Supporting Information

To Study Surface and Sub-surface Nanomechanical Properties of Electrospun Polyacrylonitrile (PAN) Nanofibers/Polydimethylsiloxane (PDMS) Composites

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I) Determination of crosslinking density by Mooney-Rilvin equation

Dumbbell shaped tensile test pieces were fabricated according to ASTM D412 Type C standard as described in Materials and Method section. The samples were immersed with certain amount of ethyl acetate until fully swollen (around 4days). The volume fraction of composites can be obtained by following equation (1)

$$V_{r} = \frac{(w_{1}/\rho_{1})}{(w_{1}/\rho_{1}) + (w_{2}/\rho_{2})} \quad (1)$$

Where, w_1 and w_2 are weights of sample and solvent respectively; and ρ_1 and ρ_2 are densities of composites and solvent respectively. From swelling experiment, it was found that the samples were swelled by approximately 30%. Samples were further used for crosslinking density measurement via stress-strain measurement under similar conditions mentioned in Materials and Method section. **Figure S1** shows typical Mooney-Rilvin plots of control PDMS (S0) and PAN nanofiber PDMS composites (S1 to S10). The data in **Figure S1** were experimentally determined from tensile elongation range of 50-80%.



Figure S1. Typical Mooney-Rilvin plots of control PDMS (S0) and PAN nanofiber PDMS (S1-S10) composites (S1 to S10) plot of $\frac{\sigma V_r^{1/3}}{(\lambda - \lambda^{-2})}$ against $\frac{1}{\lambda}$ for determination of constant $C_{I_{-}}$

From the plot of $\frac{\sigma V_r^{1/3}}{(\lambda - \lambda^{-2})}$ against $\frac{1}{\lambda}$ the intercept C1 was determined which is used for

calculation of crosslinking density.

II)Measurement of volume fraction (V_f) of PAN nanofibers in composites by computer aided image processing.

To determine the volume fraction of fibers in the PDMS composites through entire thickness using image analysis techniques, optical photomicrographs with magnification 5X were acquired at 4 different locations on same sample. **Figure 3** in Material and Method section shows typical, photomicrograph obtained from a single location on each composite. The fibers within the PDMS elastomer appear as a brighter segments (white) embedded within elastomer (black). The optical photomicrograph was first converted into a black-and-white or 'binary' image using Segmentation plugin in ImageJ software. **Figure S2** shows typical segmented images for all prepared composites.



Figure S2. Segmented images for all prepared composites (S1-S10) using segmentation procedure in ImageJ software.

Segmentation serves to refine the image, highlighting fiber edges and eliminating isolated pixel areas. The acquired segmented binary images were analyzed by Diameter J Plugin to determine number of fibers and % porosity (void area). It involves counting the number of black pixels (PDMS matrix) and white pixels (fiber) contained in a region of a binary image, allowing the area associated with each constituent to be determined. The fiber volume fraction (V_f) was determined by multiplying the number of fibers by the fiber cross-sectional area and dividing the resultant fiber area by the total area of the image. The process was repeated for images taken at different locations on same sample to determine average volume fraction of fibers in the PDMS matrix.