

Supporting Information

A Solid-liquid Self-adaptive Composite

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1. Automated diameter measurement algorithm

To determine the distribution and average diameter of the spheres that make up the PVDF-PDMS composite, it is necessary to perform a large number of measurements over many SEM images. In order to achieve this goal, a program was written to automatically detect and compute the diameter of the spheres.

The first step of the image processing algorithm developed involved importing the picture that is to be scanned to a python development environment, using the OpenCV software library (<http://opencv.org/>). The gray-scale image is imported as a matrix, in which each pixel is represented by a number (the intensity) that varies from 0 (black) to 255 (white). For instance, the matrix representing the upper right corner of Fig. S1A is shown in Fig. S1B.

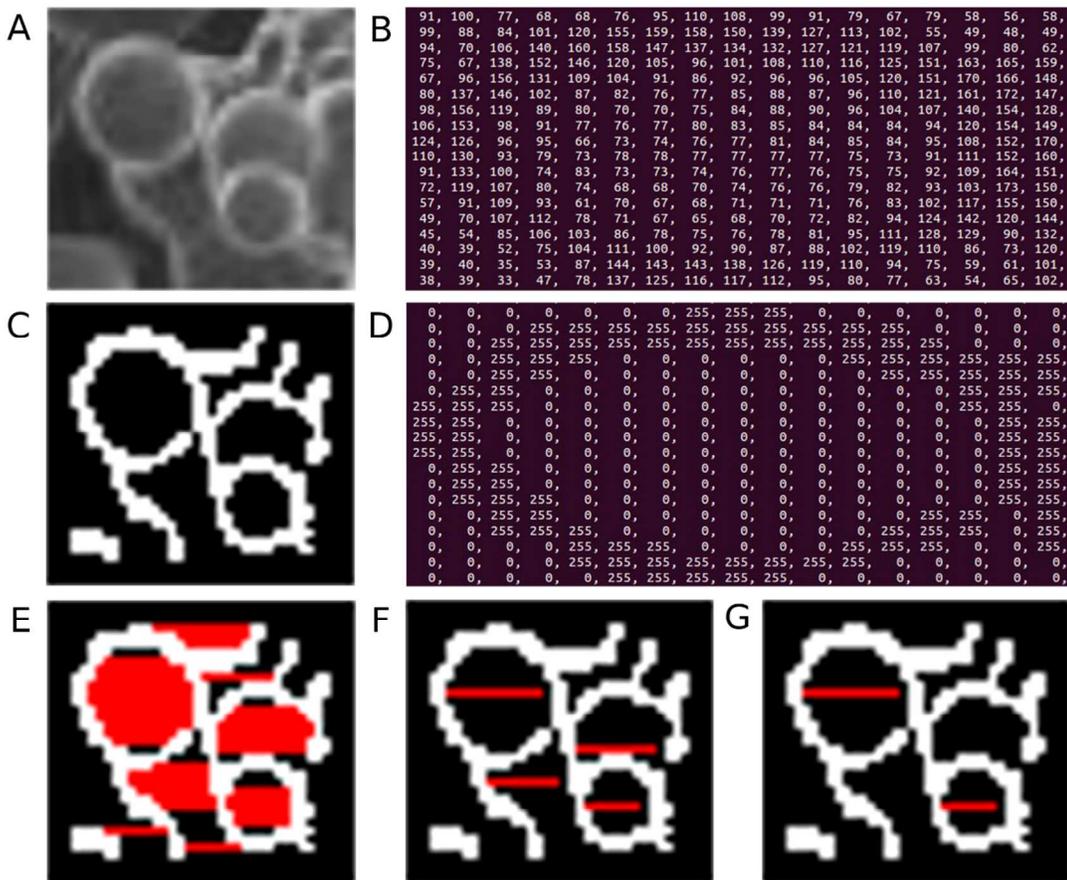


Figure S1. (A) Part of an SEM image, showing polymer spheres. (B) Part of the matrix obtained by importing (A) using the CV package. (C) Image obtained by converting the grayscale pixels from (A) to black or white. (D) The same part of the matrix from (B), after conversion. (E) Marked in red are the black segments from (C) that are confined between white pixels. Segments smaller than 6 pixels were disregarded. (F) Marked in red are segments that meet the condition of being at least as big as the segments above and below located in the same region. (G) Marked in red are the segments that were found to be diameters by the image detection code.

The basic principle used to detect spheres is that in SEM images the pixels belonging to a sphere's edge are found to be closer to white than an average pixel located in the same region of the picture. However, in initial tests it proved difficult to find these edges using the SEM images directly.

To solve this problem, in the next step of the algorithm each pixel in the microscopy image was turned either black or white to improve intensity contrast. In order to achieve this, first the average intensity around a pixel was calculated. Then, if the difference between the pixel intensity and the average was found to be greater (lesser) than a given threshold, the pixel was turned white (black). The number of pixels used to calculate the local average intensity and the threshold were parameters that needed to be tuned to ensure proper conversion. Typically, 36 pixels were used to calculate the average and a pixel had to have an intensity at least 6 points higher than the average to be turned white. Fig. S1C shows Fig. S1A after conversion, while Fig. S1D shows the converted matrix from Fig. S1B.

Starting from Fig. S1C, the detection of spheres proceeded in three steps. In the first step, every line was scanned and the black (intensity=0) intervals that were located between two white

pixels (intensity=255) were stored. To illustrate this, the pixels that met this condition were painted red in Fig. S1E.

In the second step, the length of the intervals found previously was calculated, and this length was compared to the length of the intervals located in the lines above and below. If an interval was to be considered a diameter, then its length had be at least as large as other lengths located in the same region of the picture. Intervals that didn't meet this criterion were then discarded. Fig. S1f shows in red the intervals from Fig. S1E that met this condition.

The third and final step is divided into four stages. In stage A, the center of the intervals that met the criterion described in the previous paragraph is found. In stage B, the distance from this center to the nearest white pixel in 16 different directions is calculated. If the spheres present in the picture were perfect, then each of these distances would have about the same length and they would be easy to detect. However, some of the “spheres” can be somewhat elliptical and some of them may also be partially open in the converted image, as the conversion of grayscale images to black and white is not always perfect.

So, in stage C, the distances from the previous stage are compared to half of the length of the current interval – that was measured in the second step. If the difference is too large, then this distance is discarded, otherwise it is used to calculate an average radius. This helps when dealing with partially open spheres. If more than 3 distances are discarded, then the algorithm assumes that the interval being tested is not a sphere diameter. In stage D, the distances found in stage B are divided by this average radius. If 10 or more of these ratios are found to be in the range between 0.7-1.4, then the algorithm concludes that the interval is a diameter, and stores its length (in pixels). The diameters that were found in Fig. S1C are shown in Fig. S1F.

While we won't detail it here, it is rather easy to determine how many pixels the scale bar measures using algorithms. By knowing this length, it is simple to convert the distances from pixels to a unit of distance. For example, if the scale bar length is 500 pixels and it corresponds to 1 mm, then the length of each pixel is 2 μm .

Although the above algorithm usually works well, the use of an automated measurement creates the risk of fake detections – distances detected as diameters that actually aren't. To make sure no fake detection entered the measurement statistics, after a possible diameter was found the program showed a zoomed in picture of the region in which it was found, with it drawn in red. Then, by typing one or two, a user could accept or reject the distance found.

The code described in this section was used to analyze two sets of pictures, one composed of 7 SEM images of samples that had been highly compressed and the other of 8 SEM images of uncompressed samples. In total, 109 diameters were found for the first case and 240 for the second case; the difference is believed to be due to the different thicknesses of the samples. Besides outputting the diameters, the program also generated a file showing every sphere found (marked by horizontal red lines and blue vertical lines) and also the scale bar length in green. See Fig. S2 for an example.

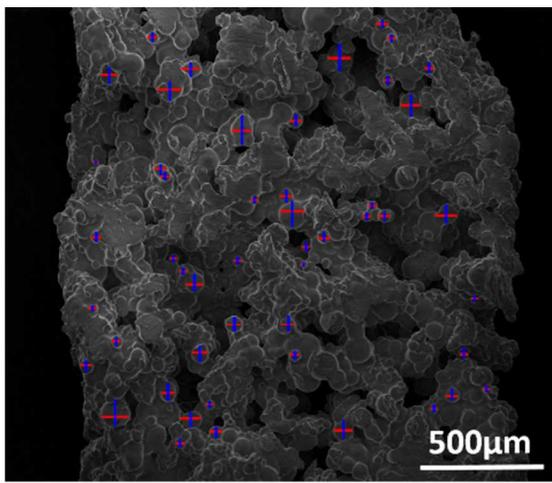


Figure S2. Image output by the image detection algorithm. Spheres are marked by red horizontal lines and blue vertical lines.

All the diameters found were then put into a single data file, and a program was used to calculate the average and standard deviation of the diameters. This result can be found on Table S1. The program also counted how often diameters appeared in certain ranges, and this information was used to plot the histogram shown below, using the R statistical computing package (<http://www.r-project.org/>).

Table S1. Average, Standard Deviation and Standard Error of sphere diameter of Soft SAC

	Pre-compression	Post-compression
Average diameter (μm)	45.2	47.2
Standard Deviation (μm)	21.9	23.2
Standard Error (μm)	1.4	2.2

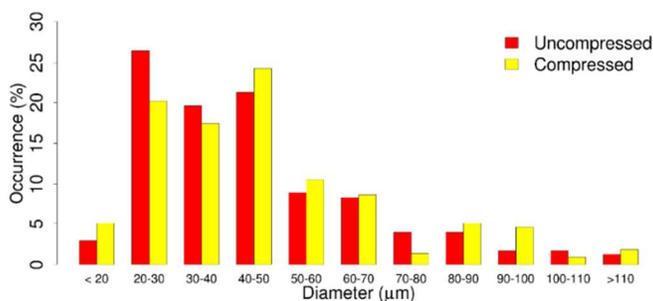


Figure S3. Histogram figure representing the diameter distribution of the spheres before and after DMA testing

From the data generated for the two sets of images, it appears that compression does not significantly change the diameter of the spheres. This indicates that either the spheres are rigid enough to resist compression or that they are able to recover their original shape after pressure is removed.

Table S2. Bead sizes of Soft SAC, Intermediate SAC and Hard SAC

	Soft SAC	Intermediate SAC	Hard SAC
Diameter (μm)	45.2 ± 21.9	35.3 ± 13.2	11.8 ± 3.5

2. XRD Results

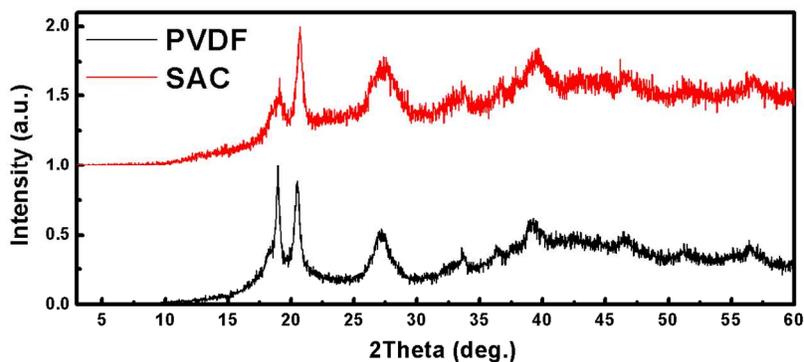


Figure S4. X-ray Diffraction (XRD) results of the PVDF and SAC. The blue dash arrow indicate the PDMS peak; while the black arrows manifest the shift of the PVDF peaks.

3. Densification (the reduction of porosity)

The self-stiffening behavior of SAC can be partially attributed to the reduction of porosity. This is proved by the changing of the sample height shown in Fig. S5, following the similar trend of the changing of the storage modulus.

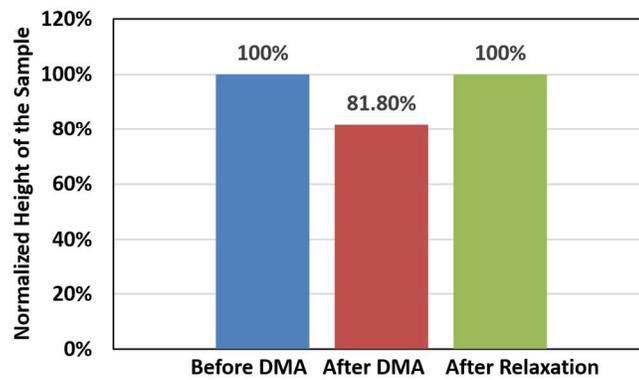


Figure S5. The normalized height of the SAC sample before, after DMA and after relaxation.