Electronic Supplementary Information (ESI)

Encapsulation of shear thickening fluid as easy-to-apply impact resistant material

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Experimental Section

1. Materials

STF was synthesized according to Chen et al.[1] Suprasec 2644, a methylene diphenyl diisocyanate based pre-polymer with average functionality of 2, was provided by Huntsman. Anhydrous toluene (0.865g/ml at 25 °C), chloroform (1.492g/ml at 25°C), ethane diol (EDO, 1.113g/ml at 25°C) and polyethyleneimine (PEI) with molecular weight (M_n) of about 600 (1.05g/ml at 25°C) were purchased from Sigma-Aldrich, and used as received.

2. Encapsulation of STF

The device for the encapsulation process is very simple, as shown in **Fig. 1**a. The STF, after being diluted and well mixed with 5wt% PEI and 10wt% EDO, was loaded into a syringe with a needle (Inner diameter of 0.61mm and outer diameter of 0.91mm) to generate droplets. The reaction solution was prepared by mixing 4.0g Suprasec 2644 with 6.0ml toluene and variable amount of chloroform (3.7ml, 4.7ml, 5.7ml, and 6.7ml) to adjust the density and the polarity of the solution. After the formation of the uniform mixture, about 1.5-2.0ml toluene was added dropwisely and gently to the surface of the mixture to form a density gradient for the better generation of spherical droplet in the solution. The STF in the syringe, with the needle located 3-4cm above the reaction solution, was slowly syringed into the reaction solution in the form of individual droplets. In order to form the uniform shell, the droplets were gently shaken using a shaker (Heidolph, Unimax 1010) in the reaction solution for different durations, ranging from 5 min to 180min. Finally the STF capsules were rinsed with pure toluene, and collected for characterization and testing.

3. Quasi-Static Compression of Individual STF Capsule

The quasi-static compressive response of the STF capsule was tested using single sphere compression apparatus as reported by Yang et al. and Zhang et al.,[2, 3] and as schematically illustrated in **Fig. S12**a. The quasi-static loading setup consists of one stepper actuator (Physik Insturment M-230S) to drive the punch rod and one load cell (0.5N, FUTEK) connected to the punch head. Loading speed of 10μm/s (strain rate of about 0.005 1/s for the STF capsule) was employed for the actuator for the tests of all the STF capsules. For each test, at least three capsules were tested to minimize the error. Curves of nominal stress versus nominal strain were recorded to characterize the quasi-static properties of the obtained STF capsules. The nominal strain (ε_n) and nominal stress (σ_n) are respectively defined as the measured displacement (Δl) divided by the diameter (d) of the capsule and the measured force (F) divided by the maximum cross-section ($S_{max} = \pi(d/2)^2$) of the capsule as follows:

$$\varepsilon_n = \frac{\Delta l}{d} \tag{1}$$

$$\sigma_n = \frac{F}{\pi(d/2)^2} \tag{2}$$

Based on this, the nominal elastic modulus is defined as the nominal stress (σ_n) divided by the nominal strain (ε_n) of the capsule.

4. Low-Speed Impact of Individual STF Capsule

The dynamic behavior of the STF capsule by low-speed impact was tested using a home-made device, as schematically shown in **Fig. S12**b. The impact setup consists of one polymer impactor with weight of 1.343g, one low level load cell (9217A, Kistler) with a charge amplifier (5015A1000, Kistler) connected to an oscilloscope (DLM2024, Yokogawa) to record the response, and one high speed camera (Fastcam SA4, Photron) with super LED light which can capture the images for the impact process with a frame rate over 40,000fps. During each test, the capsule was placed onto the testing bench on the top of the load cell, and impacted by the freely falling impactor at fixed height. Loading speed of about 3m/s and corresponding high strain rate of about 1500 1/s can be generated during the impact process.[4, 5] The force versus time curves were recorded by the oscilloscope, as typical shown in **Fig. S13**, and the impact processes were captured by the high-speed camera. Same as the quasi-static test, average value with standard deviation based on at least three pieces of capsules were obtained for comparison.

The curves of nominal stress versus nominal strain were plotted based on the original force versus time curves, and the integrated displacement based on the velocity of the impactor according to the momentum conservation equation as follows:

$$F \cdot t = m \cdot v \quad (3)$$

where the load, F, and time, t, can be obtained from the load versus time curves, and m is the weight of the polymer impactor (1.343g). The initial point and overall time duration of the impact process was determined by the high speed camera images.

5. Characterization Methods

The basic properties of the original STF and the achieved capsules were characterized by the field emission scanning electronic microscopy (FESEM, JOEL JSM-7600F). The composition of the capsules was analyzed using thermogravimetric analysis (TGA, AutoTGA Q500). In each TGA test, 10-30mg powder or liquid sample was placed in a platinum pan and heated to 600°C under nitrogen atmosphere with ramp rate of 10°C/min. In order to minimize the absorption of moisture from surroundings, the core mixture of the STF-85 capsules obtained with different reaction time in RS-5.7 was directly squeezed into the pan for TGA test. The rheological behavior of original STF, STF-85, and the core mixture from the STF capsules obtained with reaction time of 60min in RS-5.7, were tested using TA Discovery hybrid rheometer. The tested core mixture was collected by squeezing more than 60 pieces of the STF capsules in a dry cabinet to minimize the absorption of moisture.

Supplementary Figure Captions

Fig. S1 Molecular structures of PEI and Suprasec 2644, and the reaction mechanism between PEI and Suprasec 2644 to form the polyurea shell around the STF droplet.

Fig. S2 Uniformly dispersed P(St-EA) nanoparticles with narrow size distribution in the original STF.

Fig. S3 Size distribution of the P(St-EA) nanoparticles in the original STF. The nanoparticles have a narrow size distribution and have diameter of 377±34nm.

Fig. S4 Rhelogical behavior of the adopted original STF and diluted 85wt% STF (STF-85). The intial viscosity of the original STF and STF-85 are about 8.0Pa·s and 0.6Pa·s, respectively. It is observed that the viscosity of the original STF dramatically increases at shear rate of 550 1/s, which indicates the strong shear thickening effect. However, STF-85 do not show any shear thickening effect in tested range of the shear rate.

Fig. S5 TGA curves of the original STF, STF-85, pure EDO, and PEI. It is found that the weight percentage of the suspended nanoparticles in the original STF is about 50wt%.

Fig. S6 The other three possible shapes of the achieved STF-85 capsules; (a) Egg-like capsule; (b) Water-drop capsule; (c) Water-drop capsule with a sharp and long tail. The variation of the shape results from the instability of the density gradient at the top of the reaction solution due to the interdiffusion of the ingredients in the reaction solution and the disturbance by the instilled STF droplets.

Fig. S7 Smooth and dense outer polyurea wall of the STF-85 capsule to provide the impermeability for the capsule. The adhered P(St-EA) nanoparticles on the imaged outer sufrace come from the core during the washing process for the sample prepartion.

Fig. S8 (a) Robust core-shell structure which can keep the original shape after the removal of the liquid core; (b) Totally peeled outer polyurea wall away from the inner P(St-EA) nanoparticle wall.

Fig. S9 SEM images of the cross-sections for STF-85 capsules obtained in RS-5.7 with reaction time of 30min (a), 60min (b), and 120min (c), respectively. It is observed that the shell thickness increases with the increased reaction time in the reaction solution.

Fig. S10 Morphology of the P(St-EA) nanoparticles in the STF droplet with the increased immersed time in the reaction solution without Suprasec 2644 to form the shell; (a) P(St-EA) nanoparticles in the solution for 5min; (b) P(St-EA) nanoparticles in the solution for 30min; (c) P(St-EA) nanoparticles in the solution for 60min; (d) Generated polymeric network after being immersed in the solution for 60min; (e) P(St-EA) nanoparticles together with the loofah-like polymeric network after being immersed in the solution for 120min; and (f) P(St-EA) nanoparticles in the solution for 120min. The reason why Suprasec 2644 is absent rather than PEI in this control experiment is that EDO in the STF droplet can also react with Suprasec 2644 to form polyurethane to disturb the observation. The P(St-EA) nanoparticles were swollen by the chloroform and toluene in the solution without the protection of the formed polyurea wall. Some of the nanoparticles have diameter as large as 1μm.

Fig. S11 Increasing of the diameter of the P(St-EA) nanoparticles with respect to the immersion time. It can be found that the nanoparticles were gradually swollen by the solvent during the process. However, it can be seen that the nanoparticles were not swollen too much before immersion time of 60min.

Fig. S12 (a) Schematic configuration of devices for (a) the quasi-static compression and (b) the dynamic impact test.

Fig. S13 Load versus time curves for dynamic impact tests of STF-85 capsules synthesized in RS-5.7 for 5min, 30min, 60min, 120min, and 180min, respectively. The initial point of the impact process was determined using the high speed camera.

Fig. S14 Maximum nominal strain with respect to reaction time in RS-5.7 for STF-85 capsule under quasi-static compression. The nominal strain (ε_n) is defined as the measured displacement (Δl) divided by the diameter (d) of the capsule.

Fig. S15 Nominal strength, i.e. maximum nominal stress, with respect to reaction time in RS-5.7 for STF-85 capsule under quasi-static compression. The nominal stress is defined as the measured force (F) divided by the maximum cross-section ($S_{max} = \pi(d/2)^2$) of the capsule.

Fig. S16 Nominal elastic modulus with respect to reaction time in RS-5.7 for STF-85 capsule under quasi-static compression. The nominal elastic modulus is defined as the nominal stress (σ_n) divided by the nominal strain (ε_n) of the capsule.

Fig. S17 Solidified STF-85 capsule when STF-85 was encapsulated in RS-5.7 for 180min.

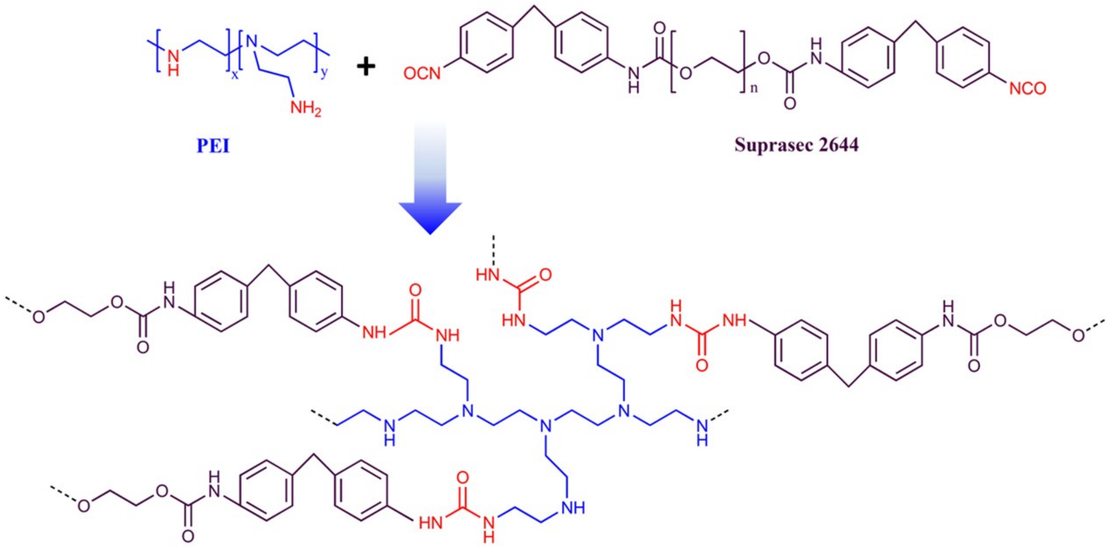
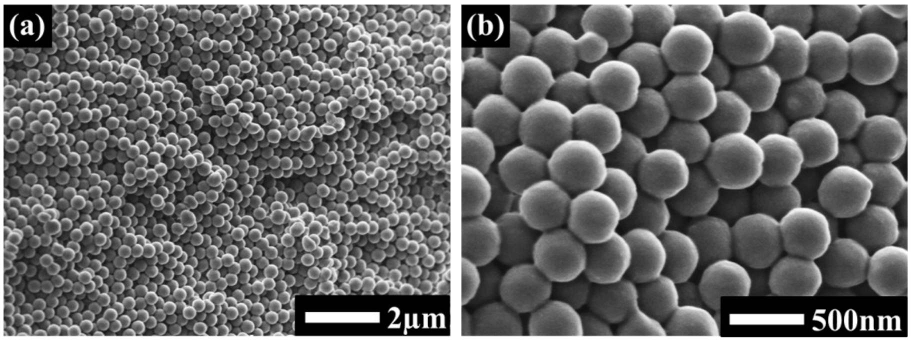


Fig. S1



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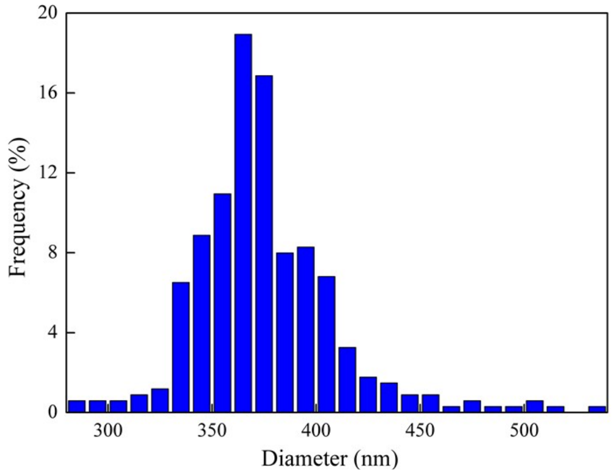
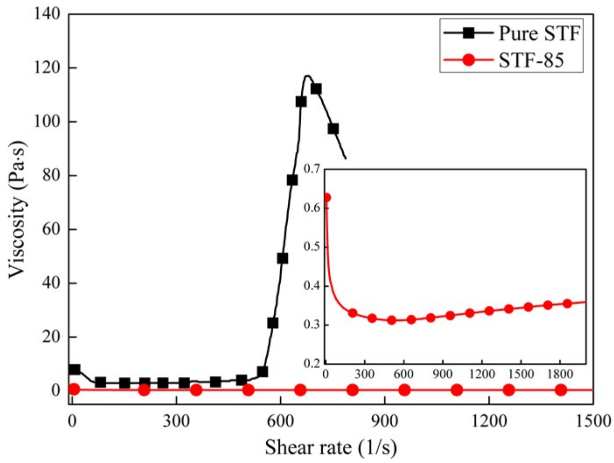


Frequency (%)
Diameter (nm)

Fig. S3



Pure STF
STF-85
Viscosity (Pa·s)
Shear rate (1/s)

Fig. S4

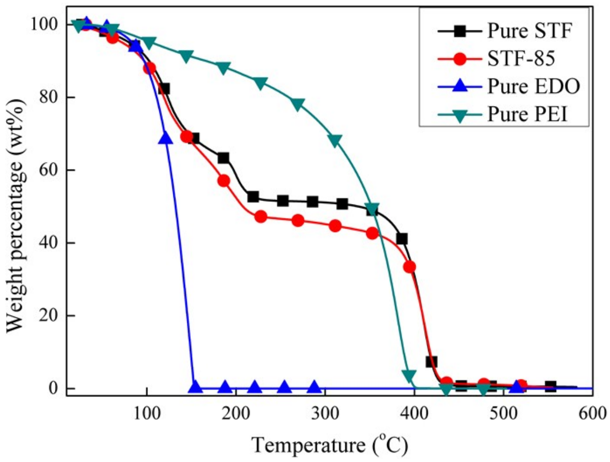
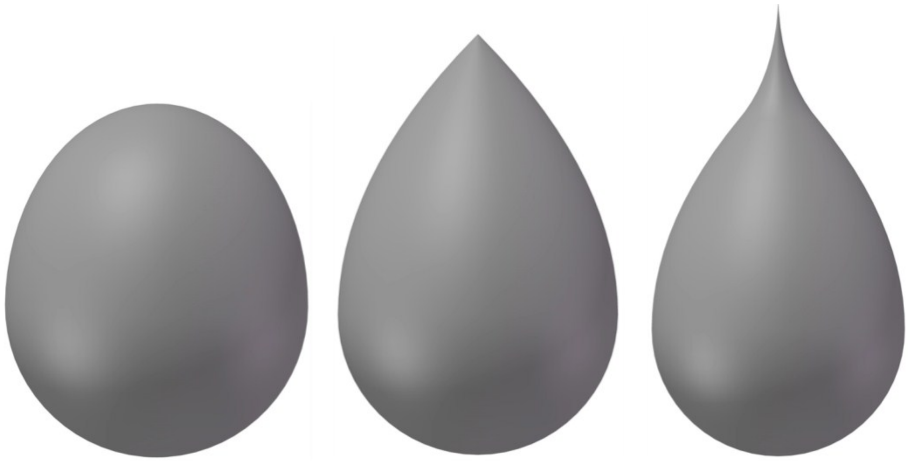
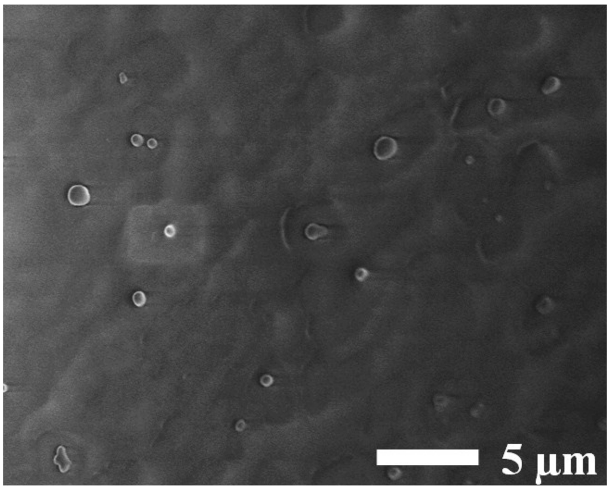


Fig. S5



(a) (b) (c)

Fig. S6



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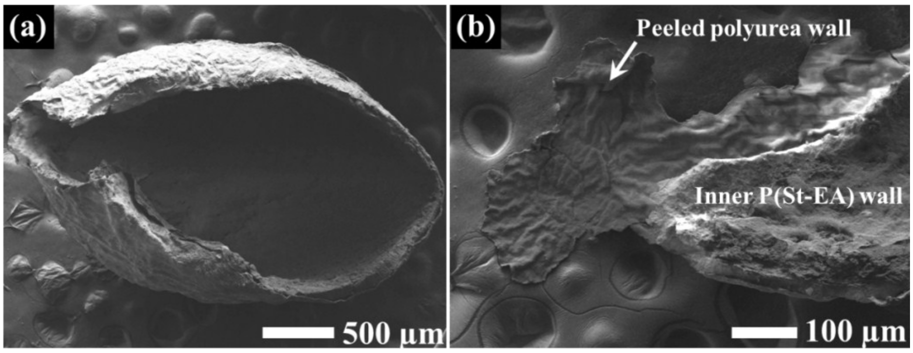

Fig. S8

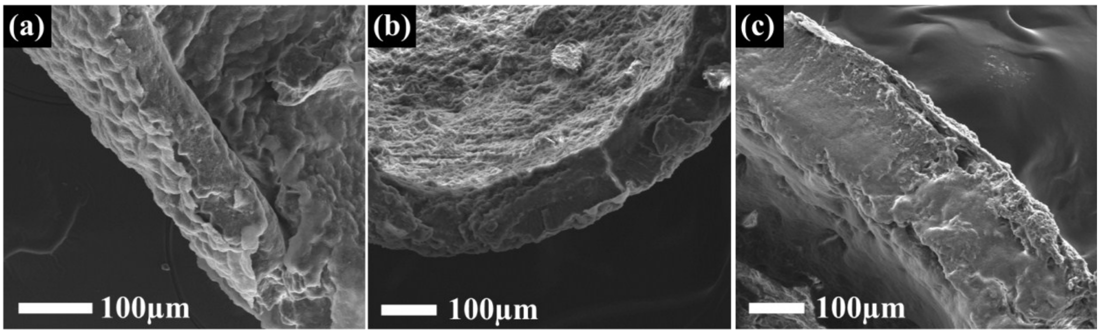

Fig. S9

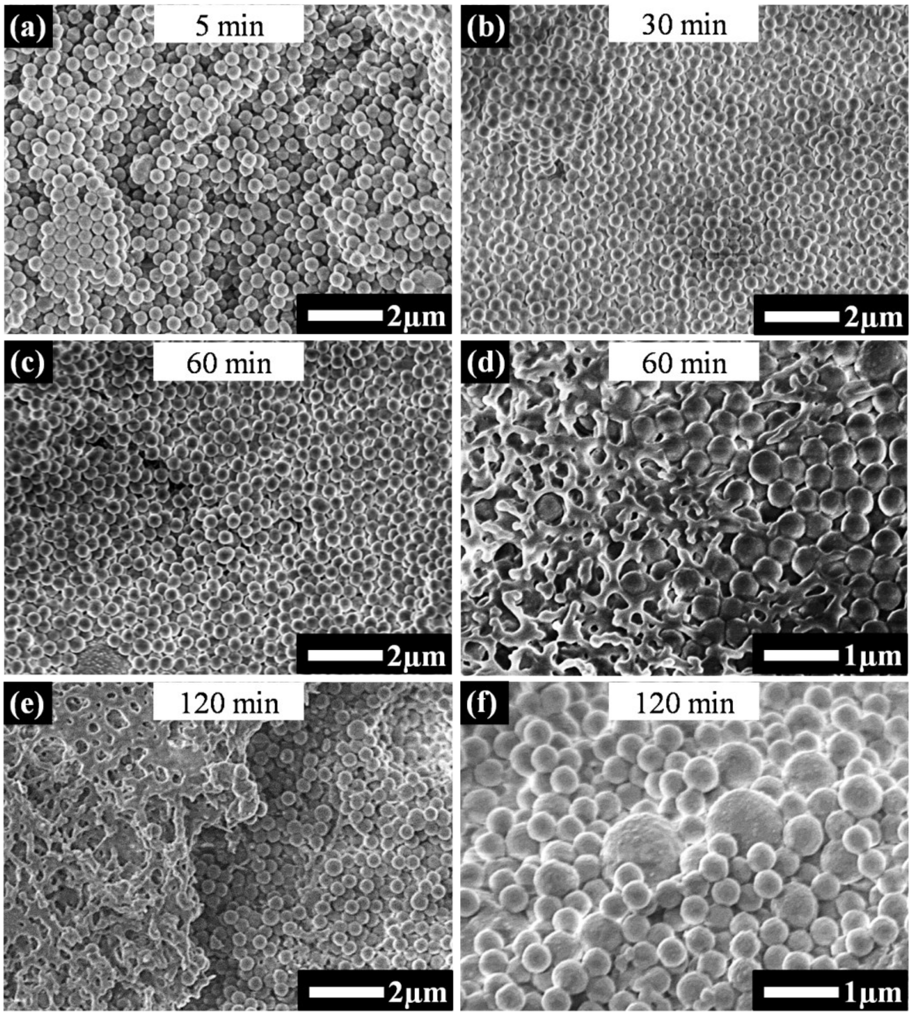

Fig. S10

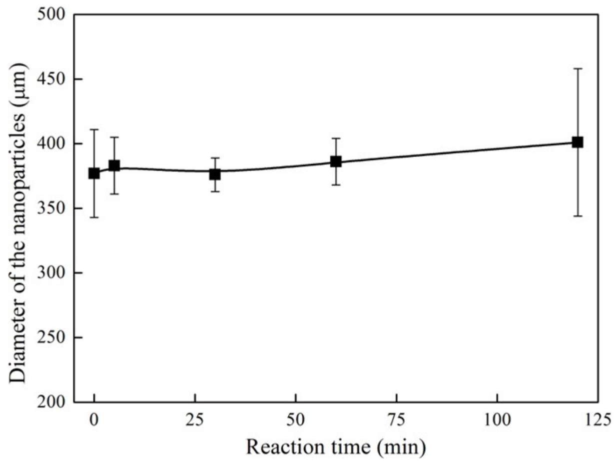

Fig. S11

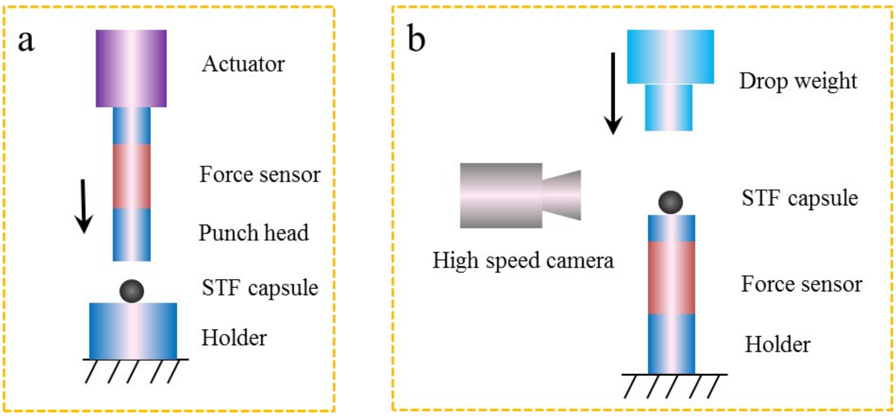

Fig. S12

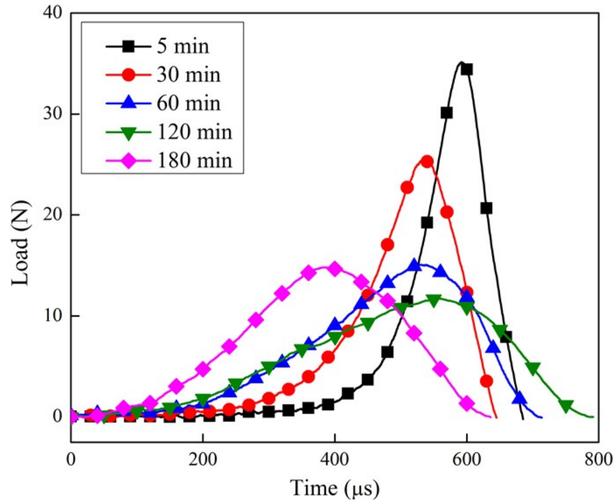

Fig. S13

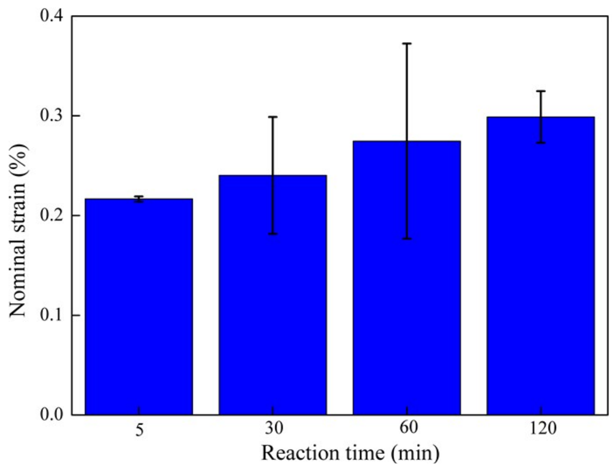

Fig. S15

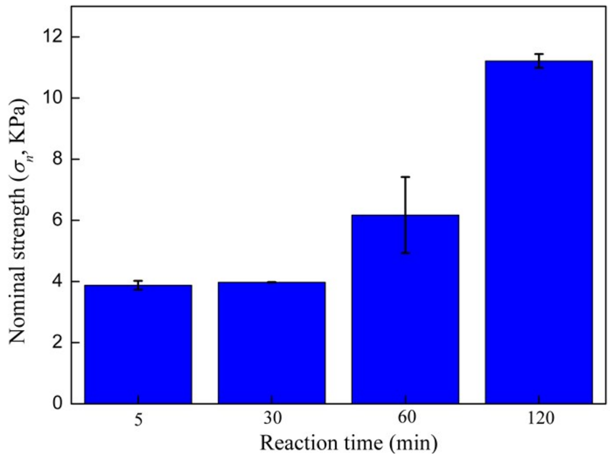

Fig. S15

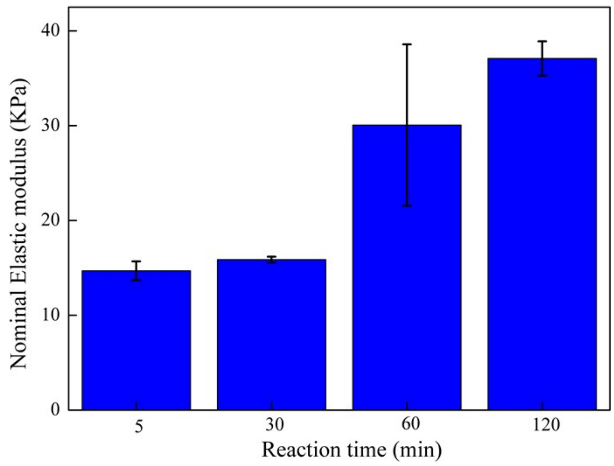

Fig. S16

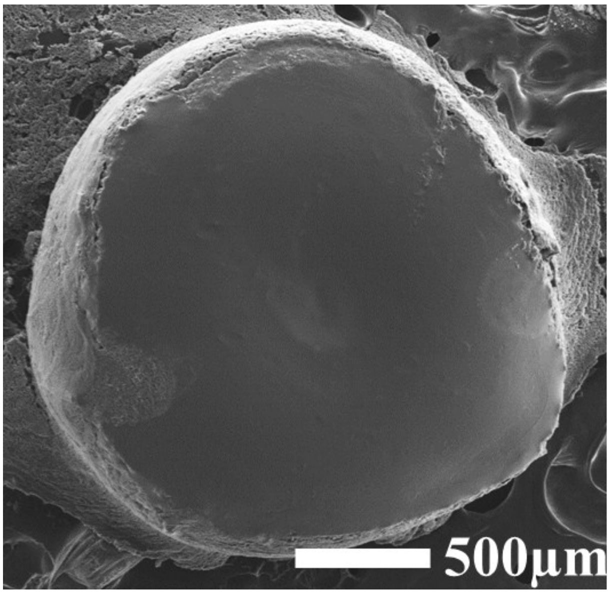

Fig. S17

Supplementary Video Captions

Video S1 Video shows the ejection of the encapsulated STF for the STF capsule with reaction time of 5min in RS-5.7 under impact testing. The total length of the video is 1.5ms in real time scale.

Video S2 Video shows the impact process of the STF capsule with reaction time of 60min in RS-5.7. The total length of the video is 0.8ms in real time scale.

Video S1.wmv

Video S1

Video S2.wmv

Video S2

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