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Study of shear-stiffened elastomers

Tongfei Tian
University of Wollongong, tt436@uowmail.edu.au

Weihua Li
University of Wollongong, weihuali@uow.edu.au

Jie Ding
Defence Science and Technology Organisation

Gursel Alici
University of Wollongong, gursel@uow.edu.au

Haiping Du
University of Wollongong, hdu@uow.edu.au

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Shear thickening fluids, which are usually concentrated colloidal suspensions composed of non-aggregating solid particles suspended in fluids, exhibit a marked increase in viscosity beyond a critical shear rate. This increased viscosity is seen as being both 'field-activated', due to the dependence on shearing rate, as well as reversible. Shear thickening fluids have found good applications as protection materials, such as in liquid body armor, vibration absorber or dampers. This research aims to expand the protection material family by developing a novel solid status shear thickening material, called shear-stiffened elastomers. These new shear-stiffened elastomers were fabricated with the mixture of silicone rubber and silicone oil. A total of four SSE samples were fabricated in this study. Their mechanical and rheological properties under both steady-state and dynamic loading conditions were tested with a parallel-plate. The effects of silicone oil composition and angular frequency were summarized. When raising the angular frequency in dynamic shear test, the storage modulus of conventional silicone rubber shows a small increasing trend with the frequency. However, if silicone oil is selected to be mixed with silicone rubber, the storage modulus increases dramatically when the frequency and strain are both beyond the critical values. © 2013 AIP Publishing LLC.

Keywords
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Study of Shear-stiffened Elastomers

Tongfei Tian[1], Weihua Li[1], Jie Ding[2], Gursel Alici[1]and Haiping Du[3]

[1]*School of Mechanical, Materials and Mechatronic Engineering, University of Wollongong, Wollongong, NSW 2522, Australia*
[2]*Defence Science and Technology Organisation, Human Protection and Performance Division, 506 Lorimer Street Fishermans Bend, VIC 3207, Australia*
[3]*School of Electrical, Computer and Telecommunications Engineering, University of Wollongong, Wollongong, NSW 2522, Australia*

Abstract. Shear thickening fluids, which are usually concentrated colloidal suspensions composed of non-aggregating solid particles suspended in fluids, exhibit a marked increase in viscosity beyond a critical shear rate. This increased viscosity is seen as being both 'field-activated', due to the dependence on shearing rate, as well as reversible. Shear thickening fluids have found good applications as protection materials, such as in liquid body armor, vibration absorber or dampers.

This research aims to expand the protection material family by developing a novel solid status shear thickening material, called shear-stiffened elastomers. These new shear-stiffened elastomers were fabricated with the mixture of silicone rubber and silicone oil. A total of four SSE samples were fabricated in this study. Their mechanical and rheological properties under both steady-state and dynamic loading conditions were tested with a parallel-plate. The effects of silicone oil composition and angular frequency were summarized. When raising the angular frequency in dynamic shear test, the storage modulus of conventional silicone rubber shows a small increasing trend with the frequency. However, if silicone oil is selected to be mixed with silicone rubber, the storage modulus increases dramatically when the frequency and strain are both beyond the critical values.

Keywords: Shear thickening, shear-stiffened, elastomer.
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INTRODUCTION

Shear thickening fluids (STFs) are a kind of non-Newtonian materials whose viscosity increases with increasing shear rate. STFs are usually concentrated colloidal suspensions composed of non-aggregating solid particles suspended in fluids, which exhibit a marked increase in viscosity beyond a critical shear rate. In addition, this increased viscosity is seen as being both 'field-activated', due to the dependence on shearing rate, as well as reversible [1-3]. STFs are mainly used as the key materials in liquid body armor, vibration absorbers or dampers [4-7].

Recently there are also some researchers focusing on the shear thickening gel. Osuji and Weitz [8] studied the gel flocculated from dilute dispersions of fractal particles in hydrocarbon solvents. They observed the shear thickening in a colloidal system with attractive interactions and found the transition to shear thickening flow is stress controlled and results in a fine suspension microstructure that produces enhanced modulus gels. Xu *et al.* [9] added bis-Pd(II) or bis-Pt(II) complexes cross-linker to semidilute unentangled solutions of poly(4-vinylpyridine) (PVP) in dimethyl sulfoxide (DMSO). They reported that the onset and magnitude of the shear thickening depend on the amount of cross-linkers added.

However, there are some disadvantages of the STF, especially for the stability and the application of the liquid [2, 5]. To overcome these drawbacks, the solid samples that show the similar shear thickening effect are required. Silicone rubber is one of the most used materials as the solid matrix. It is a rubber-like material composed of silicone containing silicone together with carbon, hydrogen, and oxygen. Silicone rubber offers good resistance to extreme temperatures, being able to operate normally from -55°C to +300°C. At the extreme temperatures, the tensile strength, elongation, tear strength and compression set can be far superior to conventional rubbers although still low relative to other materials [10]. Under dynamic test, the elastic modulus of silicone rubber was almost constant with the frequency at the low frequency range [11]. When frequency is increased to more than 500 Hz, the modulus of elasticity E has a 1.3 times increase [12]. Yu *et al.* [13] used silicone rubber as the key material in an isolator with excellent performance in vibration control.

In this paper, a series of shear-stiffened elastomers (SSEs) made of silicone rubber and silicone oil were fabricated. These SSEs' microstructures were observed through a LV-SEM. Their rheological properties under various working conditions were tested by a rheometer.

FABRICATION AND MICROSTRUCTURE OBSERVATION OF SSES

Materials And Fabrication

Materials used in this study are silicone rubber, type clear silicone sealant (Selleys Pty. LTD) and silicone oil, type 378364 (Sigma-Aldrich Pty. LTD). Silicone oil was mixed with silicone rubber in a beaker at room condition and a magnetic stirrer stirred the mixture for 2 hours. Then a vacuum chamber was used to eliminate bubbles from mixture for 2 hours. Final mixture was placed in a mould with 1mm thickness and cured at room condition for 2 days, and then cut by a punch to disks with 20mm diameter. Figure 1 shows the cured sample with 33 wt. % silicone oil before punching. It can be seen that the sample is clear and flexible. Text can be clearly seen through the flat sample while sample's other part is being bent.

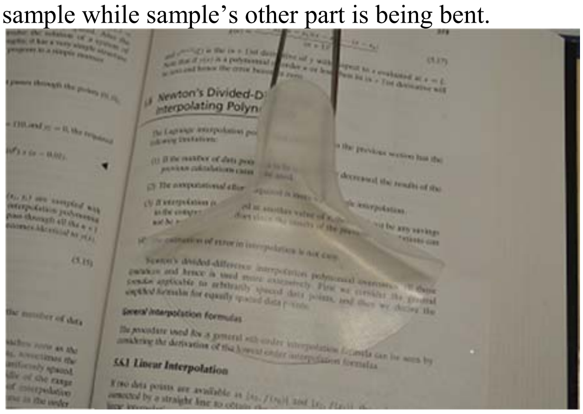

Figure 1. Photograph of the cured sample with 33 wt. % silicone oil.

A total of four isotropic samples were fabricated. Each sample has 10 g silicone rubber, but different quantity silicone oil 5g, 10 g, 15 g and 20 g. So the silicone oil weight fractions in the four samples are 33%, 50%, 60% and 67%, respectively.

Microstructure Observation

LV-SEM (JSM 6490LV SEM) was used to observe the microstructure of SSEs. Figure 2 shows the surface imaging for all samples' microstructures.

Figures 2a-d show that the silicone rubber forms clusters randomly distributed in the samples. The sample with lower percentage of silicone oil has shorter but more clusters than those with higer silicone oils. For instance, the clusters in 33 wt. %sample are around 20um long compared with 300um long in 67 wt. %sample. The crosslinking of silicone rubber forms the net-like structure which enhances the interaction within the mixture of silicone oil and silicone rubber [14].

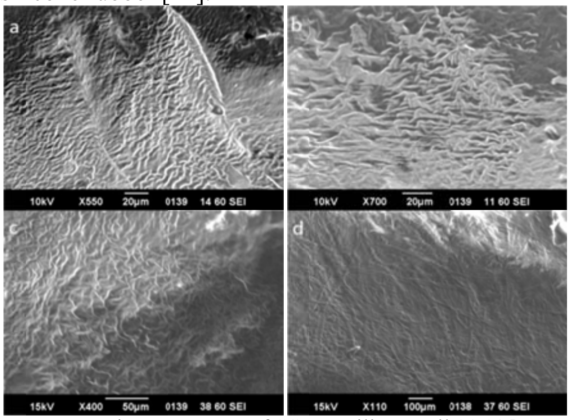

Figure 2. Microstructures of SSEs **a** silicone oil 33 % **b** silicone oil 50 % **c** silicone oil 60 % **d** silicone oil 67 %.

RHEOLOGICAL MEASUREMENT AND RESULTS

The shear-strain dependent rheology of SSEs was measured by a parallel-plate rheometer (MCR 301, Anton Paar). A temperature control device (Viscotherm VT2, Anton Paar) controlled measuring temperature at 25°C. Dynamic frequency sweeps were carried out using the PP-20 measuring geometry with a gap of 1 mm. The testing procedure for each measurement is illustrated below. Sample is firstly sheared at a constant initial shear rate of 1 rad/s for half a minute to preload shear condition. Then, steady shear and dynamic oscillatory shear modes were employed to measure rheological properties of samples under steady and dynamic loading conditions.

Steady State

Under rotary shear, samples' shear stress and strain relationship were measured and shown in figure 3. The shear strain range was set from 0.0001 to 500. In figure 3, the shear stress of each curve shows a linear relationship with the shear strain when the strain is within a range. This means that SSE behaves as linear viscoelastic properties when the strain is below a certain limit. Table 1 summarized the linear ranges of all samples. Also, when the strain is above the limit, the shear stress reaches a saturation (yield stress) and then decrease or goes steadily. This might be due to the sliding effect [15]. Additionally, other factors, such as the sample surface roughness and the normal force, could contribute to the resultant stress. In particular, they influence the static friction between SSE sample and upper plate, which results consequently in overshoots, as shown in figure 3. Moreover, the sample with higher silicone oil concentration has a lower yield stress, which means the higher silicone oil sample can stand a higher yield stress.

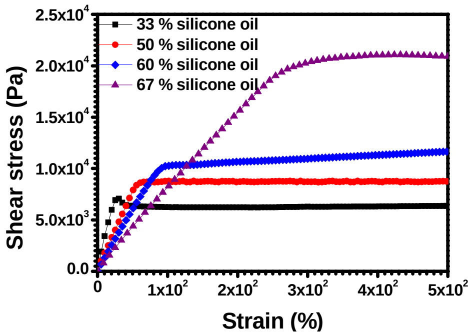

Figure 3. Strain-stress curve of all SSE samples

TABLE 1. Linear range of all samples

Samples	Linear range
33 wt.% silicone oil	25%
50 wt.% silicone oil	50%
60 wt.% silicone oil	86%
67 wt.% silicone oil	254%

The slope of strain-stress curve σ/γ represents the shear modulus of elastomer. From figure 3 we can get that the shear moduli of these four samples are 29.4 kPa, 15.6 kPa, 11.5 kPa and 7.6 kPa, respectively. Obviously, the sample with higher the silicone oil shows smaller shear modulus, which is obvious as the silicone oil tends to make SSEs softer.

Dynamic Tests Result

In order to obtain dynamic mechanical behaviour of SSEs, angular frequency sweep tests were employed in this study. Herein, the strain is set from 1% to higher values till the limitation of linear range for each SSE sample. According to the experimental equipments, angular frequency was varied from 0.01 to 628 rad/s at 25°C. Figure 4 shows storage modulus of the sample with 33 wt. % silicone oil versus angular frequency at different strains. In figure 4, SSE's storage modulus shows a slightly increasing trend with angular frequency at the beginning. However, when frequency reaches a critical value, storage modulus starts to increase abruptly, which means that the elastomer shows a shear-stiffened effect. It is noted that this phenomenon is similar to shear thickening fluid (STF), viscosity of which dramatically increases when shear rate is above a critical value. The other three SSE samples also have the same trend.

The damping factor (also called as loss factor) $\tan(\delta)$ is calculated by loss modulus/storage modulus G''/G' which defines the ratio of viscous and the elastic portion of the viscoelastic deformation behaviour [16]. Some data for damping factor are shown in figure 5.

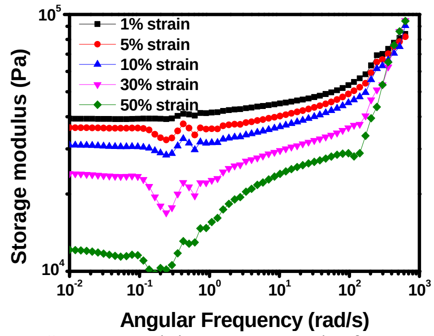

Figure 4. Storage Modulus versus angular frequency sweep (sample with 33 wt. % silicone oil)

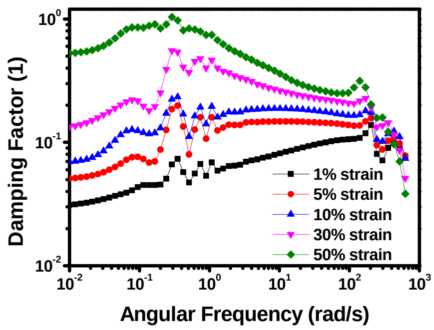

Figure 5. Damping factor versus angular frequency sweep (sample with 33 wt. % silicone oil)

In figure 5, the sample with lowest silicone oil concentrations was selected to show the damping factor curves at different strains. At low strains, the damping factor increases with the raise of angular frequency till the 100 rad/s and then starts to oscillate and drop. The higher strain leads to higher damping factor curves. However, when the strain is over a critical value, the value of damping factor can be over 1 which means the loss modulus is higher than the storage modulus. Then the damping factor decreases to less than 1 when the storage modulus is over loss modulus. The sample with 33 wt. % silicone is taken as an example and shown in figure 6.

It is clear to see that in figure 6a, the storage and loss moduli start to cross twice with each other. Before the first cross, the storage modulus dominates so the sample shows a solid state. After it, loss modulus starts to prevail and a liquid state shows up till the second crossing point, above which the storage modulus will be in charge again to let the sample perform as a solid. This phenomenon was observed in all SSE samples when a critical shear strain is reached.

When the critical strains of all samples are compared with the linear range in table 1, except for the sample with 33 wt. % silicone oil, the other three sample s' critical shear strains are all within their

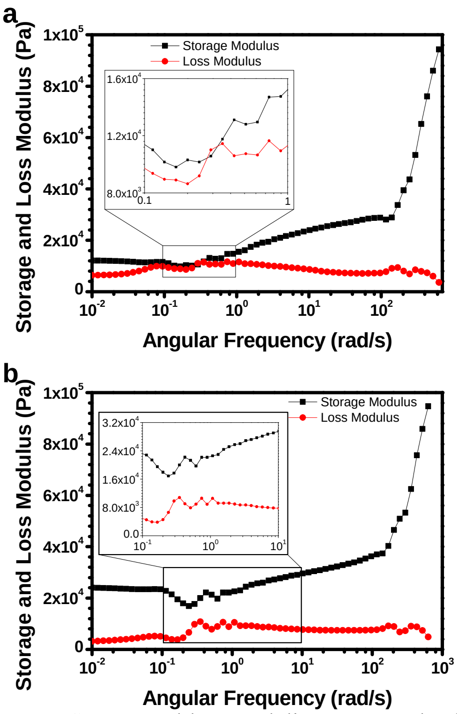

Figure 6. Storage and loss moduli versus angular frequency **a** 33 wt.% silicone oil sample at 50% strain **b** 33 wt.% silicone oil sample at 30% strain.

linear range, respectively. This means for higher silicone oil concentrated SSE, the shear-stiffened effect observe here is clearly credible. Figure 6b shows storage and loss modulus curves of the sample with 33 wt. % silicone oil at 30% strain. There is not a cross between storage and loss moduli. However, at 0.1 rad/s to 1 rad/s, the gap of loss and storage modulus is smaller than the other range, where can be said as the closest to liquid state.

Table 2. Relative shear-stiffened factors of all samples

Strain	33 wt.% silicone oil	50 wt.% silicone oil	60 wt.% silicone oil	67 wt.% silicone oil
1%	2.13	2.80	2.97	3.48
5%	2.26	2.88	3.15	3.65
10%	2.92	3.41	3.27	4.01
30%	3.94	5.41	3.87	4.75
50%	7.77	5.99	4.67	5.61
70%		6.64	5.99	7.42
100%			8.53	9.21
150%				16.17
200%				20.86
250%				23.08
300%				23.50

For all the data curves, either there is a cross of storage and loss modulus or not, the highest values of loss modulus always show up from 0.1 rad/s to 1 rad/s angular frequency, where SSE is liquid state or the closest to liquid state. The angular frequency of 0.4 rad/s is a middle value in this range which can be used as the separation. Before 0.4 rad/s, the SSE is from solid to liquid; after the separation, SSE behaves from liquid to solid state. The storage modulus at 1 rad/s G'_0 and 628 rad/s G'_f are the values at two relative ends of the measurement range. We define their ratio G'_f / G'_0 to be the relative shear-stiffened factor (SSF), which is shown in table 2. We can see that the sample with more silicone oil exhibits relative larger SSF. The closer to critical strain for SSE, the bigger SSF it has.

CONCLUSION

Four SSE sample with 33 wt. % - 67 wt. % silicone oil weight fractions were fabricated in this study. LV-SEM was used to observe their microstructures. This observation shows that the rubber clusters disperse randomly in SSEs and the sample with more silicone has longer silicone rubber clusters.

The steady state and dynamic tests were used to test the rheology of SSEs. Rheological tests show that the sample with higher silicone oil concentration has a longer linear range and a lower shear modulus. In dynamic frequency sweep tests, when shear strain is above a critical value, SSE sample can be observed as the solid to liquid transition and the liquid to solid transition which is the shear-stiffened. Test result also shows that the sample with 67 wt. % silicone oil has the biggest relative shear-stiffened factors.

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