Electronic Supplementary Material (ESI) for Soft Matter.

Supporting information

A constriction resistance model of conjugated polymer based piezoresistive sensors for electronic skin applications

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Digital image of the surface of the as-synthesized hydrogels

The hydrogels were fabricated through an exothermic multiphase reaction with a high reaction rate. When the three solutions are mixed, the resulting hydrogel is synthesized via a reaction the result of which is the release of hydrogen gas. Figure S1 demonstrates digital images of the surface of the gels after the reaction and it can be well observed that by increasing the fraction of CNT the amount of released gas decreases (less pores on the surface) which is associated with the fraction of pyrrole polymerized.

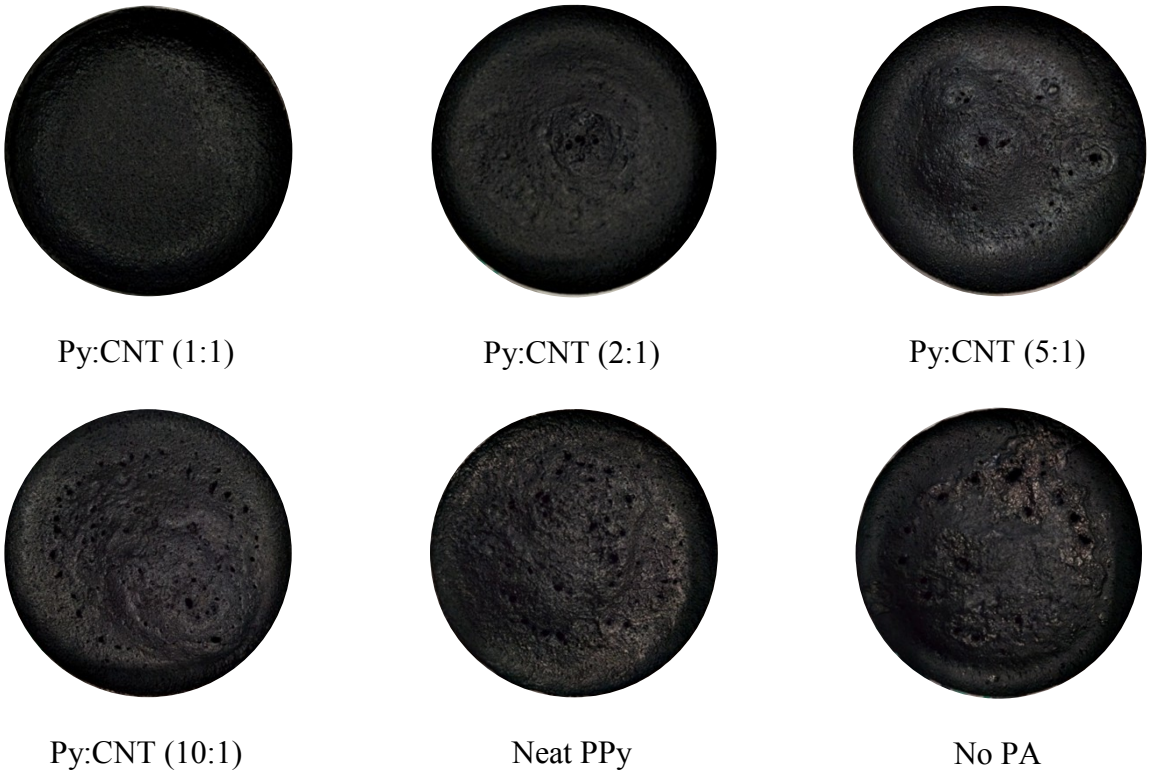


Figure S1. Surface of the resulting hydrogels after the tri-component reaction indicating the decrease in the amount of PPy produced by increasing the weight ratio of CNT in the third solution

Water content measurement results

The water content of the PPy/CNT gels was measured by drying in the ambient air following by the vacuum oven at 70℃ . Figure S2 shows the weight percentage of the gels and it can be inferred from the values that by decreasing the fraction of CNT in the structure of the hydrogel, its water content increases and a maximum water content of 92.5 percent. It is also worth mentioning that the addition of CNT to the gels increased their water content by more than 3 percent. Moreover, the sample fabricated using no cross linker slightly exhibited higher water content while it had poor mechanical properties.

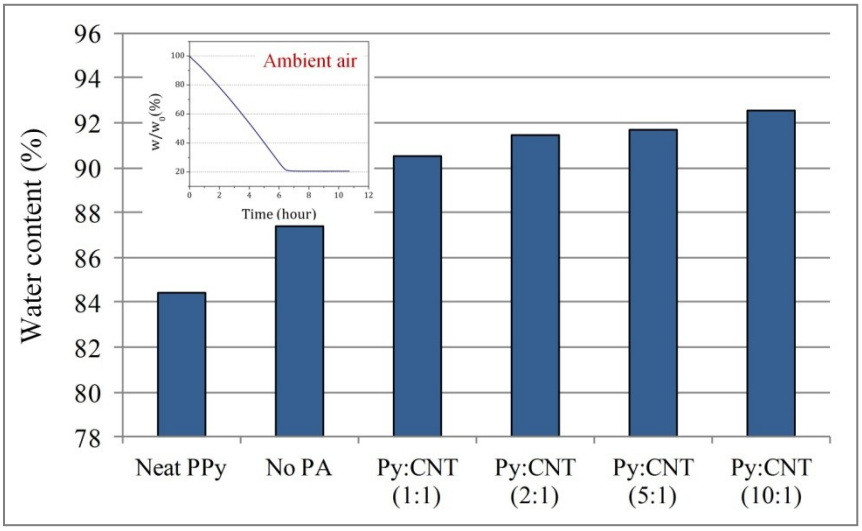
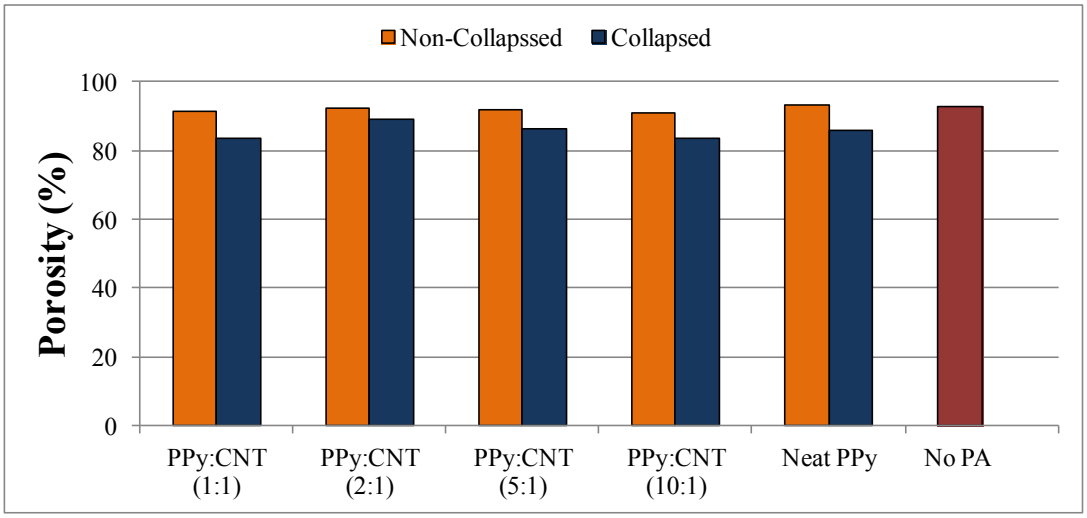


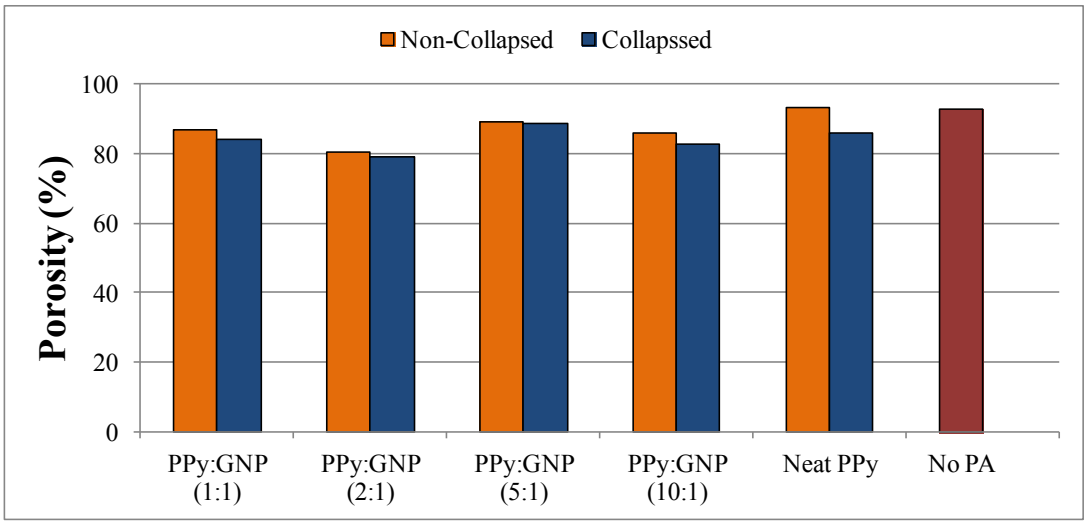
Figure S2. Water content of the neat PPy, No PA, and PPy/CNT samples dried in ambient air following by drying at 70℃. The graph on top left shows the drying time of a neat PPy sample in dried in ambient air.

Porosity measurement results

The porosity of the dehydrated gels in both their non-collapsed (before applying the compression load) and collapsed state was measured Nitrogen gas and the results are shown in Figure S3. It is noticeable that their porosity did not show a drastic drop which originates from the elasticity of the gels in their dehydrated state. This highly porous structure enhances the piezoresistive response of the PPy based gels along with an elastic structure able to deform after applying mechanically induced external loads.



(a)

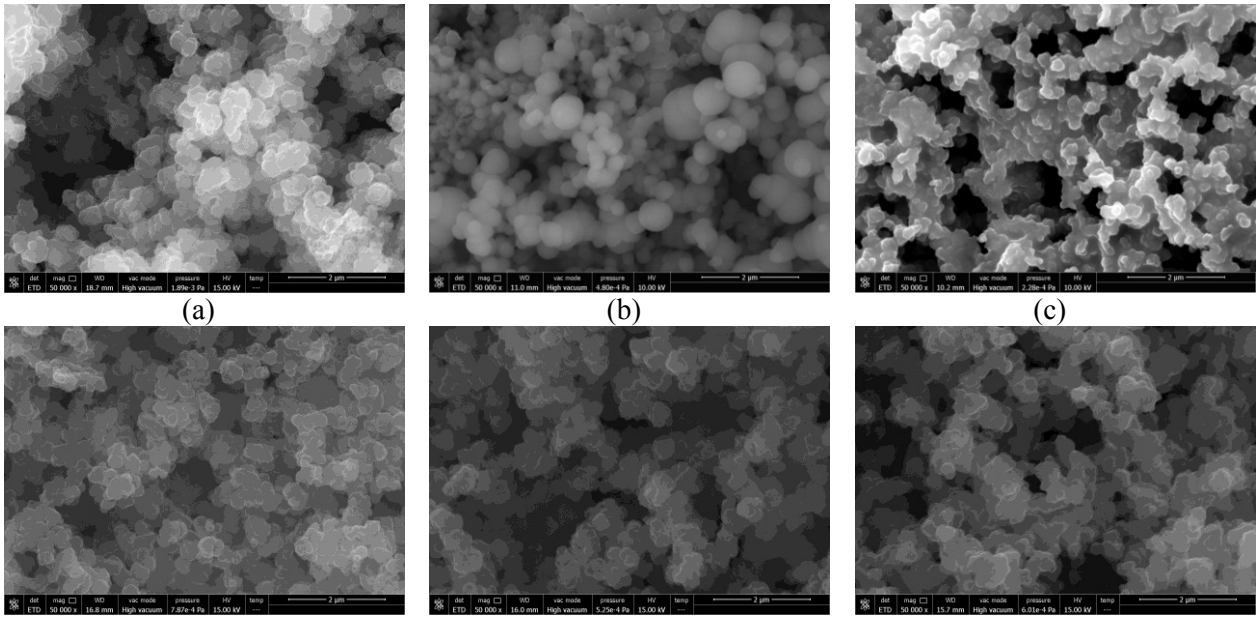


(b)

Figure S3. Porosity of the gels in their dehydrated state (a) PPy/CNT gels, (b) PPy/GNP gels

SEM micrographs of the dehydrated PPy/CNT and PPy/GNP samples

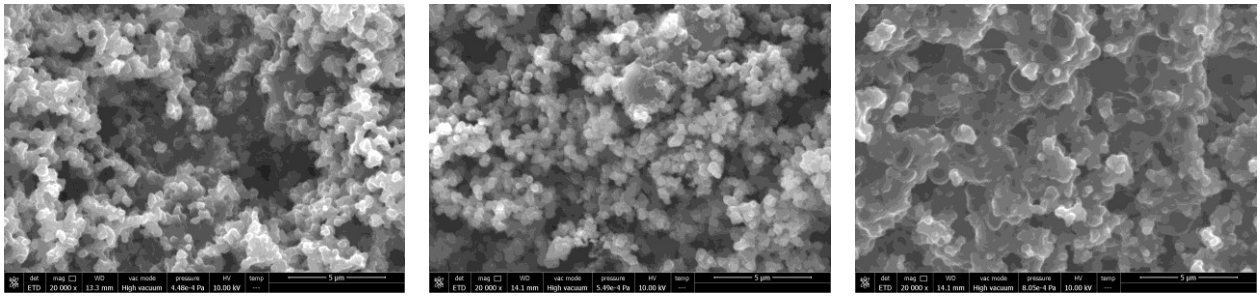
The microstructures of the PPy/CNT and PPy/GNP hydrogels with varying Py:CNT and Py:GNP ratios are depicted in Figure S4 and Figure S5, respectively. The hollow spherical structures observed in the resulting neat PPy hydrogel facilitates the transport of ions. It can be seen that by incorporation of CNT and GNP particles, the hollow spherical structure of the gels disappears while particle-like PPy still dominates. The interconnected hollow spherical microstructures of the gels change to smaller particles with a plate-like structure due to addition of CNT and GNP. This results in a more 3-dimentional microstructure with a highly porous hierarchical network.



(a) (b) (c)

(d) (e) (f)

Figure S4. SEM micrographs of (a) No PA, (b) Neat PPy, (c) Py:CNT ratio of 10:1, (d) Py:CNT ratio of 5:1, (e) Py:CNT ratio of 2:1, and (d) Py:CNT ratio of 1:1



(a) (b) (c)

Figure **S5.** SEM micrographs of PP/GNP hydrogels with Py:GNP ratio of (a) 10:1, (b) 5:1, and (c) 2:1

FTIR spectra of PPy/CNT hydrogels with varying Py:CNT ratio

The Fourier Transform Infrared Spectroscopy of the PPy/CNT gels (Figure S6) indicates the characteristic peaks of the pyrrole ring. Considering that the typical peaks for PPy have not changed in the PPy/CNT samples, it can be inferred that the chemical structure of PPy is well maintained by adding CNT. The good mechanical properties of the as-synthesized hydrogel stemming from its microstructure is shown by the inset photo in Figure S6.

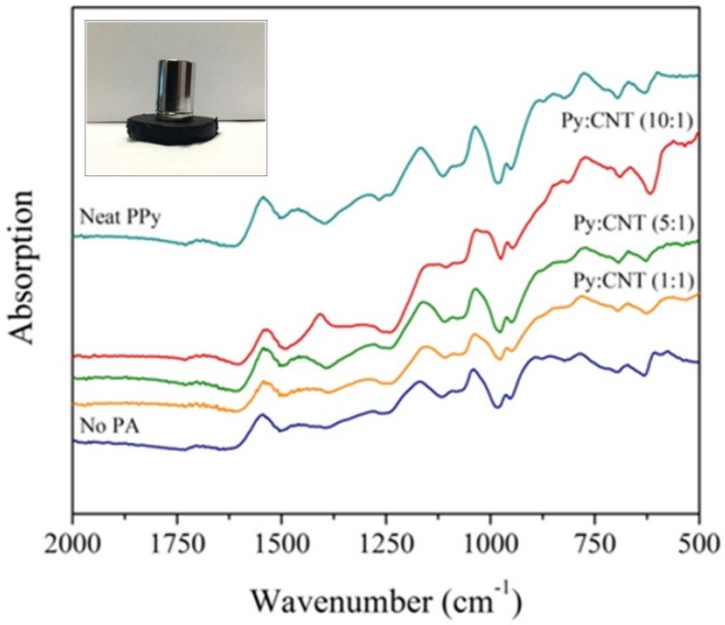


Figure S6. FTIR spectra of the neat PPy, PPy/CNT, and no PA hydrogels

Effect of the contact resistance on the piezoresistive response of the sensor

In order to validate the assumption that the major mechanism of the piezoresistive response of the fabricated PPy based hydrogels is the change in the contact resistance, their response to change of the applied load was measured with and without the contact resistance between the sample and the electrode. The elimination of the contact resistance was carried out using a layer of platinum sputter coated on both sides of the sample. Covering the lateral surface of the sample, a layer of platinum was coated on its two sides and used as the electrode. A glass slide was then placed on the upper and lower side of the sample to locate the point to apply pressure (Figure S7a). The response of a PPy/CNT hydrogel with and without the effect of the contact resistance is demonstrated in Figure S7b. It can be then concluded that the change in the constriction resistance of the sample and the electrode plays a key role in the response of these sensors and the effects of inner resistance change and tunneling of the fillers can be negligible.

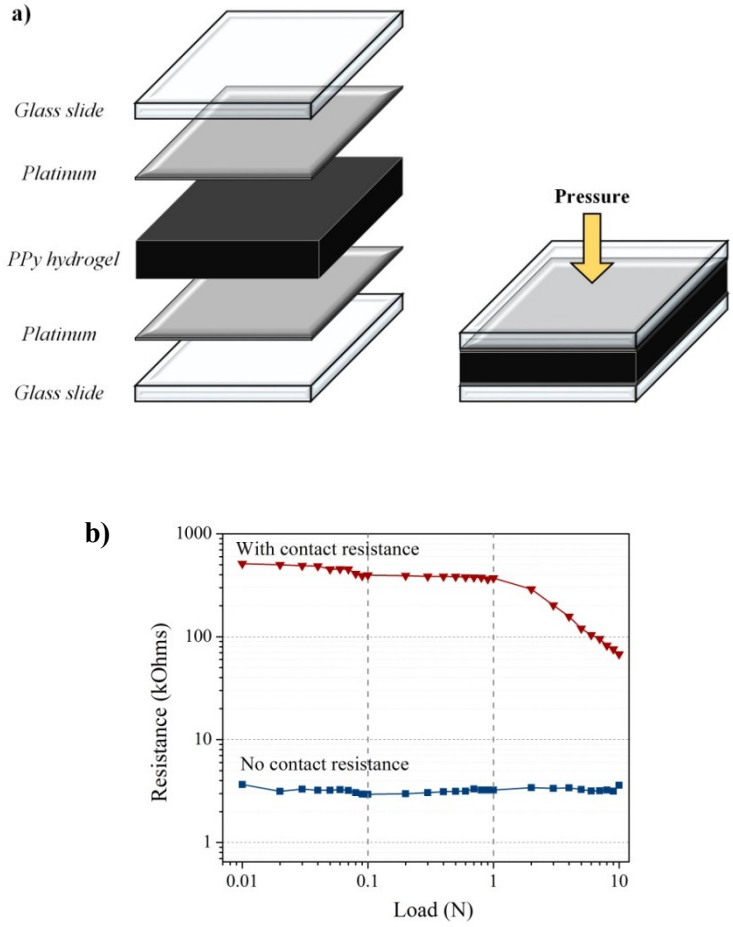


Figure S7. a) Schematic of the measurement setup to eliminate the contact resistance effect, and b) Piezoresistive response of a PPy/CNT hydrogel with and without the contact resistance effect

The relative resistance change and sensitivity of the piezoresistive sensors

The pressure response of the as-synthesized hydrogels was measured as the change of the resulting resistance. Figure S8a and Figure S8b show respectively the relative resistance change of the PPy/CNT and PPy/GNP gels, from which it can be inferred that by increasing the Py:CNT and Py:GNP ratios, the overall resistance between the sample and the electrode decreases due to higher electrical conductivity. Another term that would exemplify the sensitivity of these stimuli-responsive sensors is the slope of the their relative resistance change obtained as $\frac{d}{dF}(\frac{\Delta R}{R_0})$. By increasing the Py:CNT, the sensor exhibit higher sensitivity for lower ranges of the applied load due to the dominant hollow spherical structure of PPy. The same trend was observed in the PPy/GNP samples with lower overall sensitivity to the applied compression load.

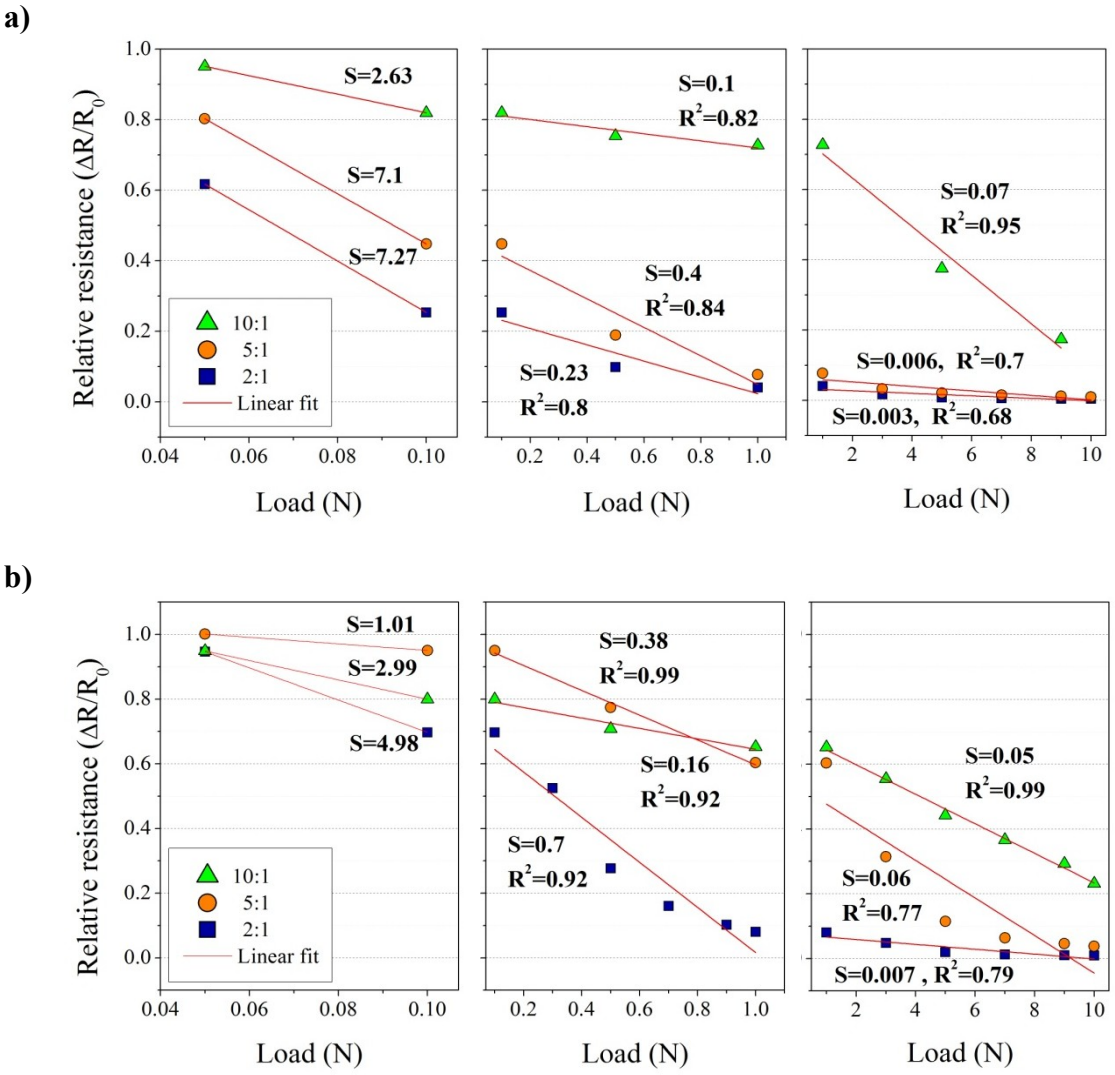


Figure S8. The relative resistance change and sensitivity of a) PPy/CNT, and b) PPy/GNP gels

Cluster distributions resulted from the proposed constriction resistance model

The randomly distributed clusters within the geometry of the tested samples (circular samples of 10mm in diameter) are depicted in Figure S9 using Weibull and Gamma distributions. The number of the obtained clusters and their minimum and maximum distance are also shown in the figure.

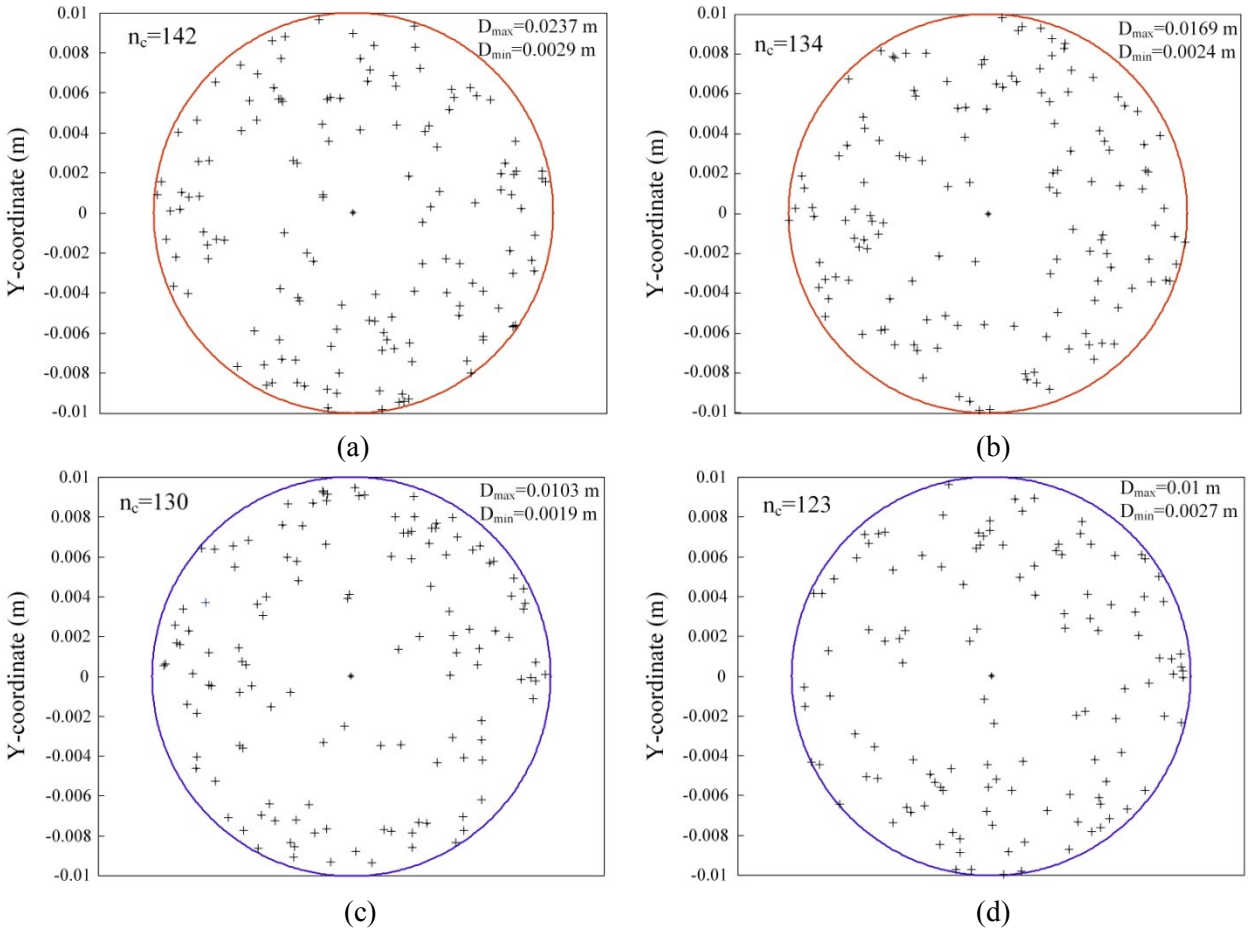


Figure S9. Cluster distributions (a) and (b) Weibull distribution, (c) and (d) Gamma distribution