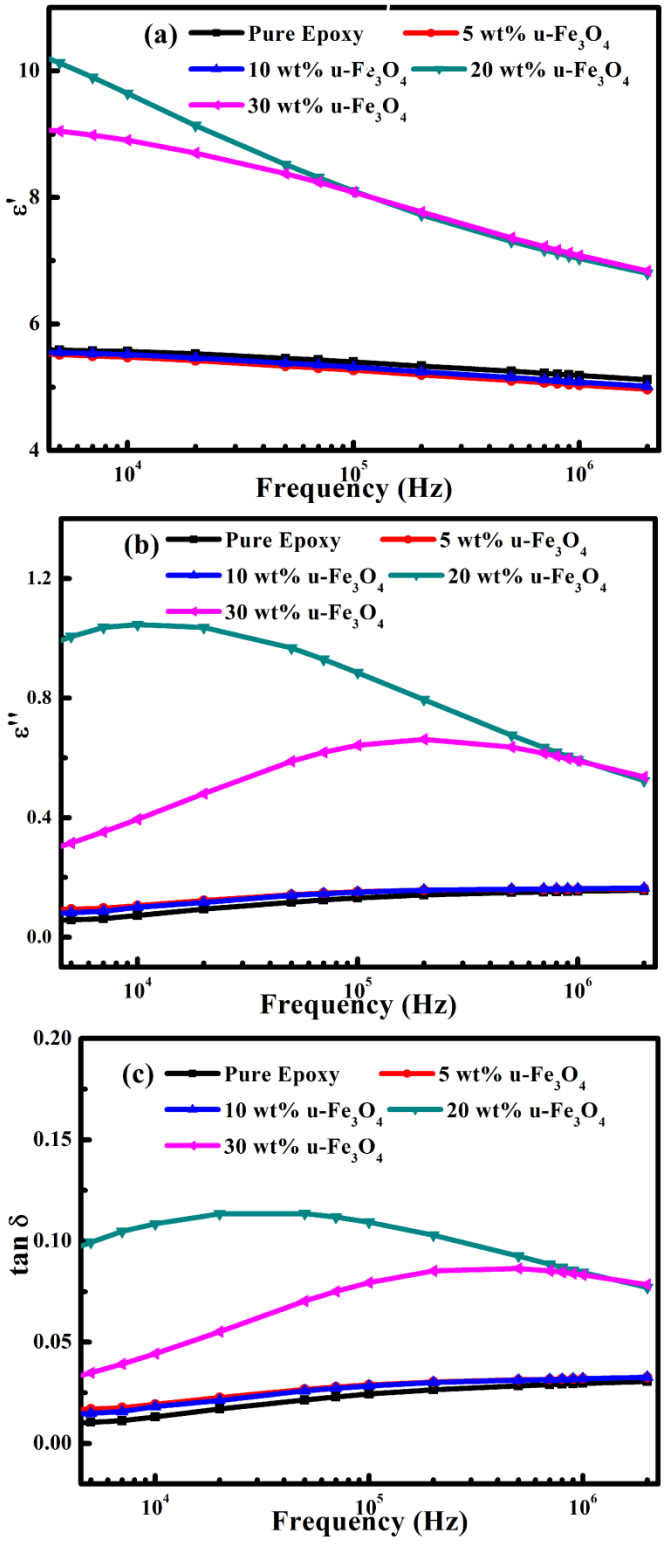

Fig S6. (a) Real permittivity (ε'), **(b)** imaginary permittivity (ε''), and **(c)** dielectric loss tangent (tan δ) as a function of frequency for the cured pure epoxy and epoxy PNCs with different loadings of u-Fe_3O_4 nanoparticles.

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