Electronic Supplementary Information

Enhancement of the Dielectric Response in Polymer Nanocomposites with Low Dielectric Constant Fillers

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Composite Models:

The following models were used for two-phase dielectric composites:

The **Maxwell model** for the dielectric constant of composite K_m for spherical inclusions in a continuous matrix[19].

$$K_m = K_1 \frac{K_2 + 2K_1 - 2V_2(K_1 - K_2)}{K_2 + 2K_1 + V_2(K_1 - K_2)}$$

where K_m, K_1, and K_2 represent the dielectric constants of the composite, phase 1, and phase 2, respectively, V_1 and V_2 are the volume fractions of phases 1 and 2 ($V_1 + V_2 = 1$).

Series and parallel mixing models represent the extreme cases. The series model corresponds to alternating layers of each phase in the direction perpendicular to the applied field (two capacitors in series). The parallel model corresponds to alternating layers of each phase in the direction parallel to the applied field (two capacitors in parallel)[20].

(a) Series model:

$$\frac{1}{K_m} = \frac{V_1}{K_1} + \frac{V_2}{K_2}$$

(b) Parallel model

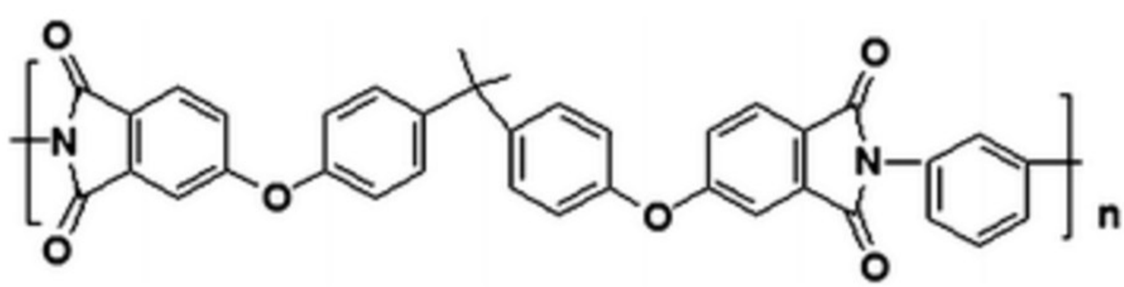
$$K_m = V_1 K_1 + V_2 K_2$$

Lichtenecker model represents a widely used empirical relationship without any concern for the physical geometry of the composite system[21].

$$lnK_m = V_1 lnK_1 + V_2 lnK_2$$

Dipoles in PEI:

The molecular structure of PEI is shown in Scheme S1. As shown by Bendler and Takekoshi[17], the phthalimide group has a large dipole moment, ~ 4.2 Debye, which is arranged along the polymer main chain.



Scheme S1. Molecular structure of the polyetherimide.

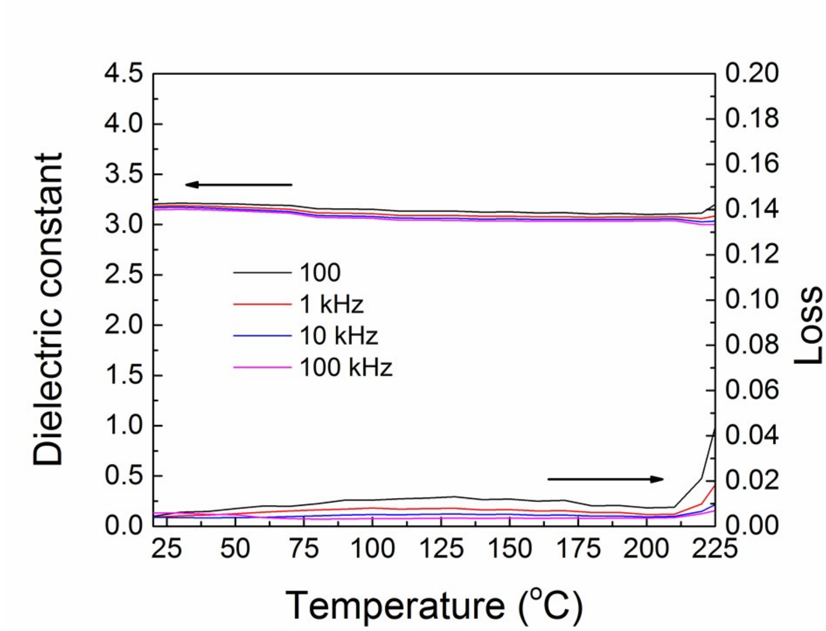


Figure S1. Dielectric properties at different frequencies of neat PEI as a function of temperature.

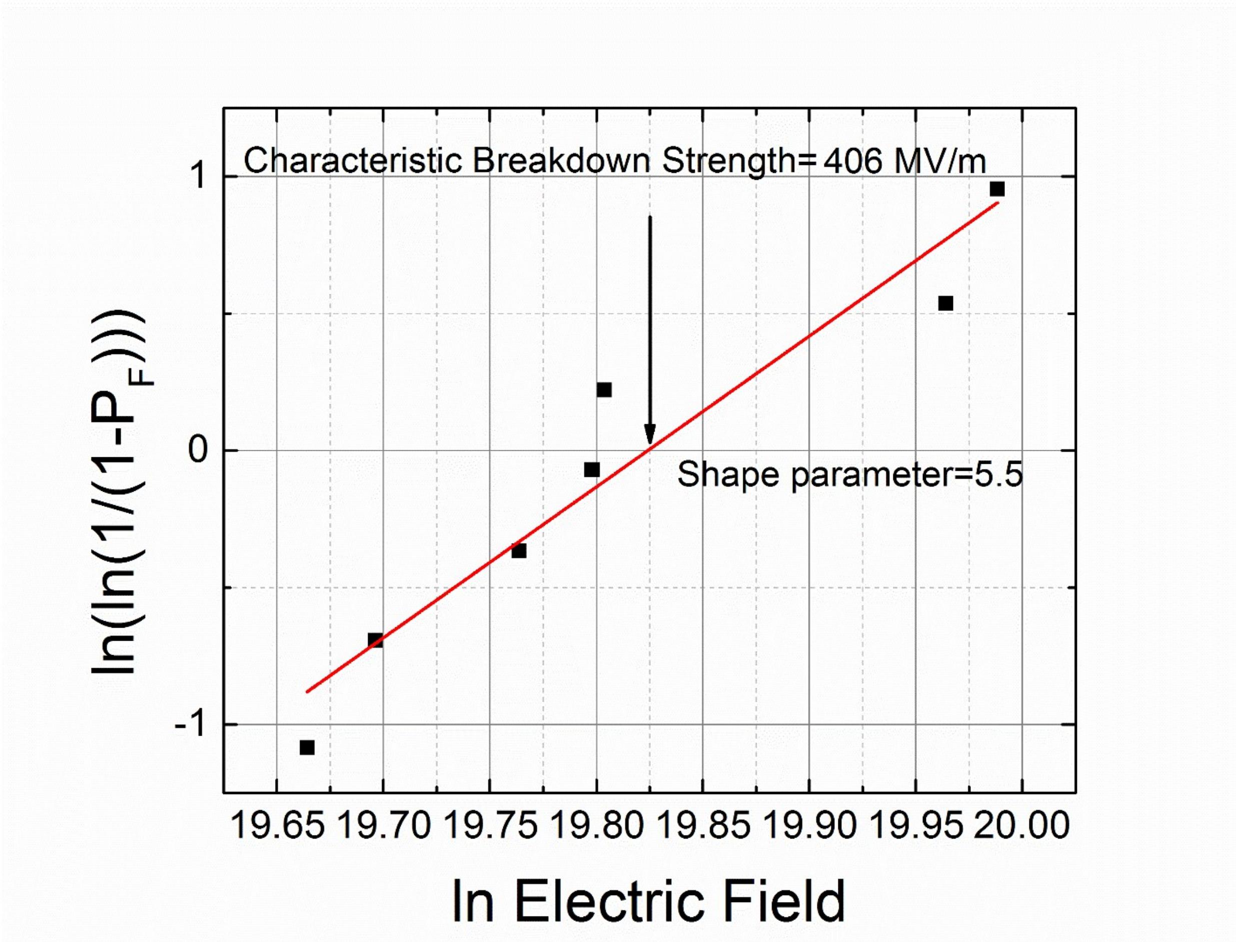


Figure S2. Weibull plot showing failure distribution for PEI-0.32 vol.% Al_2O_3 nanocomposite film

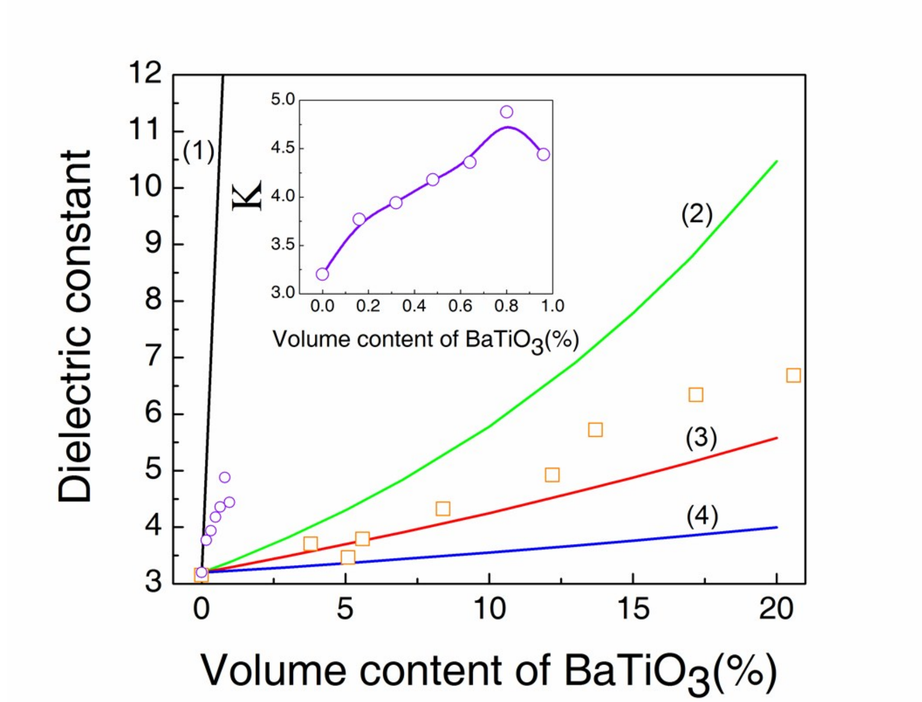


Figure S3. Dielectric constant of PEI/$BaTiO_3$ (50 nm size) nanocomposites vs. $BaTiO_3$ volume content (experimental data points are shown and for > 3 vol.% nanocomposites (orange squares) the data are from Ref. 11). Experimental data are compared with several commonly used composite models (Refs. 19-21): (1) Parallel model (black), (2) Maxwell model (red), (3) Lichtenecker model (green), and (4) series model (blue), assuming the dielectric constant of $BaTiO_3$ is 100X of that of PEI. Inset is an expanded view of the enhanced dielectric response of nanocomposites at very low volume content (< 1 vol.%) due to nanofiller interfacial effects, experimental data points are shown and solid curve is drawn to guide the eye.

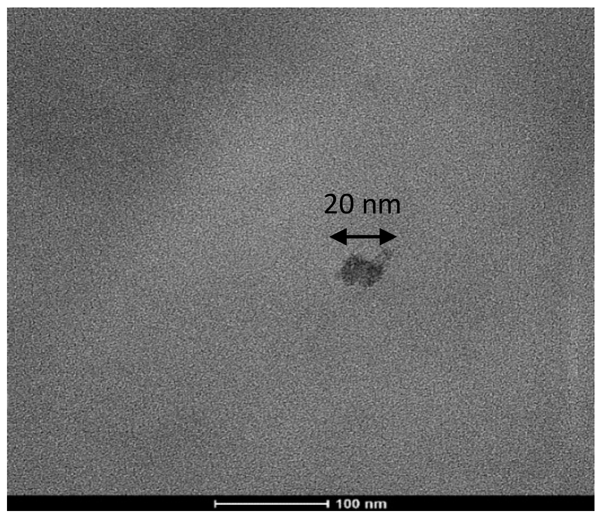
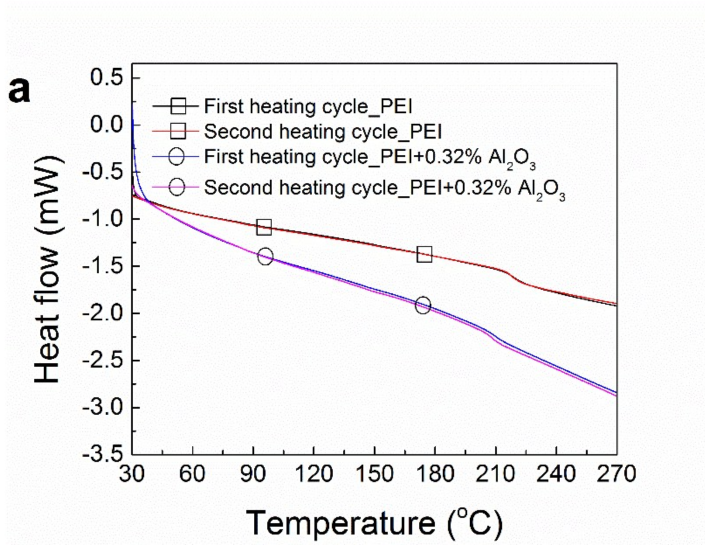


Figure S4. A representative TEM image of the PEI nanocomposite with 0.32 vol.% alumina (20 nm particle size). Due to low volume content of nanofiller in the composite, only one nanoparticle is seen in the image area, as indicated.



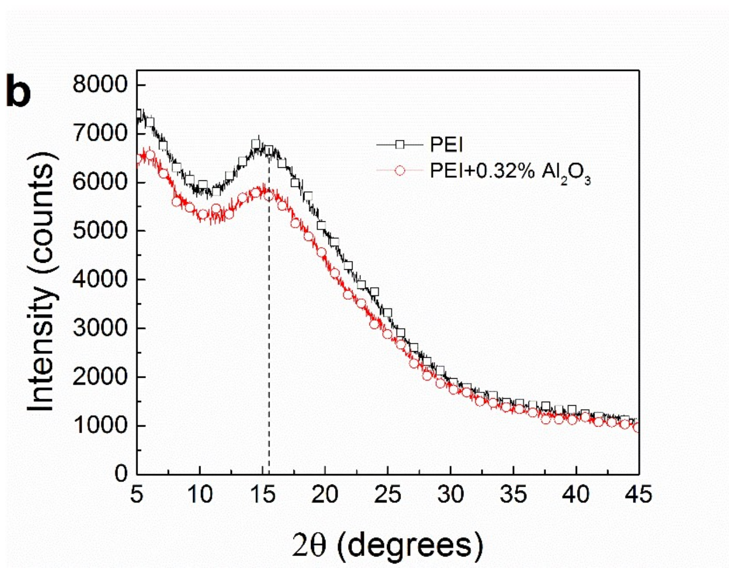


Figure S5. (a) DSC and (b) X-ray diffraction data of PEI and the PEI nanocomposite with 0.32 vol.% of alumina.

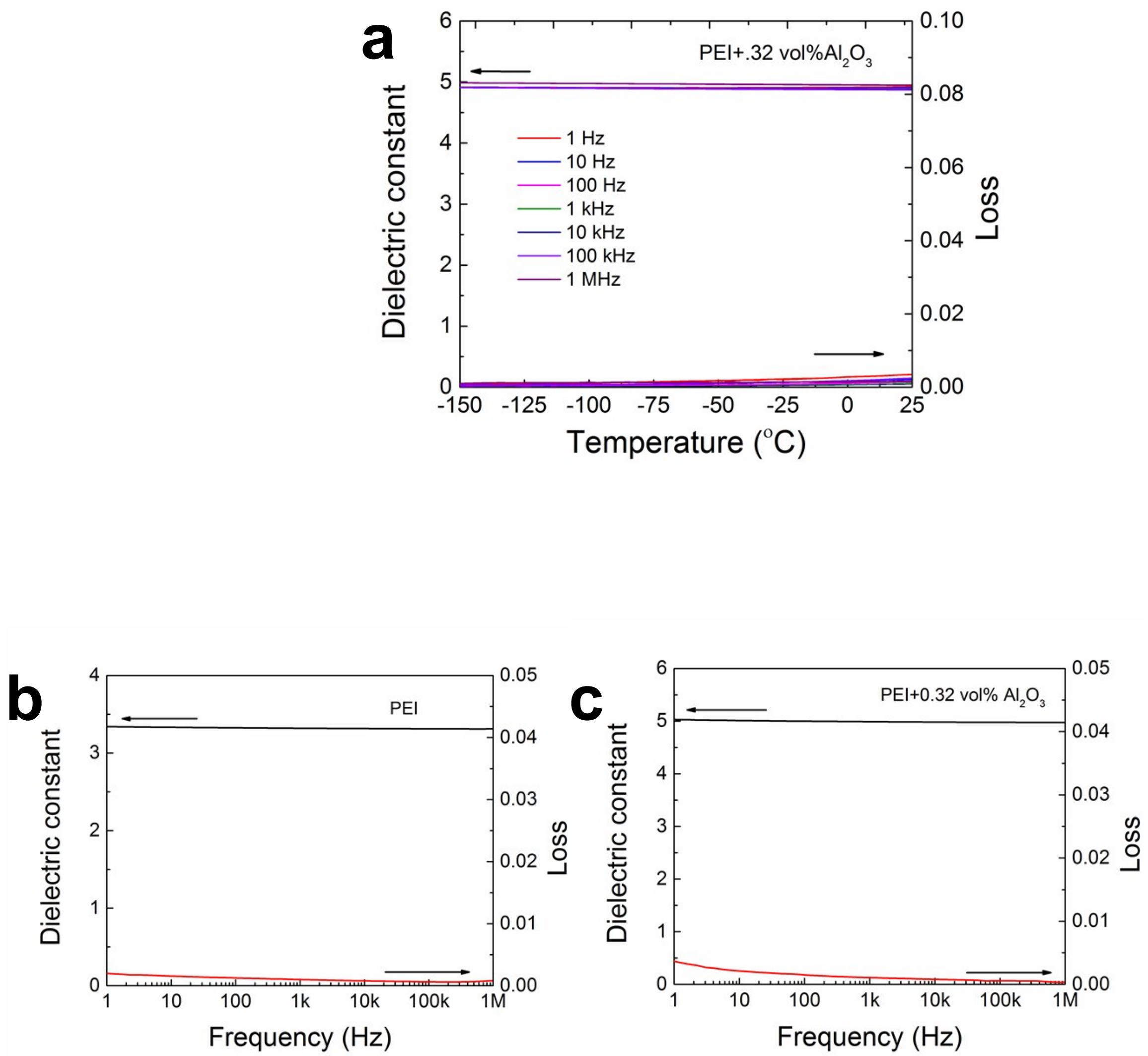


Figure S6. (a) Dielectric data at different frequencies of PEI+0.32 vol.% Al_2O_3 20 nm as a function of temperature, (b) Dielectric data of PEI and (c) PEI+0.32 vol.% Al_2O_3 20 nm nanofiller as a function of frequency at room temperature.

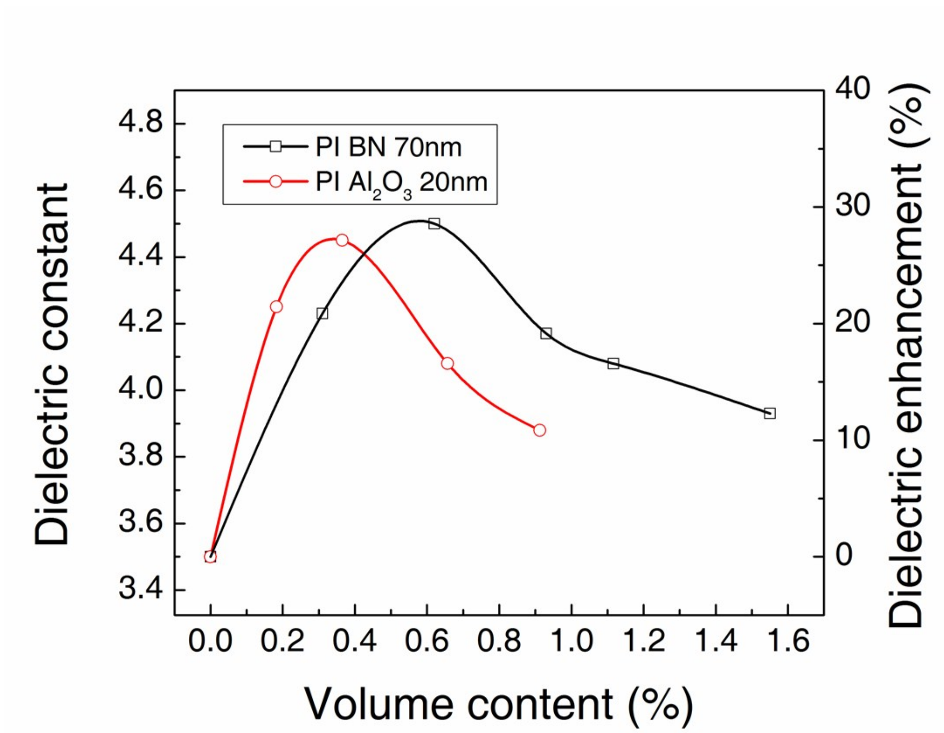


Figure S7. Dielectric constant measured at 1 kHz and room temperature vs. the volume content of the nanofiller for PI nanocomposites. Data points are shown and solid curves are drawn to guide the eye.

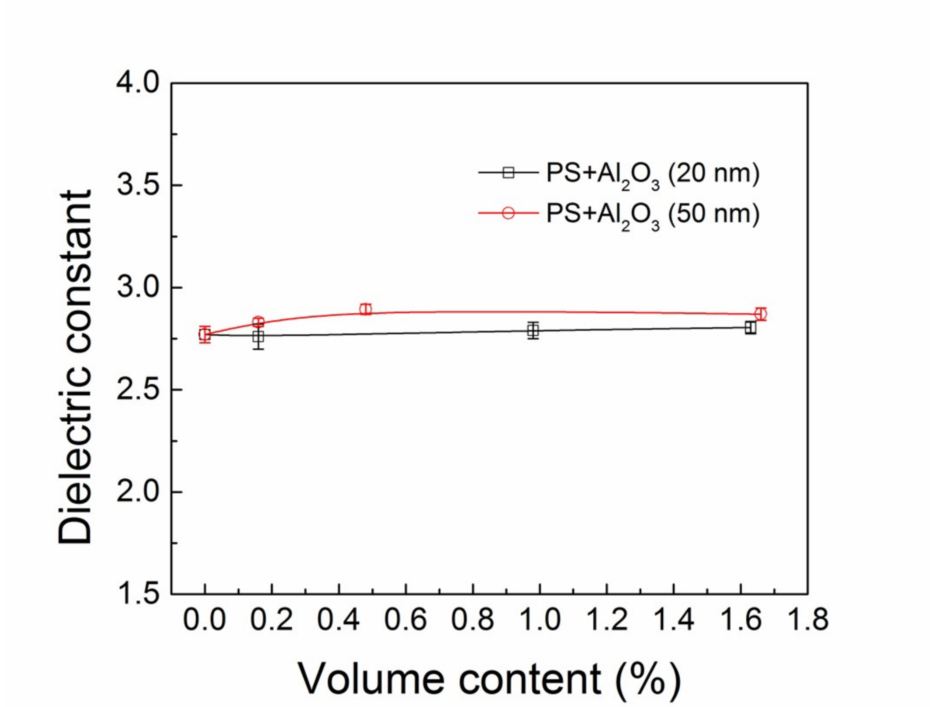


Figure S8. Dielectric constant measured at 1 kHz and room temperature vs. the nanofiller content for PS nanocomposites. Data points are shown and solid curves are drawn to guide the eye.

Table S1. Summary of dielectric data of polyetherimide (PEI) nanocomposite films

Neat Polymer Film	Dielectric constant (1 kHz)	Loss (1 kHz)
Neat PEI	3.17	0.29%
Nanocomposite Film	Dielectric constant (1 kHz)	Loss (1 kHz)
PEI with Al_2O_3 (5 nm)		
PEI+0.08% Al_2O_3 (5 nm) (by vol.)	4.02	0.48%
PEI+0.16% Al_2O_3 (5 nm) (by vol.)	4.44	0.38%
PEI+0.24% Al_2O_3 (5 nm) (by vol.)	5.0	0.42%
PEI+0.32% Al_2O_3 (5 nm) (by vol.)	3.93	0.25%
PEI+0.48% Al_2O_3 (5 nm) (by vol.)	3.65	0.15%
PEI with Al_2O_3 (20 nm)		
PEI+0.16% Al_2O_3 (20 nm) (by vol.)	4.56	0.46%
PEI+0.32% Al_2O_3 (20 nm) (by vol.)	5.0	0.46%
PEI+0.48% Al_2O_3 (20 nm) (by vol.)	4.74	0.5%
PEI+0.64% Al_2O_3 (20 nm) (by vol.)	4.05	0.27%
PEI+1.28% Al_2O_3 (20 nm) (by vol.)	4.01	0.68%
PEI+1.63% Al_2O_3 (20 nm) (by vol.)	3.93	0.61%
PEI with MgO (20 nm)		
PEI+0.17% MgO (20 nm) (by vol.)	4.36	0.55%
PEI+0.35% MgO (20 nm) (by vol.)	4.95	0.23%
PEI+0.70% MgO (20 nm) (by vol.)	4.09	0.49%
PEI with SiO_2 (20 nm)		
PEI+0.26% SiO_2 (20 nm) (by vol.)	4.88	0.24%
PEI+0.79% SiO_2 (20 nm) (by vol.)	3.84	0.43%
PEI with Al_2O_3 (50 nm)		
PEI+0.27% Al_2O_3 (50 nm) (by vol.)	3.92	0.63%

PEI+0.32% Al_2O_3 (50 nm) (by vol.)	4.18	0.29%
PEI+0.64% Al_2O_3 (50 nm) (by vol.)	4.27	0.35%
PEI+0.83% Al_2O_3 (50 nm) (by vol.)	4.88	0.43%
PEI+1.1% Al_2O_3 (50 nm) (by vol.)	4.29	0.61%
PEI+1.66% Al_2O_3 (50 nm) (by vol.)	3.82	0.53%
PEI with $BaTiO_3$ (50 nm)		
PEI+0.16% $BaTiO_3$ (50 nm) (by vol.)	3.77	0.35%
PEI+0.32% $BaTiO_3$ (50 nm) (by vol.)	3.94	0.43%
PEI+0.48% $BaTiO_3$ (50 nm) (by vol.)	4.18	0.23%
PEI+0.64% $BaTiO_3$ (50 nm) (by vol.)	4.36	0.24%
PEI+0.80% $BaTiO_3$ (50 nm) (by vol.)	4.88	0.40%
PEI+0.96% $BaTiO_3$ (50 nm) (by vol.)	4.44	0.45%
PEI with BN (70 nm)		
PEI+0.27% BN (70 nm) (by vol.)	3.73	0.25%
PEI+0.55% BN (70 nm) (by vol.)	3.97	0.58%
PEI+0.83% BN (70 nm) (by vol.)	4.71	0.89%
PEI+1.1% BN (70 nm) (by vol.)	4.55	0.19%
PEI+1.66% BN (70 nm) (by vol.)	4.21	0.18%

Table S2. Summary of dielectric data of polyimide (PI) nanocomposite films

Neat Polymer Film	Dielectric constant (1 kHz)	Loss (1 kHz)
Neat PI	3.5	0.5%
Nanocomposite Film	Dielectric constant (1 kHz)	Loss (1 kHz)
PI with Al_2O_3 (20 nm)		
PI+0.18% Al_2O_3 (20 nm) (by vol.)	4.22	0.50%
PI+0.36% Al_2O_3 (20 nm) (by vol.)	4.45	0.69%
PI+0.65% Al_2O_3 (20 nm) (by vol.)	4.08	0.75%
PI+0.91% Al_2O_3 (20 nm) (by vol.)	3.88	0.62%
PI with BN (70 nm)		
PI+0.31%BN (70 nm) (by vol.)	4.23	0.74%
PI+0.62%BN (70 nm) (by vol.)	4.48	0.76%
PI+0.93%BN (70 nm) (by vol.)	4.17	0.79%
PI+1.11%BN (70 nm) (by vol.)	4.08	0.87%
PI+1.55%BN (70 nm) (by vol.)	3.93	0.74%

Table S3. Summary of dielectric data of non-polar polystyrene (PS) nanocomposite films

Neat Polymer Film	Dielectric constant (1 kHz)	Loss (1 kHz)
Neat PS	2.77±0.04	0.30%
Nanocomposite Film	Dielectric constant (1 kHz)	Loss (1 kHz)
PS with Al_2O_3 (20 nm)		
PS+0.16% Al_2O_3 (20 nm) (by vol.)	2.76±0.06	0.13%
PS+0.98% Al_2O_3 (20 nm) (by vol.)	2.79±0.03	0.14%
PS+1.63% Al_2O_3 (20 nm) (by vol.)	2.80±0.03	0.43%
PS with Al_2O_3 (50 nm)		
PS+0.16% Al_2O_3 (50 nm) (by vol.)	2.83±0.02	0.33%
PS+0.48% Al_2O_3 (50 nm) (by vol.)	2.89±0.02	0.27%
PS+1.66% Al_2O_3 (50 nm) (by vol.)	2.87±0.03	0.24%

Table S4. Effect of particle size and volume fraction on the distance between the neighboring nano-particles

Particle diameter (nm)	Volume fraction (%)	Distance between neighboring particles (nm)
20	0.1	141
20	0.3	92
20	0.9	57
50	0.3	230
50	0.9	144