

Supplementary Information

A strategy to achieve high electromagnetic interference shielding and ultralow percolation in multiwall carbon nanotube/polycarbonate composites through selective localization of carbon nanotube

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1S. Optical Microscopy

A slight reduction in bead size of the PC was evident in the optical image of the composites. This could be due to partial swelling and thus, surface etching of the beads to some extent by the solvent during composites preparation. If this is true, one would expect more surface etching and hence significant reduction in bead size when the composites were prepared with relatively low loading of the PC bead, using same amount of the solvent. To check this, we compared the optical images of MWCNT/PC composites, prepared with the same method, containing 0.1 wt% of MWCNT in the presence of 60 wt% (Figure 1Sa) and 40 wt% PC bead (Figure 1Sb), which are shown in Figure 1S. As evident, the size of the beads (white regions) in optical images of the composites with 60 wt% and 40 wt% PC bead is smaller as compared to that in case of the composites with 70 wt% PC bead.

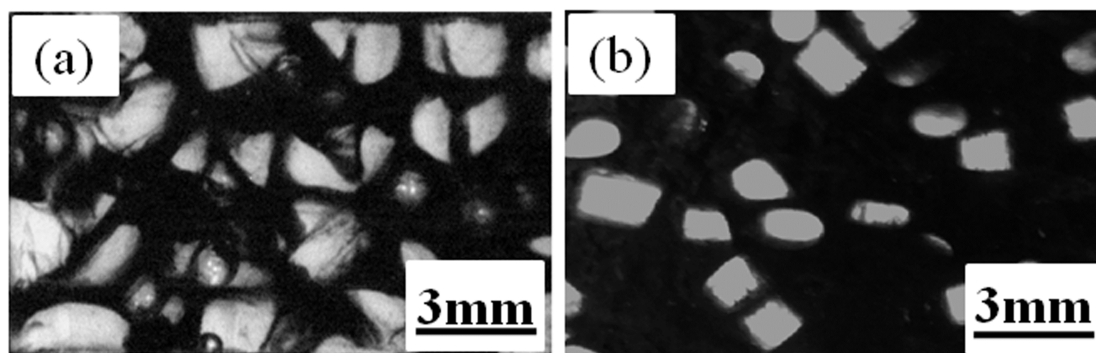


Figure 1S: Optical micrograph of MWCNT/PC composites with (a) 60 wt% PC bead and 0.1 wt% MWCNT loading and (b) 40 wt% PC bead and 0.1 wt% MWCNT loading.

2S. Measurement of σ_{AC}

The variation of σ_{AC} with f for the MWCNT/PC composites is shown in figure 2Sa. The variation of σ_{AC} of the composites with f at various PC bead loading (0 to 70 wt%) and constant MWCNT loading (0.10 wt%) was measured at room temperature, as shown in figure 2Sa. It is noted that the value of σ_{AC} for pure PC increases with increasing f which is the general

phenomena of insulating materials. In addition, the value of σ_{AC} for MWCNT/PC composites at constant MWCNT loading (0.10 wt%) increases with increasing the amount (up to 70 wt%) of PC bead loading. This indicated that with increasing the PC bead loading in the composites, effective concentration of the MWCNT increases in the solution blended PC phase. This high concentration of the MWCNT with increasing the PC bead loading makes an interconnected continuous conductive network path throughout the solvent dried PC region and thus, the value of σ_{AC} increases with increasing the PC bead loading in the composites. From the figure, it is clearly shown that the value of σ_{AC} for the composites remains almost constant up to a certain f , known as critical frequency (f_c). Beyond f_c , the value of σ_{AC} of the composites increases with increasing the f . The value of f_c shifted towards higher f region with increasing the loading of PC bead in the composites. This is because of formation of strong network structure of CNT–CNT by increasing the effective concentration of MWCNT with the incorporation of more amount of PC bead in the solution blended MWCNT–PC region. This result is also well supported by previous observations.^{1,2}

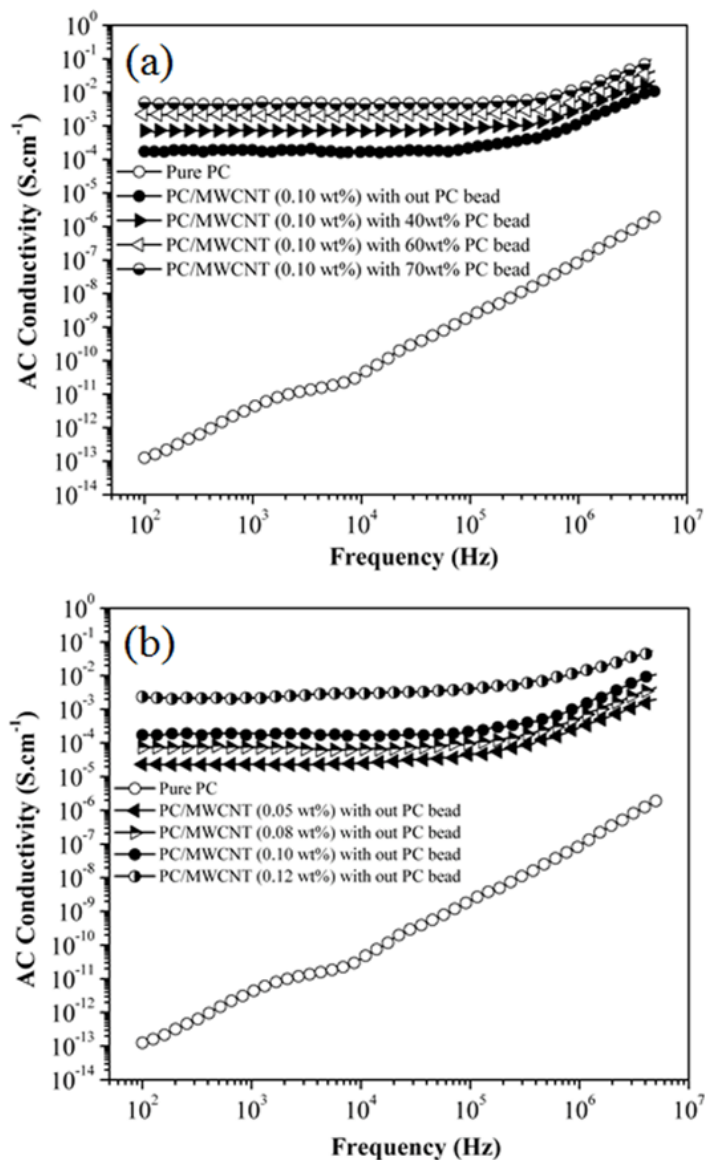


Figure 2S: AC conductivity of the MWCNT/PC composites versus frequency at (a) different loading of PC bead at constant CNT loading and, (b) different MWCNT loadings without PC bead.

Figure 2Sb shows the variation of σ_{AC} with f for the MWCNT/PC composites with various loadings (0.05 to 0.12 wt%) of MWCNT at constant PC bead content. It is observed that the value of σ_{AC} for pure PC increases with increasing f , consistent with the general

characteristic of insulating materials. Furthermore, the value of σ_{AC} increases with increasing the MWCNT loading in the composites.

From the figure, it is clearly seen that the value of σ_{AC} is independent on f at low f region and beyond f_c , this value increases with increasing the f . AC conductivity of any dielectric material below f_c can be expressed as:

$$\sigma_{\downarrow AC} = \sigma_{\downarrow DC} + \omega \varepsilon'' \quad (S1)$$

Where σ_{AC} and σ_{DC} are the AC and DC conductivity of the sample, respectively; ω is angular frequency (i.e. $\omega = 2\pi f$) and ε'' is dielectric loss factor. The σ_{AC} of any dielectric material is the combination of two components, as shown in equation S1. The first component σ_{DC} generate from conduction of charge carriers (i.e. ion or electrons), whereas, the second component $\omega \varepsilon''$ comes from dipole movement (permanent or induced) of dielectric material and accumulated charge at the interface. Below f_c all dipole (permanent or induced) get sufficient time to orient themselves with the direction of applied electric field, whereas, at high f (above f_c), speed of electric field is higher than the dipole movement of the material and remaining polarization at this stage is only due to accumulated interfacial charge between MWCNT and polymer. Thus, the value of σ_{AC} depends only on the flow of electron through the conductive network in the matrix. Furthermore, hopping and tunneling of electron through the polymer barrier between CNT become easier which increase the σ_{AC} value.

3S. Dielectric permittivity

The variation of dielectric permittivity (ε') of MWCNT/PC composites with the f was measured at room temperature with changing the PC bead loading (0 to 70 wt%) at a constant MWCNT loading (0.10 wt%), as shown in figure 3Sa. As can be seen, the value of ε' for the composites decreases with increasing f in the region $\sim 10^1$ to $\sim 10^7$ Hz. This is the well-known

phenomena of any dielectric materials. This kind of phenomena could be explained with the help of polarization effect. Accordingly, the dielectric permittivity of a material is proportionally varied with polarizability.³ The polarization effect is more prominent at low f region as the molecules of dielectric materials get sufficient relaxation time to orient them in the direction of the applied electric field. Thus, the value of ϵ' of the composites increases. The value of ϵ' of the composites decreases with the increase in f , indicating the dominant nature of electronic polarization at higher f . With increase in f , polarization effect in the dielectric material become insignificant as the molecules are getting less relaxation time for orientation themselves in the direction of applied alternative electric field.

The variation of ϵ' with the f of the MWCNT/PC composites without any PC bead with increasing content of MWCNT (0.05 to 0.12 wt%) is shown in figure 3Sb. The value of ϵ' of pure PC does not depend on the f . At low f region, the value of ϵ' of the composites is high and it is going to decrease at higher f region. In high f region, a relaxation process took place that helps to a drastic drop in the value of ϵ' . Similar result of the dielectric response was found by Potschke et al.⁴ where dielectric constant decreased with increasing the f in CB/elastomer composites above the p_c . This improvement of dielectric property indicated that the incorporation of nanofiller in the polymer plays a great role to increase the dielectric permittivity of the composites.

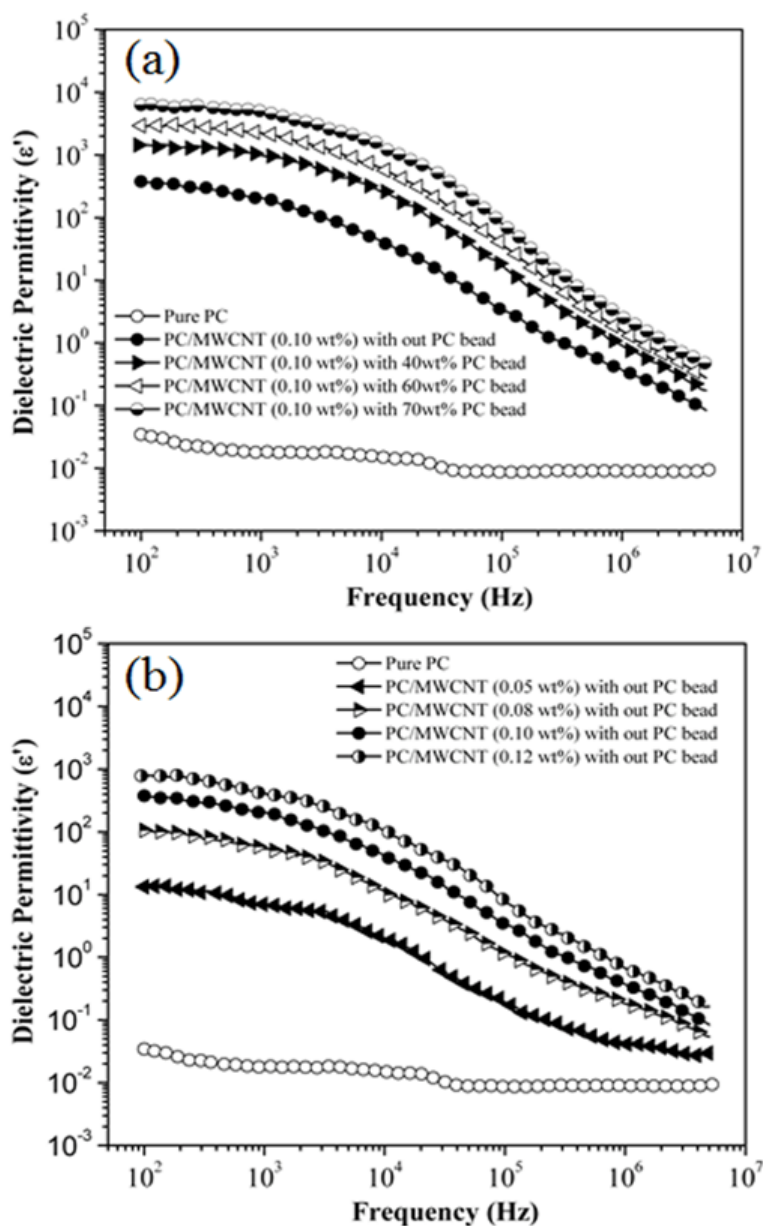


Figure 3S: Dielectric permittivity vs. frequency of MWCNT/PC composites (a) with variation of PC bead loading at constant CNT loading and (b) with variation of CNT loading without any PC bead.

The enhancement of dielectric permittivity of the composites with the incorporation of nanofiller could be due to several factors, such as (i) the large surface area of nanofiller modifies the morphology of the polymer in the composites, (ii) the large surface area and very high aspect

ratio of nanofiller which creates a large interaction zone in the polymer composites, (iii) a reduction in the internal field due to nano-sized of the fillers in the composites, (iv) high electrical conductive nano-sized fillers changes the space charge distribution,⁵ and (v) also scattering mechanism of the composites. In the case of nanofiller filled materials, the nano-sized of the filler leads to an exceptionally large interfacial area in the composites. Since nanofiller have a greater surface area to volume ratio due to its nano-sized and high aspect ratio, they possess a much greater interface with their neighbors compared to the macrofiller. Thus, the degree of interfacial interaction among the nanofiller and the host polymer has been controlled by this interface and also controls the electrical and physical properties of the composites. Dissado et al.⁶ studied the dielectric permittivity of polymer composites and where dielectric permittivity was shown to increase at low f region due to ‘quasi-dc’ conduction which is well explained by Lewis⁷ with the help of O’Konski’s model⁸ and a double layer approach. According to the model, the charge carriers are efficiently moved around the interface by the field leading to an induced polarization at the polar ends of the fillers or particles.⁷ This could be the reason behind a high dielectric permittivity value in the composites. Since these double layer effects are likely to be prominent in composites, the slope of the permittivity is steeper than that for the micro-composites in the low f region.

4S. DMA study

Figure 4Sa shows the storage modulus of the MWCNT/PC composites with different loading of the PC bead (0 to 70 wt%) at constant MWCNT loading (0.10 wt%). The storage modulus of the composites was increased with increasing the PC bead (up to 70 wt%) loading. With the addition of PC bead in the composites, the effective concentration of MWCNT in the composites increases. Thus, a strong continuous conductive interconnected network path of

CNT–CNT was developed throughout the continuous phase which helps to restrict the chain mobility of the polymer and hence, increased the storage modulus of the composites.

The storage modulus of MWCNT/PC composites was measured in the temperature range from room temperature to 180 °C with different loadings (0.05 to 0.12 wt%) of MWCNT without any PC bead, as shown in figure 4Sb. From the figure, it is clearly seen that storage modulus of the MWCNT/PC composites was increased with increasing the MWCNT loading in the composites. Since, nanofillers have a much higher surface area than larger particles; they hold a much greater interface with their environment. Thus, the extent of interaction between the matrix phase and nanofillers was greatly controlled by this interface. Sternstein et al.⁹ studied the visco-elastic behavior of the nano-filled materials and suggested that particulates of nanometric dimensions contribute to the process of tether chain entanglement, which might have significant impact on this interaction zone. Since, the surface area was increased with incorporation of nanofillers in the composites, tethered zones will become more important and movement of the polymeric chain in the composites will be restricted. This reduction in chain mobility (in addition to the physical and chemical bonding of the polymer chain with nanofillers) might contribute to the reduction in polymer chain relaxation by the formation of cross linking physical bonds between the polymers and fillers in the composites. Thus, MWCNT retards the chain mobility of the polymer and enhanced the storage modulus of the composites.

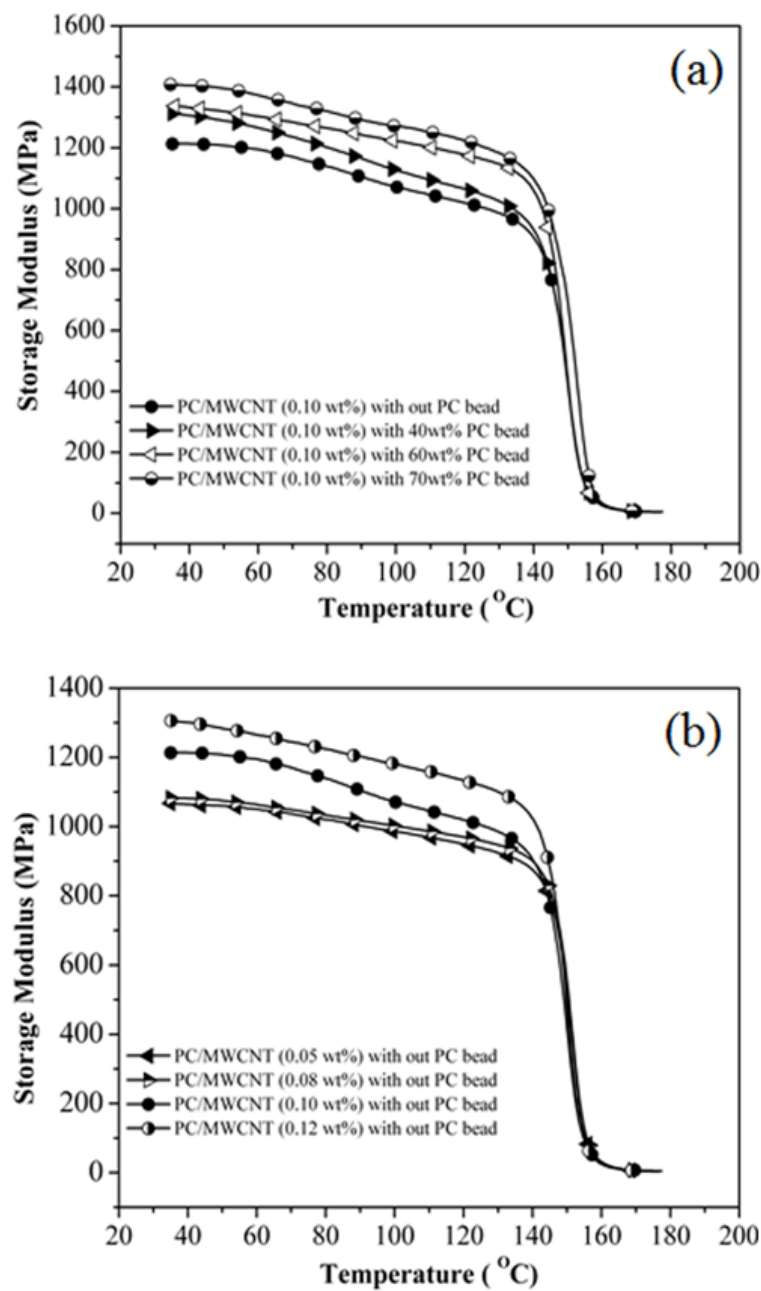


Figure 4S: DMA study of the MWCNT/PC composites at (a) different loading of PC bead at constant MWCNT loading (0.10 wt%) and (b) different MWCNT loading without any PC bead.

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