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Mechanical response of encapsulated shear thickening fluid*

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Abstract: In this investigation, the hard-to-handle shear thickening fluid (STF) is successfully encapsulated for easy handling and re-processing in the application of promising impact resistant material. Double-walled macroscopic STF capsules are synthesized using a convenient process by instilling the diluted STF droplets into reaction solution. The obtained STF capsules show significant shear thickening response to dynamic impact in comparison to quasi-static compression in terms of 154 times higher absorbed nominal strain energy. This innovative method opens a new window to design and manufacture versatile impact resistant materials and structures.

Keywords: Shear thickening fluid (STF); encapsulation; impact resistance; energy absorption

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0 Introduction

Materials with good impact resistance is increasingly demanding for applications for the safety of personnel or equipment at a risk of encountering impact ranging from military use, like body armors, armoured vehicles, protective bastions, etc. to civil commodity, like sports equipment, motor vehicles, sophisticated but delicate electronic devices, etc[1]. Tremendous efforts have been put into the investigations on how to improve the impact resistance of materials as high as possible[2].

However, besides the primary consideration of higher impact resistance, it is necessary for the applied impact resistant material to balance the flexibility of the material for normal body movements and the protectiveness of the material upon accidentally low-speed or high-speed impacts. Shear thickening fluid (STF), a non-Newtonian liquid whose viscosity increases rapidly with the increase of shear rate especially after a threshold shear rate[3-5], can deliver this perfect balance as a unique impact resistant material[6-8]. However, the practical applications of STF are restricted by its own physical and chemical properties, such as high viscosity, hydroscopicity, hard to handle or integrate into structures, etc. In order to overcome these disadvantages and increase the stability of STF during its service life, it is important to explore the techniques for the packaging of this highly viscous fluid.

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Investigations have been focused on resolving, or partially resolving this challenge. For example, the STF alone or the fabrics impregnated with STF as a whole can be packaged and sealed using polyethylene film to minimize the external influence from the surroundings[9-11]. In order to incorporate STF into polymer composites, other porous structures[12, 13], like foam, cellular solids, fibrous matrices, scaffolds, etc., were adopted to carry and reserve STF in the composites. While these approaches solve the problem caused by the external environment, they cannot eliminate the mutual interaction between STF and the fabrics or polymers.

In order to completely overcome the above-mentioned disadvantages and increase the stability of STF during its service life, it is of great significance to explore the techniques to tightly package this highly viscous fluid. However, due to the high viscosity, the shear thickening effect, and the feature of multiple ingredients of STF, till now there are no investigations on the encapsulation of liquids with high viscosity like STF[14-17].

In this study, a convenient method by a simple device consisting of a syringe for the generation of STF droplets and a container with reaction solution for the encapsulation using a simple process is proposed for the encapsulation of STF. The mechanical properties of fabricated STF capsules at quasi-static and dynamic loading were studied systematically. Meanwhile, the fracture mechanism of the STF capsule during impact was further discussed.

1 Materials and method

1.1 Materials and encapsulation

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, chloroform, ethane diol (EDO) and polyethyleneimine (PEI) with molecular weight (Mn) of about 600 were purchased from Sigma-Aldrich, and used as received.

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 5.7ml chloroform 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 to the surface of the mixture to form a density gradient. The STF in the syringe 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 in the reaction solution for different durations, ranging from 5min to 180min.

The proposed mechanism for the shell formation is illustrated in Fig. 1(b). Upon instillation of the diluted STF into the reaction solution, the PEI near the interface between STF droplet and reaction solution will diffuse across the interface and react with Suprasec 2644 immediately because of the extremely high reactivity between isocyanate and amine to form the outer wall. Although EDO is insoluble in toluene, it is partially miscible with chloroform. Accompanied with the diffused EDO, the P(St-EA) nanoparticles migrate to the interface due to the high affinity with toluene and chloroform in the reaction solution. It is necessary of this step for the robustness of the STF capsule considering the size of the generated STF droplets of up to several millimeters and the maximum thickness of the formed polyurea shell of only several or several tens microns. Fig. 1(c) shows the optical image of the capsules synthesized with reaction time of 60min in the reaction solution, and the capsule in the yellow frame was enlarged to show the general appearance. By counting more than 50 individual capsules, the average diameter of the capsules is 2.7±0.2mm. One of the STF capsule was broken using a steel plate, it is found that the amount of liquid inside the capsule is very high, as shown and indicated in Fig. 1(d).

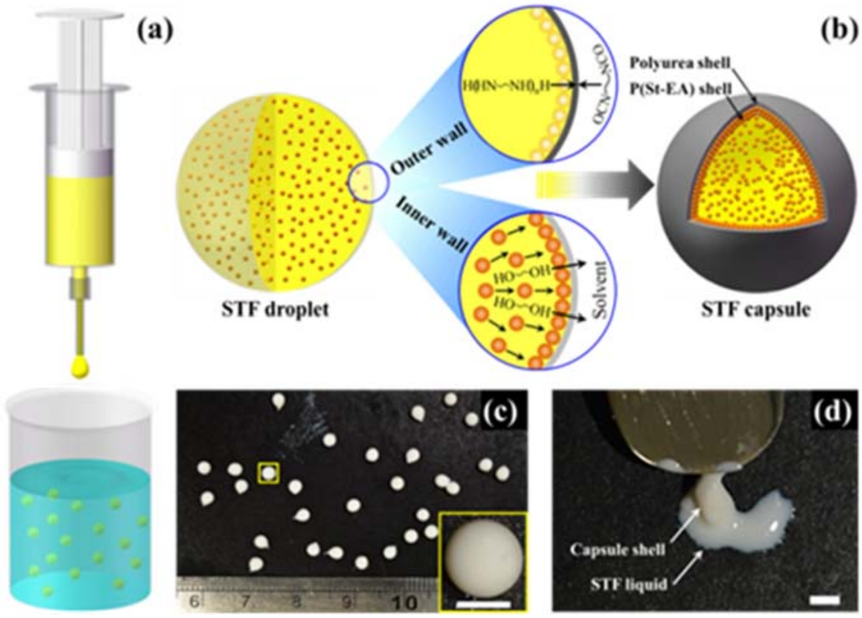

Fig. 1 (a) Schematic setup for the encapsulation of STF; (b) Schematic formation mechanism of the outer wall and inner wall of STF capsule; (c) Optical image of the obtained STF capsules with one enlarged at the bottom right; and (d) One broken STF capsule. The scale bars in the inset of (c) and (d) represent 2mm.

1.2 Experiments

1.2.1 Quasi-static compression

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. 2(a). The quasi-static loading setup consists of one stepper actuator to drive the punch rod and one load cell connected to the punch head. Loading speed of 10μm/s was employed for the actuator for the tests of all the STF capsules. For each test, at least three capsules were tested to obtain an average value with standard deviation to minimize the error.

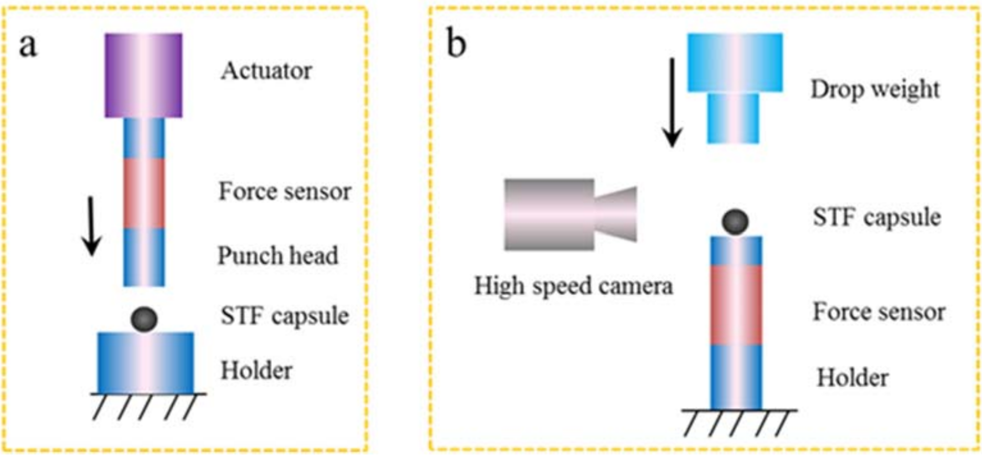

Fig. 2 Configurations of devices for (a) quasi-static compression and (b) dynamic impact

1.2.2 Low speed impact

The dynamic behavior of the STF capsule was tested using a home-made device, as schematically shown in Fig. 2(b). The impact setup consists of one polymer impactor with weight of 1.343g, one low level load cell with a charge amplifier connected to an oscilloscope to record the response, and one high speed camera which can capture the images for the impact process with a frame rate over 40000fps. Same as the quasi-static test, average value with standard deviation based on at least three pieces of capsules were obtained for comparison.

The integrated displacement of the STF capsule can be calculated based on the velocity of the impactor according to the momentum conservation equation as follows:

$$F \cdot t = m \cdot v \tag{1}$$

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. This deduced displacement of the STF capsule fits well with the displacement measured through the images obtained from high speed camera.

2 Results and discussion

The mechanical properties of fabricated STF capsule can be tested by using the above mentioned devices. Fig. 3(a) and b respectively show the typical curves of nominal stress versus nominal strain from the quasi-static compression and dynamic impact of single STF capsule. The capsules were synthesized in the reaction solution for different reaction time, and 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 area ($S_{max} = \pi(d/2)^2$) of the capsule as follows:

$$\varepsilon_n = \frac{\Delta l}{d} \tag{2}$$

$$\sigma_n = \frac{F}{\pi(d/2)^2} \tag{3}$$

Fig. 3(c) shows the absorbed nominal strain energy (E_n) of STF capsule with respect to the reaction time under both quasi-static and dynamic loading, as well as the ratio of the absorbed energy under dynamic impact to quasi-static compression. The nominal strain energy under quasi-static loading is integrated till the catastrophic failure of the tested capsule. However, for the nominal strain energy under dynamic impact, it is integrated till the strain of 0.4 (before the vertical dash line in Fig. 3(b)) since it is hard to identify the catastrophic failure strain. It is observed that the ratio increases from about 34 for reaction time of 5min to about 154 for reaction time of 60min and then decreases to about 120 for reaction time of 120min. The huge difference, especially at reaction time of 60min, indicates that the STF after encapsulation can absorb much more energy during dynamic impact than quasi-static loading due to the strain rate effect which is dominated by the shear thickening effect in the case here.

Fig. 4(a)-(e) and (f)-(j) respectively show the freeze frames of the videos with a time interval of 200μs to study the deformation and failure process of the STF capsules. As shown in Fig. 4(b) and the schematic illustration in Fig. 4(k), a shape similar to conical frustum can be observed during the early stage (~200μs) of the impact process, which reveals a non-homogeneous deformation. However, for the STF capsule with reaction time of 60min, a shape similar to a Chinese drum with homogeneous deformation can be observed under the same impact test, as shown in Fig. 4(g) and the schematic illustration in Fig. 4(l). The deformation of the STF capsule is much similar to that of a gulf ball hitting on a steel target with an impact velocity[19]. It indicates that the STF capsule comes to an equilibrium state immediately during the impact, which means the encapsulated STF transfers from

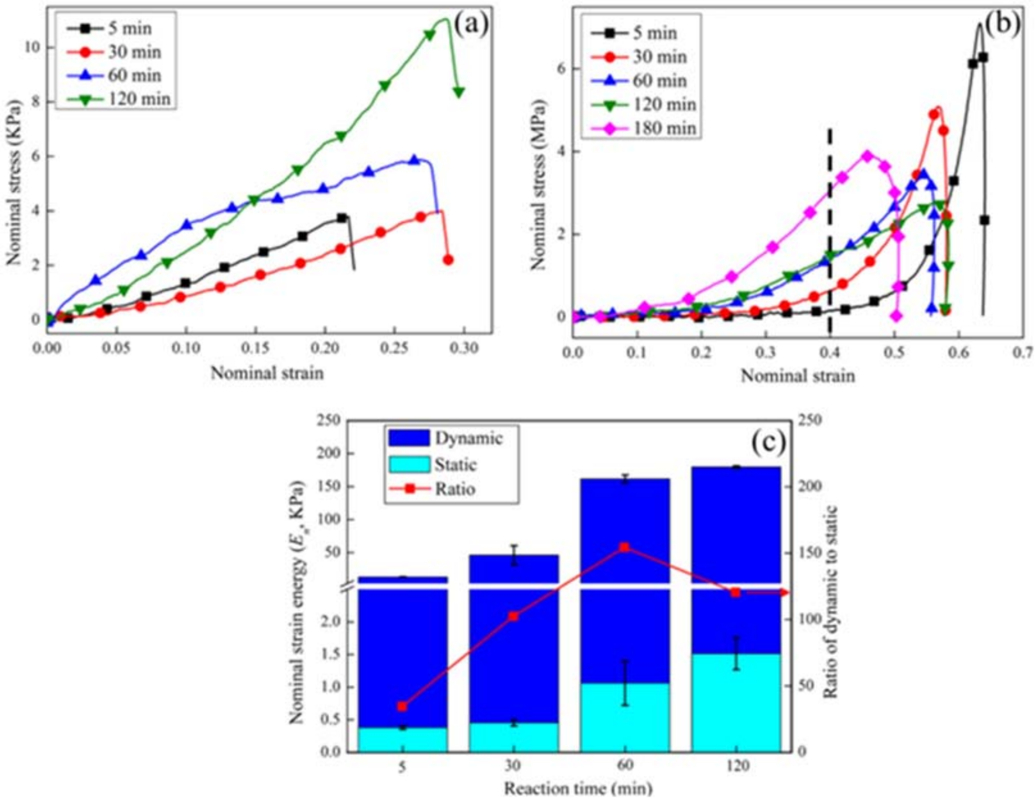

Fig. 3　Typical curve of nominal stress versus nominal strain of single STF capsule (a) under quasi-static compressive loading; (b) under dynamic loading; (c) comparison of the absorbed nominal strain energy for STF capsule with respect to reaction time under quasi-static compression and dynamic impact

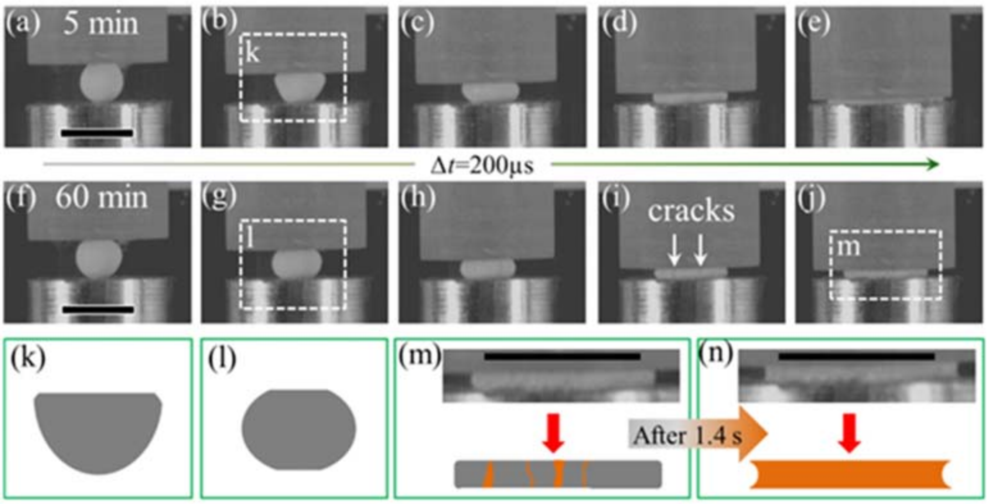

Fig. 4　Response of STF capsule under impact loading. (a-e) and (f-j) digital images from high speed camera with time interval of 200μs for the impact behavior of STF capsules with reaction time of 5min and 60min, respectively; (k) and (l) schematic shapes of STF capsule with reaction time of 5min and 60min at the early stage of impact (～200μs); (m) and (n) flow behavior of STF in the capsule at the end of the impact (～800μs) and after the impact (～1.4s)

liquid to solid during the impact process.

As can be seen from Fig. 4(i), quite a few cracks, indicated by the arrows in Fig. 4(i), appear during the impact process and the STF inside remains solid rather than being squeezed to spray out like liquid. However, after 1.4s, this solid material turns to liquid finally and covers the damaged sample, as illustrated by the increased light reflection from the LED light of the high speed camera as shown in Fig. 4(n). Moreover, different from the raised curve of the damaged sample between the impactor and holder right after the impact process as shown in Fig. 4(m), a hyperbolic contour of the damaged sample was observed alternatively after 1.4s as shown in Fig. 4(n). It indicates that the leaked STF from the capsule turned to liquid to wet the surface of the damaged sample and form the shape due to the capillary effect in the small gap. The phenomena captured by the high speed camera is consistent with the behavior recorded by the stress-strain curves, which both demonstrate the effectiveness of shear thickening for the STF after being encapsulated. The reversible change of the encapsulated STF from liquid to solid upon dynamic impact and from solid to liquid after the impact process means that the encapsulation process does not influence the behavior of the nanoparticles in STF.

3 Conclusion

Macroscopic STF capsules possessing significant shear thickening effect were successfully synthesized using a simple process by instilling the diluted STF droplets into reaction solution in this investigation. Double-walled shell was achieved with the outer polyurea wall resulted from the interfacial reaction between the PEI diffused from the core and the diisocyanate pre-polymer and the inner wall by the deposited P(St-EA) nanoparticles. It is found that much higher strain energy can be absorbed under dynamic impact loading compared with the quasi-static compression loading, which demonstrates that the STF after encapsulation still keeps the shear thickening effect to absorb the impact energy. The encapsulation technique to produce STF capsules with high robustness and ability to absorb more strain energy opens a new window to design and manufacture versatile impact resistant materials and structures.

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