Supporting materials for

Magnetoresistive Polyaniline-Silicon Carbide Metacomposites: Plasma Frequency Determination and High Magnetic Field Sensitivity

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Materials and Methods

S1. Materials

Aniline (C_6H_7N), ammonium persulfate (APS, $(NH_4)_2S_2O_8$), and *p*-toluene sulfonic acid (PTSA, $C_7H_8O_3S$) were purchased from Sigma Aldrich. The silicon carbide (SiC) nanoparticles with an average diameter of 45 ~ 55 nm (SiC, *β*-SiC, 97.5%) were obtained from Nanostructured & Amorphous Materials, Inc. All the chemicals were used as-received without any further treatment.

S2. Fabrication of *β*-Silicon Carbide (*β*-SiC)/PANI Nanocomposites

The *β*-SiC/PANI nanocomposites were prepared with a surface initiated polymerization (SIP) method. Briefly, the *β*-SiC nanoparticles (0.186-2.511 g), PTSA (15 mmol) and APS (9 mmol) were firstly added into 100 mL deionized water in an ice-water bath for one-hour mechanical stirring (SCILOGEX OS20-Pro LCD Digital Overhead Stirrer, 300 rpm) combined with sonication (Branson 8510). Then aniline solution (18 mmol in 25 mL deionized water) was mixed with the above solution and mechanically stirred and sonicated continuously for additional one hour in an ice-water bath for further polymerization. The product was vacuum filtered and washed with deionized water. The final dark green *β*-SiC/PANI nanocomposite powders were dried at 60 ^{o}C in an oven overnight. The *β*-SiC/PANI nanocomposites with a nanoparticle loading of 10.0, 20.0, 40.0, and 60.0 wt% were prepared. The nanoparticle loadings were calculated based on the weight of aniline monomers and nanoparticles. Pure PANI was also synthesized following the above procedures without adding any nanoparticles for comparison.

S3. Characterizations

The Fourier transform infrared (FT-IR) spectra of the products were obtained on a Bruker Inc. Vector 22 (coupled with an ATR accessory) in the range of 500 to 2500 cm^{-1} at a resolution of 4 cm^{-1}. The thermogravimetric analysis (TGA) was conducted by TA instruments TGA Q-500 with a heating rate of 10 ^{o}C min^{-1} under an air flow rate of 60 mL min^{-1} from 30 to 800 ^{o}C. X-ray diffraction (XRD) analysis was carried out with a Bruker AXS D8 Discover diffractometer with General Area Detector Diffraction System (GADDS) operating with a Cu-K_{α} radiation source filtered with a graphite monochromator (λ = 1.5406 Å). Data were collected in a range of 10 to 80 ^{o}. The morphologies of the synthesized nanocomposites were observed on a field emission scanning electron microscope (SEM, JEOL, JSM-6700F system). The samples were prepared by adhering the powders onto an aluminum plate.

Dielectric properties were investigated by a LCR meter (Agilent, E4980A) equipped with a dielectric test fixture (Agilent, 16451B) in the angular frequency range from 1.26×10^{2} to 1.3×10^{7} rad s^{-1} at room temperature. The β-SiC/PANI nanocomposite powders were pressed in a form of disc pellet with a diameter of 25 mm by applying a pressure of 50 MPa in a hydraulic presser and the average thickness was about 1.0 mm. The same sample was used to measure the resistivity by a standard four-probe method from 50 to 290 K. The four probes were 0.002 inch diameter platinum wires, which were attached by silver paste to the sample. The temperature dependent resistivity was used to determine the electrical transport mechanism in the β-SiC/PANI nanocomposites. Magnetoresistance (MR) was carried out using a standard four-probe technique by a 9-Tesla Physical Properties Measurement System (PPMS) by Quantum Design at room temperature. The magnetic field was perpendicular to the current.

S4. FT-IR Analysis

Figure S1 shows the FT-IR spectra of the as-received β-SiC nanoparticles, pure PANI and its nanocomposites filled with different β-SiC nanoparticle loadings. The sharp absorption peak at around 800 cm^{-1} with a shoulder at 913.4 cm^{-1}, observed in the as-received β-SiC nanoparticles, is attributed to the Si-C stretching vibration of the crystalline β-SiC,[1, 2] Figure S1(a). The strong absorption peaks at 1560 and 1481 cm^{-1} for pure PANI, Figure S1(f), correspond to the C=C stretching vibration of the quinoid and benzenoid rings, respectively.[3] The band at 1292 cm^{-1} is related to the C-N stretching vibration of the benzenoid unit.[4] The peak at 1228 cm^{-1} is assigned to the C-H in-plane vibration of the quinoid rings.[5] The out-of-plane bending of C-H in the substituted benzenoid ring of PANI is reflected in the peak at around 792 cm^{-1}.[6] These characteristic peaks of PANI (1560, 1481, 1292, 1228, and 792 cm^{-1}), also observed in the FT-IR spectra of the β-SiC/PANI nanocomposites, Figure S1(b-e), confirm that the synthesized pure PANI and PANI nanocomposites are conductive emeraldine salt (ES) form. Generally, PANI has completely reduced state of “leucoemeraldine base” (LEB) form, half-oxidized state of “emeraldine base” (EB) form, and fully oxidized state of “pernigraniline base” (PB) form.[7] Normally, the LEB and PB forms are insulating even after doping; only EB form can become conductive after doping/protonation process and be converted to emeraldine salt (ES) form.[7]

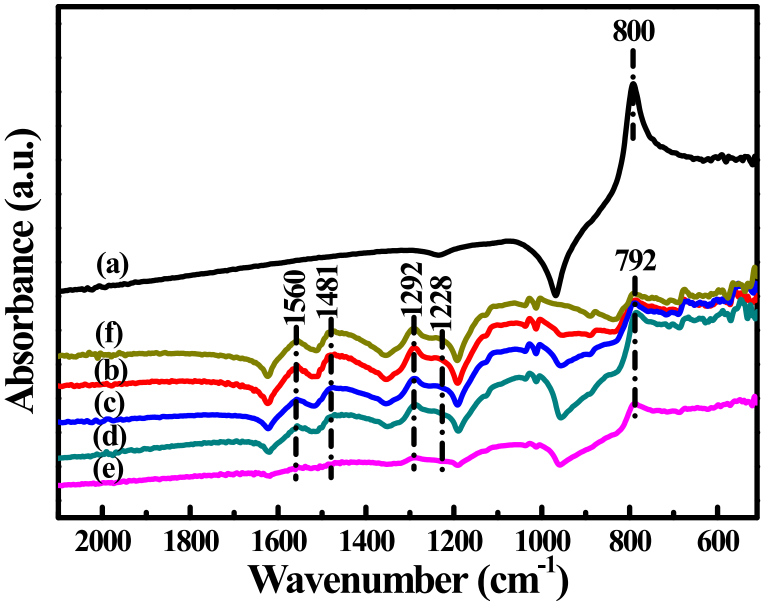


Fig. S1 FT-IR spectra of (a) the as-received *β*-SiC; *β*-SiC/PANI nanocomposites with a *β*-SiC loading of (b) 10.0, (c) 20.0, (d) 40.0, and (e) 60.0 wt%; (f) pure PANI.

S5. X-ray Diffraction Analysis

The X-ray diffraction (XRD) results of the as-received *β*-SiC nanoparticles, pure PANI and *β*-SiC/PANI nanocomposites are shown in Fig. S2. The strong intensity of the diffraction peaks in the XRD curves indicates a highly crystallized structure[3] of the as-received *β*-SiC nanoparticles and *β*-SiC/PANI nanocomposites, Fig. S2(a-e). The diffraction peaks at around 2θ = 35.35, 40.95, 59.70, and 71.60° in the as-received *β*-SiC nanoparticles, Fig. S2(a), are indexed to (1 1 1), (2 0 0), (2 2 0) and (3 1 1) crystallographic planes of moissanite SiC (standard XRD file PDF#29-1129).[8] The broad peak at around 20 and 25° in the pure PANI is attributed to the (1 0 0), and (1 1 0) crystallographic planes of the partially crystallized PANI,[9] Fig. S2(f). The intensity of these broad peaks decreases with increasing the *β*-SiC nanoparticle loadings in the *β*-SiC/PANI nanocomposites and disappears in the *β*-SiC 60.0 wt% loading of *β*-SiC/PANI nanocomposites, Fig. S2(e).

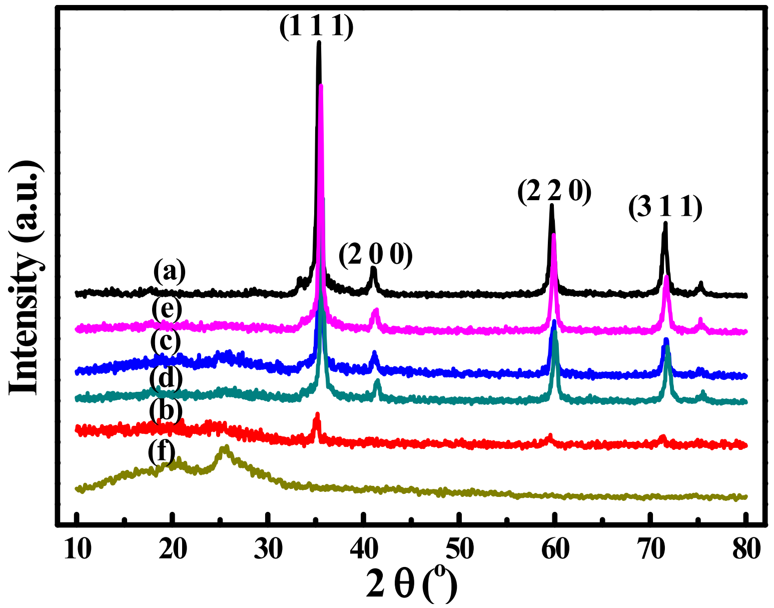


Fig. S2 XRD patterns of (a) the as-received β-SiC; β-SiC/PANI nanocomposites with a β-SiC loading of (b) 10.0, (c) 20.0, (d) 40.0, and (e) 60.0 wt%; (f) pure PANI.

The average crystallite size of as-received β-SiC nanoparticles and β-SiC/PANI nanocomposites is estimated through XRD pattern using the Scherrer Equation (S1):[5]

$$\beta = \frac{k\lambda}{L\cos\theta} \tag{S1}$$

where λ is the X-ray wavelength (λ = 0.154 nm), L is the average crystallite size, k is the shape factor, β is the full-width at half-maximum, and θ is Bragg angle in degree. The shape factor k depends on several factors including the miller index of the reflection plane and the shape of the crystal and normally is 0.89. The peak at 2θ=59.70° is chosen to calculate the average crystallite size of as-received β-SiC nanoparticles and β-SiC/PANI nanocomposites. The obtained average crystallite size of the as-received β-SiC is about 44.6 nm. In the β-SiC/PANI nanocomposites, the calculated average crystallite size is 38.7, 31.3, 31.5 and 39.1 nm for the β-SiC/PANI with a β-SiC loading of 10.0, 20.0, 40.0 and 60.0 wt%, respectively. The average crystallite size is decreased a little bit after adding the β-SiC nanoparticles into the PANI matrix.

S6. Thermogravimetric Analysis

Fig. S3 shows the TGA curves of pure PANI and its *β*-SiC nanocomposites with different *β*-SiC nanoparticle loadings in the air condition.

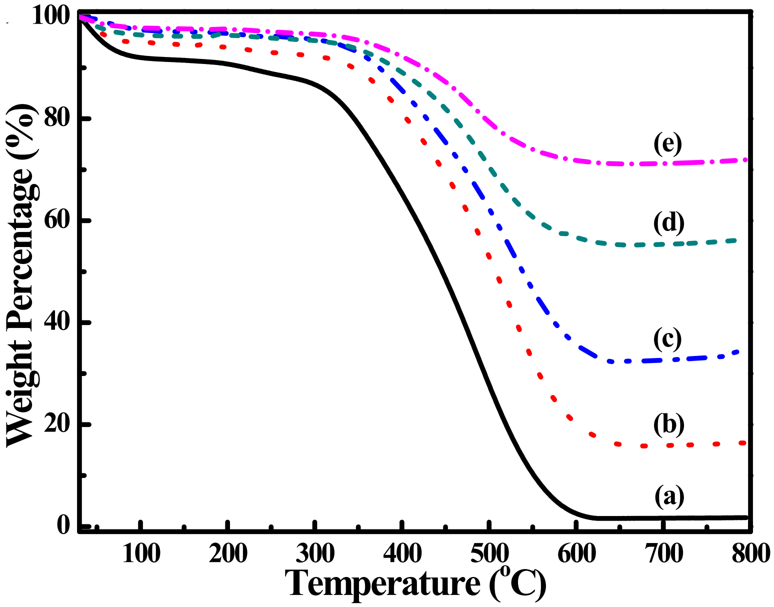


Fig. S3 TGA curves of (a) pure PANI; *β*-SiC/PANI nanocomposites with *β*-SiC loading of (b) 10.0, (c) 20.0, (d) 40.0, and (e) 60.0 wt%.

There is two-stage weight loss observed in the pure PANI and its *β*-SiC nanocomposites. The first stage in the temperature range from room temperature to 250 °C is due to the elimination of moisture and doped PTSA in PANI.[10] The major weight loss of all the samples from 250 to 600 °C is due to the large scale thermal degradation of the PANI chains.[11] The thermal stability of the *β*-SiC/PANI nanocomposites is observed to increase with increasing the *β*-SiC nanoparticle loading. The 15 wt% loss decomposition temperature for pure PANI and its *β*-SiC nanocomposites with a *β*-SiC nanoparticle loading of 10.0, 20.0, 40.0, and 60.0 wt% is 317, 380, 403, 431, and 465 °C, respectively. This indicates that the adding of *β*-SiC nanoparticle into the polymer matrix can improve the thermal stability of the polymer matrix. The pure PANI is almost completely decomposed at 800 °C with only 1.7 wt% left due to the carbonized PANI, indicating that the PANI cannot easily get completely decomposed in air even at high temperature.[6] The weight residues of the nanocomposites with an initial *β*-SiC nanoparticle loading of 10.0, 20.0, 40.0 and 60.0 wt% at 800 °C are 16.45, 34.39, 56.34 and 71.97%, respectively. The difference in the weight residues from the initially calculated nanoparticle loading based on the aniline monomers and nanoparticles is associated with the incomplete polymerization of the aniline monomers.[5, 12]

S7. Microstructures of *β*-SiC/PANI Nanocomposites

Fig. S4 shows the SEM microstructures of the as-received *β*-SiC nanoparticles and its PANI nanocomposites with a *β*-SiC loading of 20.0, 40.0 and 60.0 wt%.

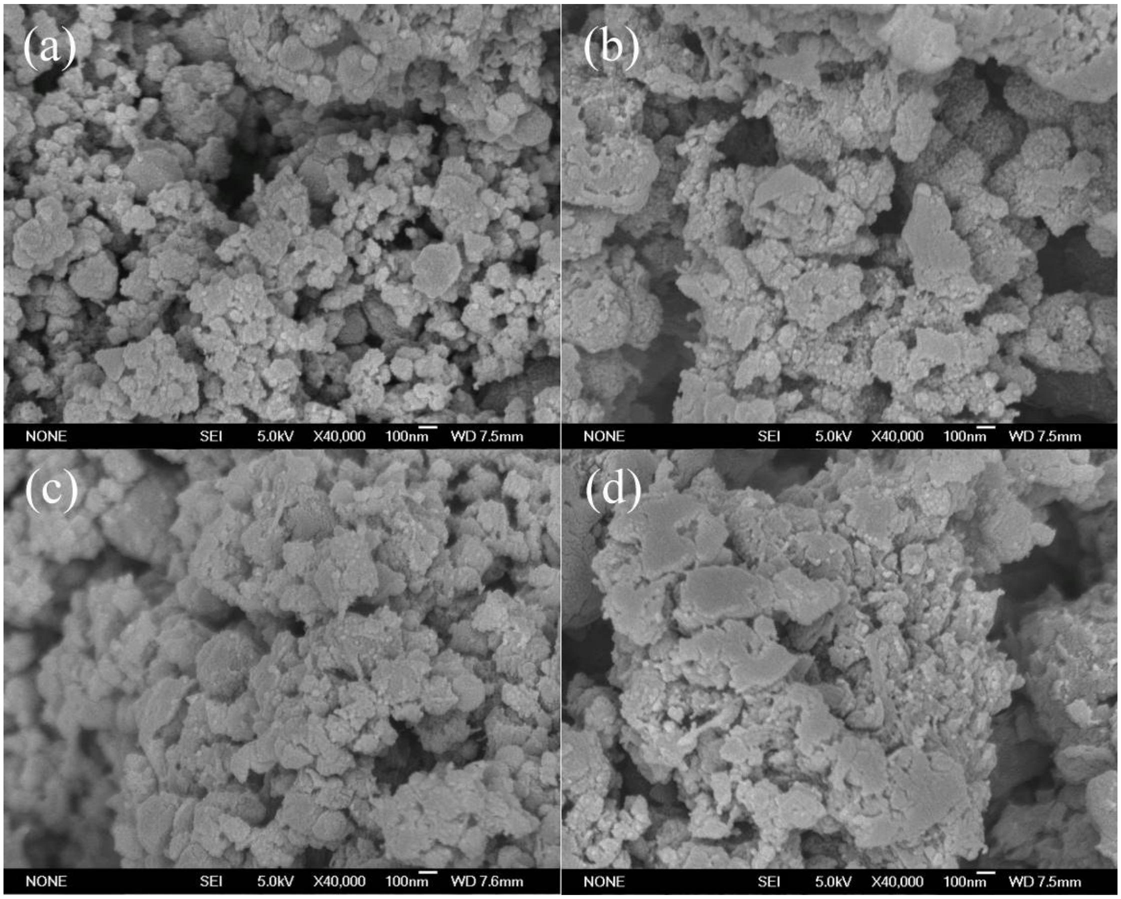


Fig. S4 SEM microstructures of (a) as-received *β*-SiC; and *β*-SiC/PANI nanocomposites with *β*-SiC loading of (b) 20.0, (c) 40.0, and (d) 60.0 wt%.

The as-received β-SiC nanoparticles have a fairly smooth surface, Fig. S4(a). In the SiC/PANI nanocomposites, Fig. S4(b), (c)&(d), the smooth and ball-like surface of the β-SiC nanoparticles are observed to become rough and flake-like surface, indicating the polymerization of PANI occurred on the β-SiC nanoparticle surface.[4]

S8. Angular Frequency (ω) Dependent Real Permittivity (ε') of Pure PANI

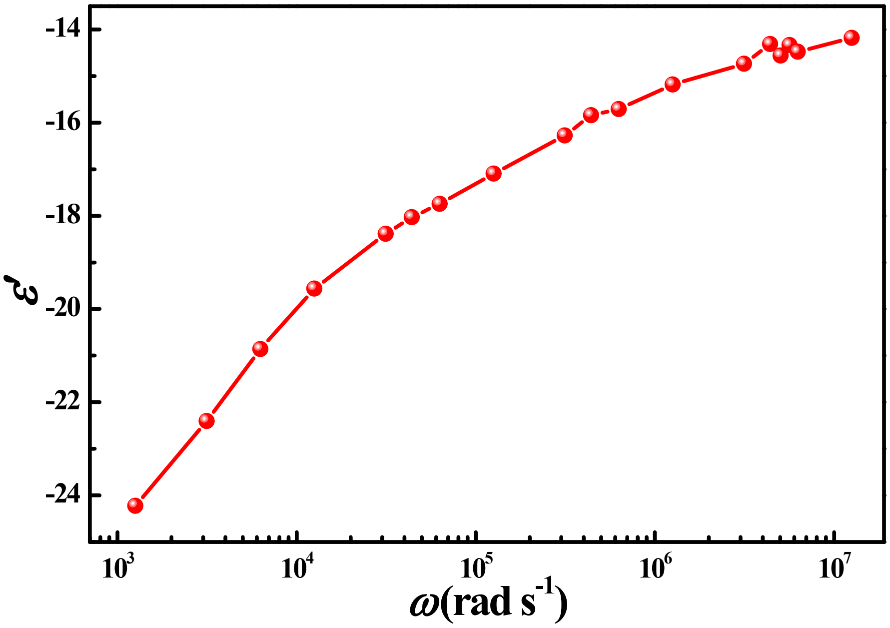
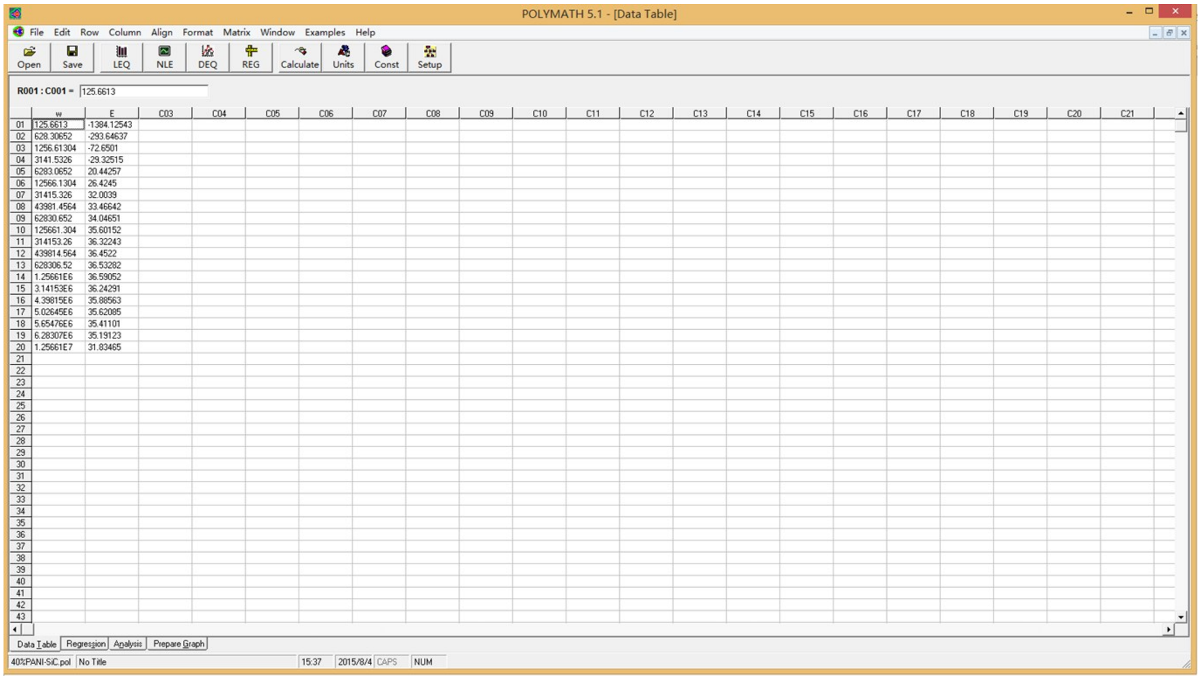


Fig. S5 Real permittivity as a function of angular frequency of PANI.

S9. Polymath Software Fitting Process

For example: angular frequency dependent real permittivity of 40.0 wt% β-SiC:

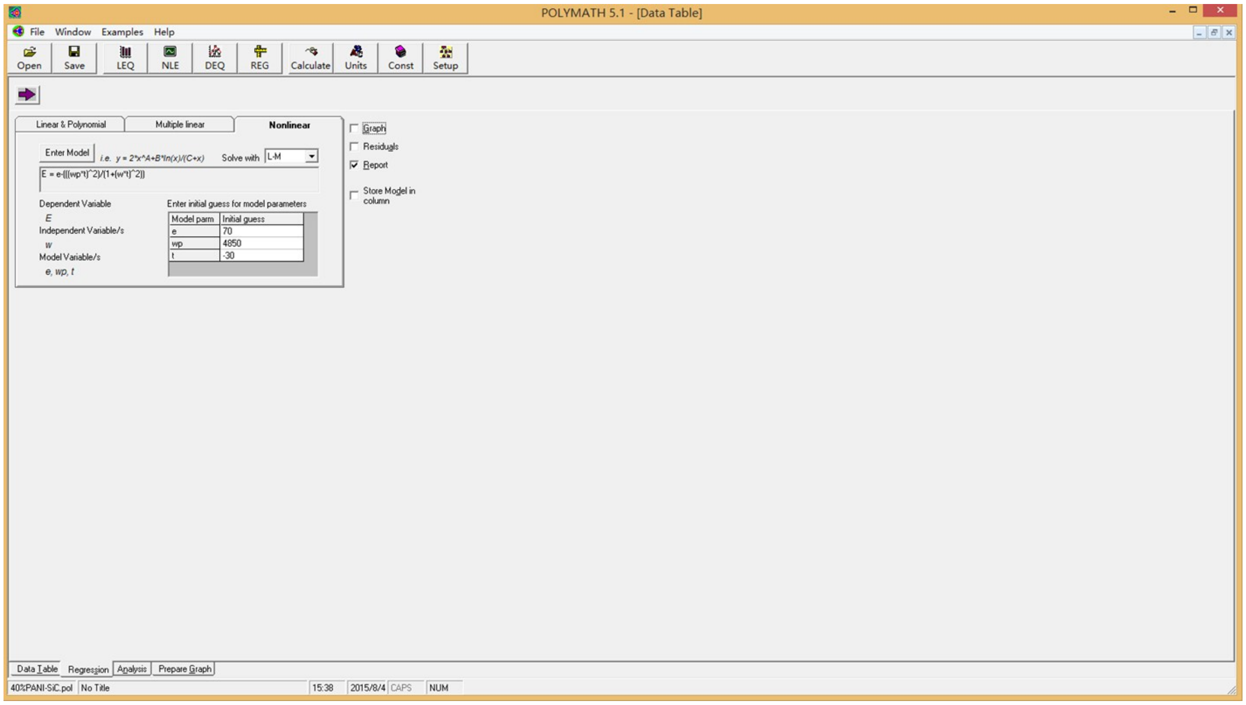
Step 1:



R001 : C001 = 125.6613

	w	E
01	125.6613	-1384.12543
02	628.30652	-293.64637
03	1256.61304	-72.6501
04	3141.5326	-29.32515
05	6283.0652	20.44257
06	12566.1304	26.4245
07	31415.326	32.0039
08	43981.4564	33.46642
09	62830.652	34.04651
10	125661.304	35.60152
11	314153.26	36.32243
12	439814.564	36.4522
13	628306.52	36.53282
14	1.25661E6	36.59052
15	3.14153E6	36.24291
16	4.39815E6	35.88563
17	5.02645E6	35.62085
18	5.65476E6	35.41101
19	6.28307E6	35.19123
20	1.25661E7	31.83465

Step 2:



Solve with L-M

```
E = e-(((wp*t)^2)/(1+(w*t)^2))
```

Dependent Variable: E

Independent Variable/s: w

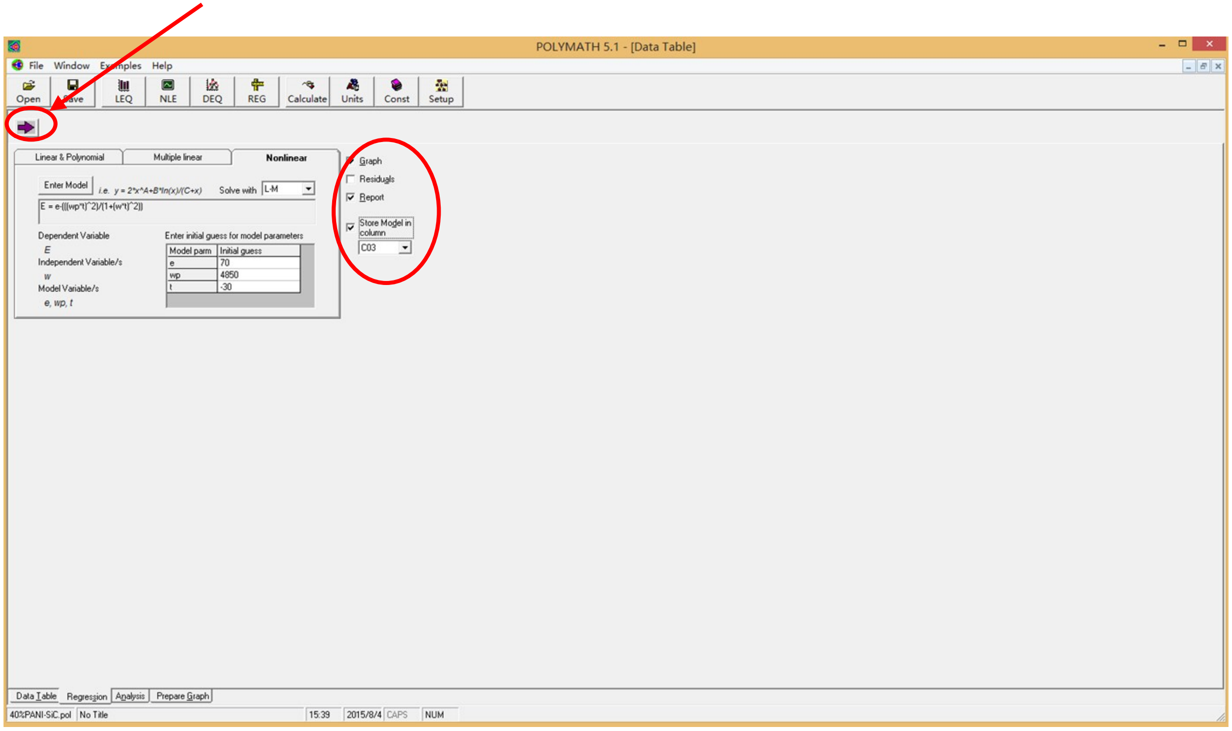
Model Variable/s: e, wp, t

Enter initial guess for model parameters

Model parm	Initial guess
e	70
wp	4850
t	-30

☐ Graph
☐ Residuals
☑ Report
☐ Store Model in column

Step 3:



Solve with L-M

E = e-(((wp*t)^2)/(1+(w*t)^2))

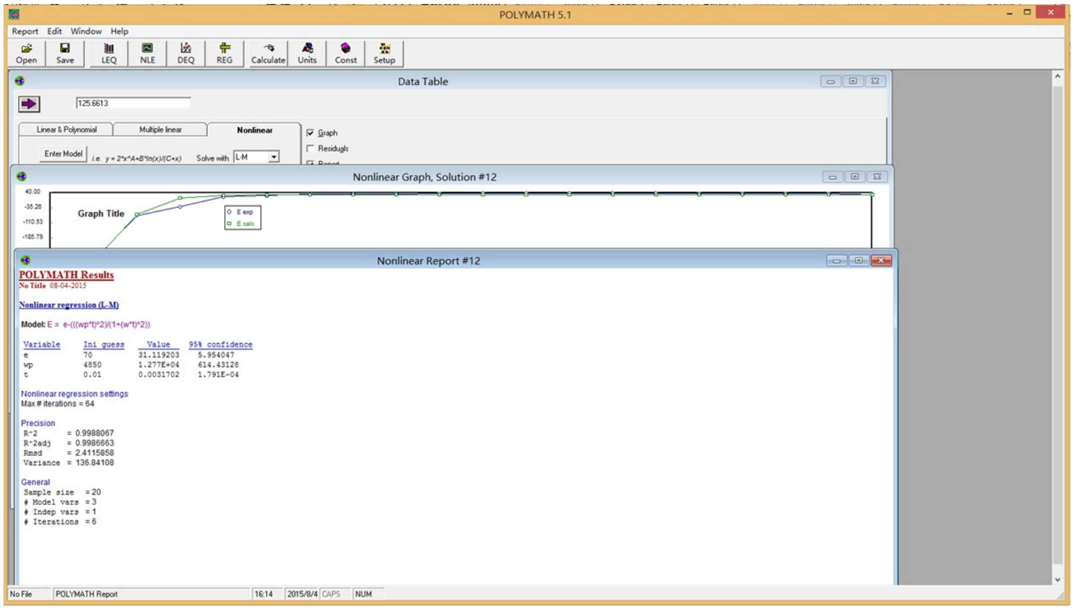
Dependent Variable
E
Independent Variable/s
w
Model Variable/s
e, wp, t

Enter initial guess for model parameters

Model parm	Initial guess
e	70
wp	4850
t	-30

☑ Graph
☐ Residuals
☑ Report
☑ Store Model in column C03

Step 4:



```
POLYMATH Results
No Title  08-04-2015

Nonlinear regression (L-M)

Model: E =  e-(((wp*t)^2)/(1+(w*t)^2))

Variable      Ini guess     Value       95% confidence
e             70            31.119203     5.954047
wp            4850          1.277E+04     614.43128
t             0.01          0.0031702     1.791E-04

Nonlinear regression settings
Max # iterations = 64

Precision
R^2        = 0.9988067
R^2adj     = 0.9986663
Rmsd       = 2.4115858
Variance   = 136.84108

General
Sample size   = 20
# Model vars  = 3
# Indep vars  = 1
# Iterations  = 6
```

S10. Fitting Results Obtained from Polymath Software for *β*-SiC/PANI nanocomposites

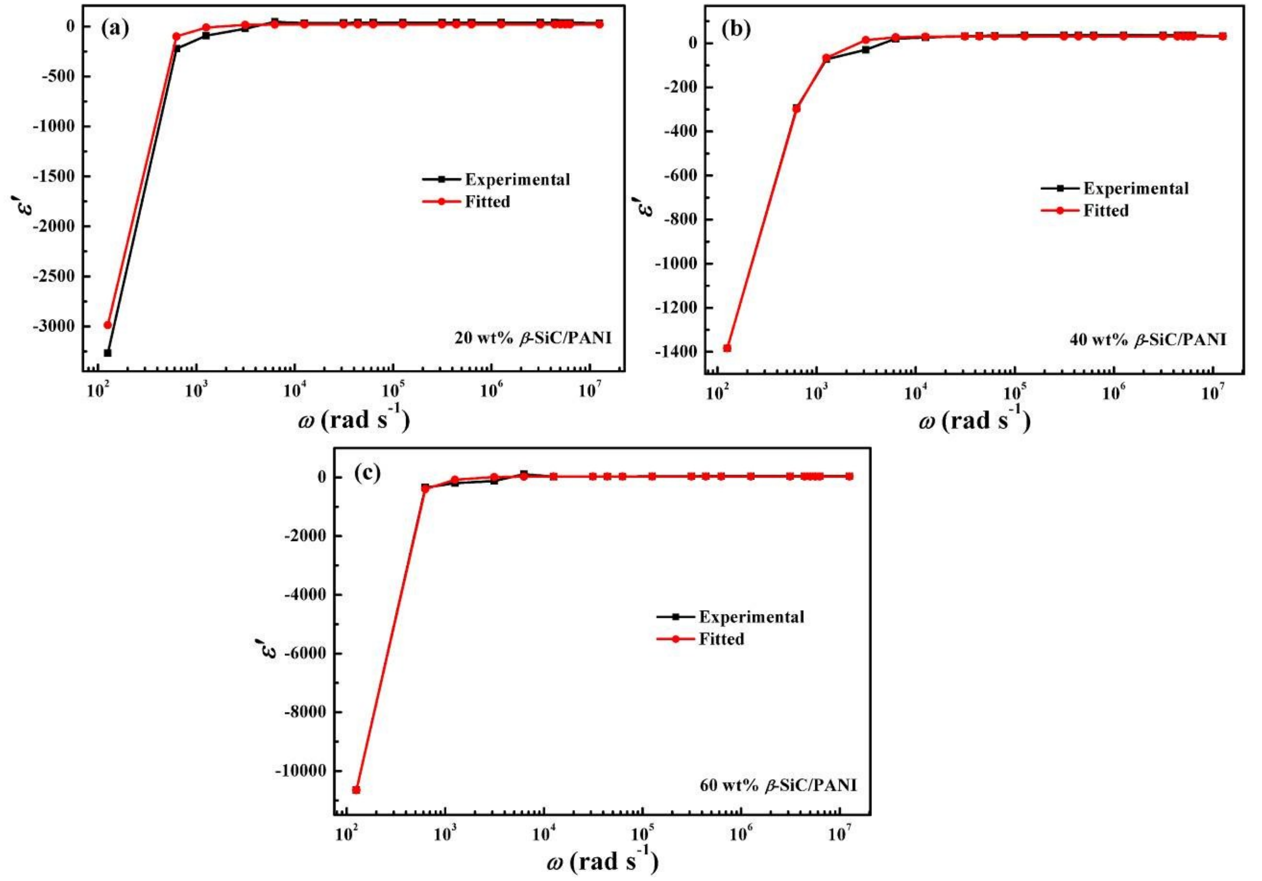


Fig. S6 Experimentally measured and calculated ε' as a function of angular frequency ω for 10.0 wt% *β*-SiC/PANI.

References

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