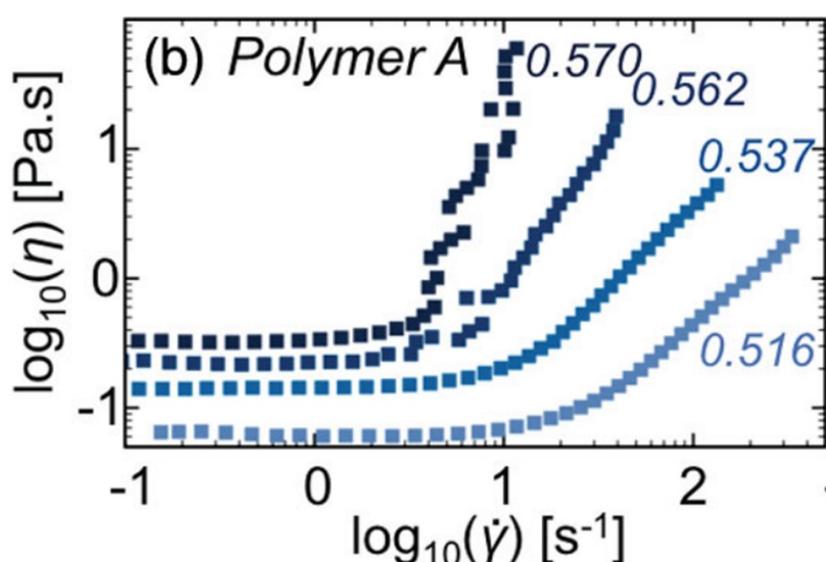


## Supporting Information

The relevant description of STF

In the reference *Microscopic Mechanism for Shear Thickening of Non-Brownian Suspensions*, the importance of volume fractions for shear thickening of non-Brownian suspensions is revealed. Through calculation, the volume fraction of the STF system we adopted is completely combined with the STF volume fraction range of excellent performance in the literature during the whole experiment, and it is confirmed again through the experiment.



**Figure (1) Viscosity versus shear rate with adsorbed polymer A for various  $\Phi$  of quartz microparticle suspensions.**

In the reference, the author proposed the optimal volume fraction of shear thickening effect in silica suspension system through experiments and simulations. By formula (1), the mass fraction of our silica and polyethylene glycol 200 is converted into volume fraction. ( $\rho_{\text{SiO}_2}=1.900\text{g/cm}^3$ ,  $\rho_{\text{PEG}}=1.125\text{g/cm}^3$ )

$$\Phi_{SiO_2} = \frac{m_{SiO_2}/\rho_{SiO_2}}{m_{SiO_2}/\rho_{SiO_2} + m_{PEG}/\rho_{PEG}} \quad \#(1)$$

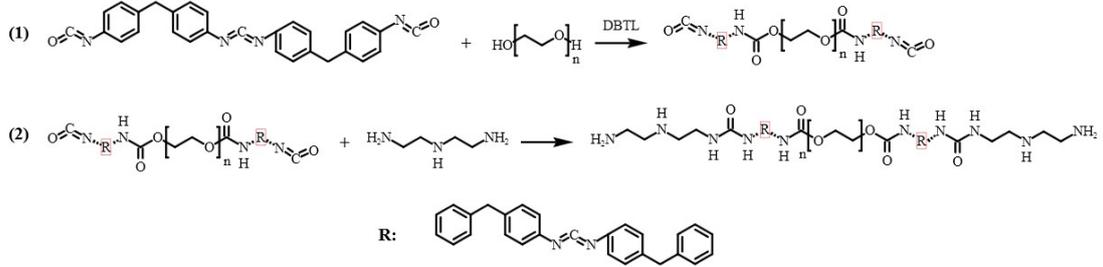
The volume fraction interval of the system is obtained:  $\Phi(\omega=62.0)=0.491$ ,  $\Phi(\omega=68.5)=0.562$ , The results are in full agreement with the STF volume fraction range of excellent performance in the references and the excellent shear thickening performance obtained by our experiments.

Of course, both microspheres with different particle size and STF system may achieve excellent shear thickening performance. However, if you choose micron-scale coating method to coat STF, the particle size of microspheres needs to be small enough because enough silica microspheres are needed to form particle clusters. In addition, the 150 nm granulated silica can play a good shear thickening effect in the polyethylene glycol 200 system. As can be seen from the STF curve of 68.5% black microsphere content in Figure 1 (f), the viscosity of the system rapidly increases by 28 times. Finally, the purpose of our research is mainly to apply STF's mechanical properties in a wider range of scenarios through the coating of STF. We believe that the most important thing is to ensure the same performance advantages of STF in microcapsules as in other application scenarios. Therefore, we have realized the effective coating of STF in polymer shells through repeated experimental regulation. For example, PEG decomposition peak shown in the thermogravimetric graph in Figure 2 (c); PEG liquid can be isolated from STF capsules formed by direct drop addition.

Therefore, STF with excellent shear thickening effect tested by rotary rheometer was used as the core material for cladding, including suitable silica microspheres with

excellent shear thickening performance, SiO<sub>2</sub>-polyethylene glycol 200 system and suitable silica system concentration, etc.

The STF system changes in the reaction process



$$n_{PEG1} = \frac{m_{STF1} * (1 - 0.62)}{M_{PEG}} = 1.9 * 10^{-3} mol$$

$$n_{CD-MDI} = \frac{V_{CD-MDI} * \rho_{CD-MDI}}{M_{CD-MDI}} = 8.32 * 10^{-4} mol$$

$$n_{\Delta PEG} = \frac{1}{2} n_{CD-MDI} = 4.16 * 10^{-4} mol$$

$$m_{\Delta PEG} = n_{\Delta PEG} * M_{PEG} = 8.32 * 10^{-2} g$$

$$n_{PEG2} = n_{PEG1} - n_{\Delta PEG} = 1.48 * 10^{-3} mol$$

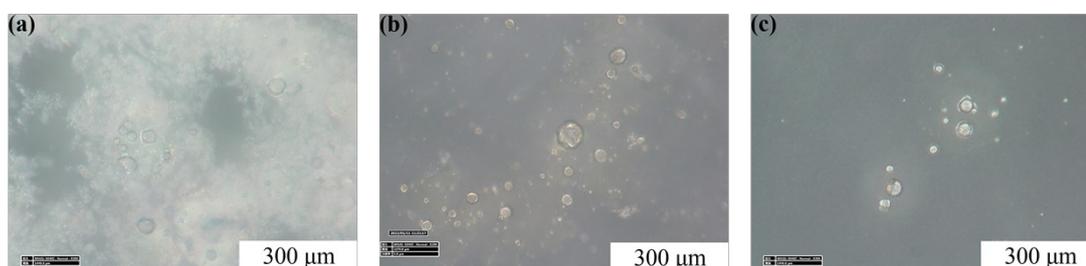
$$\omega_{SiO2} = \frac{m_{SiO2}}{n_{PEG2} * M_{PEG} + m_{SiO2}} = 67.69\%$$

(STF mass before reaction:  $m_{STF1}=1$  g,  $M_{PEG}=200$ ,  $V_{CD-MDI}=0.1$  ml,  $\rho_{CD-MDI}=1.19$  g/mol,  $M_{CD-MDI}=143$ ,  $m_{SiO2}=0.62$ g.)

It can be seen from the calculation results that the consumption of polyethylene glycol in the reaction process is  $8.32*10^{-2}$  g, and the concentration of silica nanoparticles after the reaction is about 67.69%, which is close to the optimal concentration of shear thickening effect in this system (Figure 1 (f)), so that STF with excellent shear thickening performance can be coated in the microcapsules.

Description of microcapsule size and wall thickness

The preparation of micron-scale STF microcapsules has always been the goal of our project. At present, only millimeter-scale STF capsules have been prepared in literature reports. Micron-scale STF microcapsules can be used in a wider range of applications, such as the new impact resistant material that is composite with polyurea itself in the original manuscript, which is why we adopt the method of emulsifying STF, all in order to get smaller microcapsules rather than capsules. Our microcapsule size is mainly determined by the emulsification effect of STF in liquid paraffin. We studied the droplet sizes at different rotational speeds, and comprehensively considered that the microcapsules would not be destroyed or adhere to the bottom in the reaction process. Finally, we obtained 800 rpm/min in the emulsification process and 300 rpm/min in the reaction process as the most appropriate speed, which made the prepared microcapsule length 190  $\mu\text{m}$ . Both the size of the microcapsule and the thickness of the polymer shell do affect its mechanical properties, and our team is exploring in this direction. Here's what we've done so far: We've added different amounts of isocyanate to the reaction, and the goal is to get microcapsules of different polymer shell thicknesses. The following are the microcapsule morphologies observed in the coating process under the optical microscope, (a) 0.2 mlCD-MDI, (b) 0.1 mlCD-MDI(manuscript), (c) 0.05 mlCD-MDI.

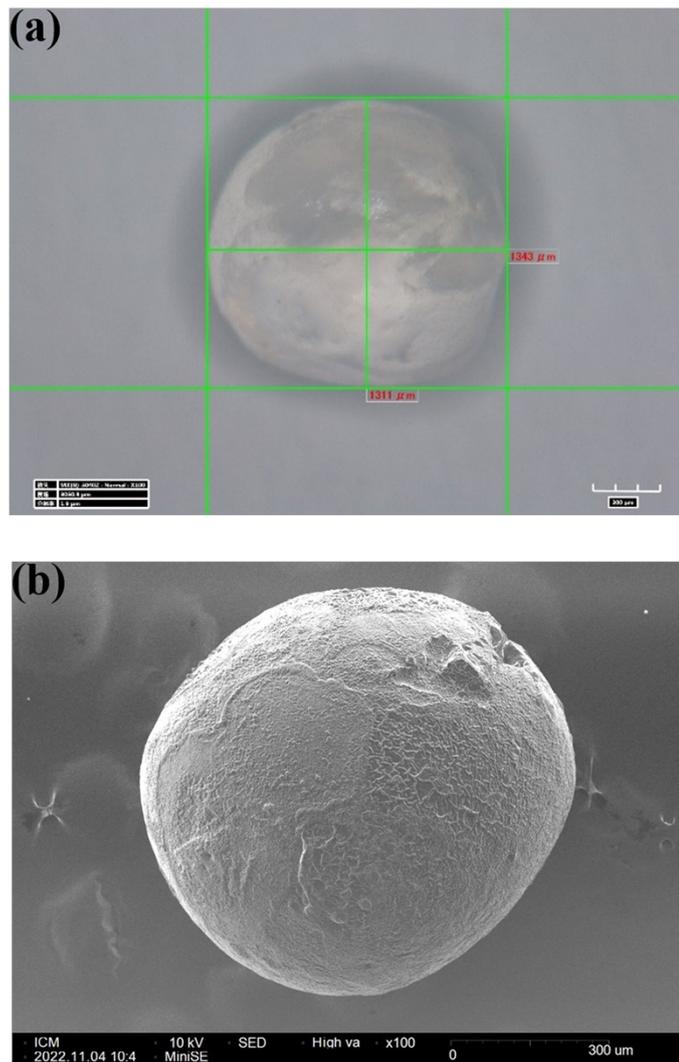


**Figure (2) Microcapsules with different amounts of isocyanate during the reaction (a) 0.2 mlCD-MDI, (b) 0.1 mlCD-MDI(Original manuscript), (c) 0.05 mlCD-MDI.**

As can be seen from Figure (2), 0.2 mlCD-MDI will generate a large amount of polymer impurities in the reaction solution, while 0.1 mlCD-MDI(in the original draft) and 0.05 mlCD-MDI can generate STF microcapsules.

### Description of surface roughness of microcapsules

As for the rough surface of microcapsules, we believe that there are mainly two reasons as follows: (1) There are folds on the surface of the microcapsule, which may be the result of the uneven shrinkage of the wall material caused by the rapid evaporation of solvent in the drying process. (2) Figure (3) shows STF capsules formed by direct drip addition. Its main process is to form coating in isocyanate solution by adding single STF droplets, which is completely consistent with the reaction mechanism of wall material formation in the original draft and is the content of our team's follow-up experiment. By comparison, we can find that the surface of STF capsules obtained by direct drip addition is relatively smooth. We believe that this is because there is a certain adhesion between microcapsules in the emulsion reaction, which affects the surface roughness of microcapsules. We think this is a good question, and we will continue to explore this question in future experiments.



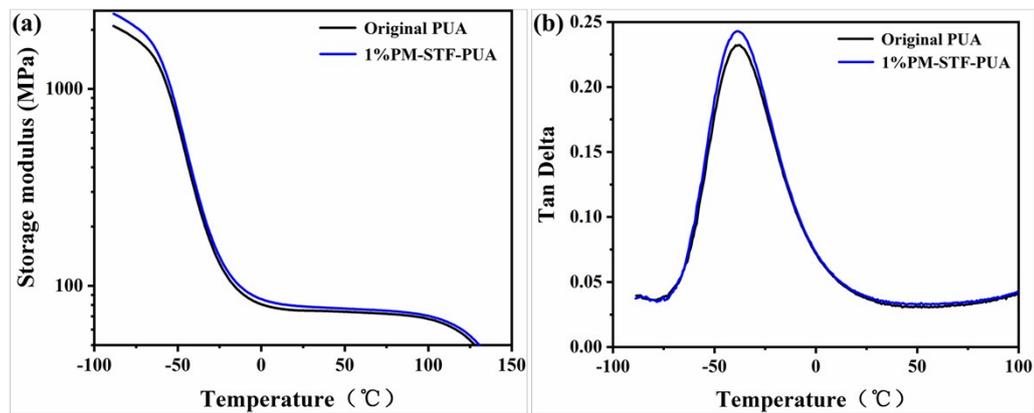
**Figure (3) STF capsules formed by direct drop addition, (a) Optical microscope image, (b) Scanning electron microscope image.**

STF capsules prepared by drip addition adopt the same chemical reaction principle and different technological means as the method in the original manuscript.

### Analysis of thermal properties of composites

The DMA curves of polyurea composites with microcapsule additions are shown in Fig. 4. The introduction of microcapsules increases the storage modulus of PUA, but has less effect on the  $T_g$  of composites. The peak intensity of  $Tan\delta$  increases with the

addition of microcapsules due to the internal friction mechanism of the composites. In general,  $Tan\delta$  represents the internal friction energy dissipation, which is related to the damping properties of materials. A larger internal loss indicates a higher damping performance. Since the strong interfacial forces between PM-STF and PUA backbone, a large amount of internal friction is dissipated under the impact force, and the loss factors exhibit an increasing trend.



**Figure (4) Curves of storage modulus and loss factor as a function of temperature for pure PUA and PUA Composites.**

#### Description of dielectric related parameters

In order to determine the characteristic relaxation times ( $\tau_{HN}$ ) of the relaxations, the isothermal dielectric losses ( $\epsilon''$ ) are fitted to the Havriliak-Negami function.

$$\epsilon'' = \epsilon_{\infty} + \frac{\Delta\epsilon}{(1 + (i\omega\epsilon_{HN})^a)^b} \quad \#(2)$$

in which  $\omega$  is the angular frequency ( $\omega = 2\pi f$ ),  $\Delta\epsilon$  is the dielectric relaxation strength, or the difference between the static dielectric constant and the infinite frequency dielectric constant ( $\epsilon_{\infty}$ ).  $\Delta\epsilon$  is related to the number density of dipoles participating in the relaxation, as well as their dipole moment. The shape of the relaxation is described by parameters  $a$  and  $b$ , which are the breadth and the high frequency asymmetry,

respectively. The  $\tau_{HN}$  is related to the maximum frequency of each process by the following equation:

$$f_{max} = \left[ \frac{1}{2\pi\tau_{HN}} \right] \left[ \frac{\sin\left(\frac{\pi a}{(2+2b)}\right)}{\sin\left(\frac{\pi ab}{(2+2b)}\right)} \right]^{\frac{1}{a}} \# (3)$$

The obtained relaxation frequencies of both relaxation processes as function of temperature for the samples are gathered in Fig. 8(d), which follow the Vogel-Fulcher-Tamman law (VFT) and the corresponding fitting parameters together with the obtained  $T_0$  values are reported in Table 1.

$$f = f_0 \exp\left(-\frac{B}{T - T_0}\right) \# (4)$$

Where the pre-exponential factor  $f_0$ , the so-called Vogel temperature  $T_0$ , and the exponential factor  $B$  (related to the fragility and to the apparent activation energy) are the fitting parameters.