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# Polydimethylsiloxane Microspheres with Poly(methyl methacrylate) Coating: Modelling, Preparation, and Characterization

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Abstract:

Polydimethylsiloxane (PDMS) microspheres are prepared by mixing homogeneous dispersions of vinyl-functional PDMS and a curing agent using mechanical stirring in a series of aqueous solutions, and curing at 80 °C for 2 h. In order to verify the experimental diameter and size distributions of the PDMS microspheres, the Hinze-Kolmogorov theory is applied to predict the mean diameter, and a population balance model as well as the maximum entropy formalism are used to describe the size distribution. Close agreement is found between experimental and theoretical results. Furthermore, vinyl functional PDMS microspheres were coated with poly(methyl methacrylate) (PMMA) by spin coating with different concentrations of PMMA

solutions. The quality of the resulting PMMA shell is investigated using rheological measurements at 50 °C with a time-sweep procedure. The results strongly suggest that PMMA-coated PDMS microspheres react around 20 times slower than the uncoated ones, and that the PMMA shell significantly hinders the reaction between the PDMS microsphere and cross-linker. Thus the thin PMMA shells are very efficient in protecting the reactive PDMS microspheres, since the PMMA shell forms an impermeable barrier up to 50 °C.

Key words: PDMS microspheres, PMMA, silicone, modelling, coating

## INTRODUCTION

Polydimethylsiloxane (PDMS) has attracted much attention due to its useful properties, such as water repellency, low surface energy, and non-toxicity.<sup>[1]</sup> Cross-linked PDMS microspheres not only possess the useful properties of PDMS, but also have the potential for versatile applications, such as drug delivery,<sup>[2]</sup> enzyme immobilization,<sup>[3]</sup> and wastewater treatment.<sup>[4]</sup> Due to these properties and the attractive potential applications, the preparation of PDMS microsphere has been investigated in several studies.<sup>[5-7]</sup> However, most of the studies focus on producing the monodisperse functional PDMS microspheres on the order of milligrams using microfluidic systems. The low productivity of PDMS microspheres from the microfluidic system constrains the potential applications of PDMS microsphere on an industrial scale. Hence, it is of considerable interest to prepare large quantities of PDMS microspheres in an easy way.<sup>[8]</sup> In this study, the preparation of PDMS microspheres by emulsion will be demonstrated, using emulsions with varying concentrations of surfactant solutions, and the resulting particle distribution of the PDMS microspheres will be further investigated.

In the preparation of the PDMS microspheres, the process involves the dispersion of the PDMS in a turbulent system. A vast amount of theoretical and experimental works can be found

concerning the mean diameter and size distribution of the droplets in turbulent systems.<sup>[9–11]</sup> However, the droplets in previous studies are obtained from physical mixtures of two immiscible liquids, which allows for no further reaction, meaning that the droplets cannot be separated from the emulsion. In the present study, cross-linked PDMS microspheres are prepared which can be separated and used in other applications. In order to interpret the mean diameter and size distribution of the PDMS microspheres, the experimental results are compared with the theoretical mean diameter predicted by the Hinze-Kolmogorov theory and the size distribution described by the population balance model as well as the maximum entropy formalism.

By changing the mixing ratio between vinyl terminated PDMS and the hydride cross-linker in the preparation process, the resulting PDMS microsphere can be functionalized with vinyl groups, which allow for further cross-linking reactions with the presence of additional hydride cross-linker. Thus, the protection of the active vinyl groups by encapsulation, which is similar to the encapsulation of the hydride cross-linker in PMMA,<sup>[12,13]</sup> is achieved by a solvent evaporation technique. Similarly, the reactive PDMS microsphere will be encapsulated with the spin-coating technique, and time-sweep rheological measurements are performed to investigate the quality of the PMMA coating.

Encapsulated elastomer microspheres can provide the basis for an elastomer system that can be activated in hard-to-access places, such as in oil reservoirs where fractures arise and cause a significant decrease in oil production. First of all, the size of the microsphere will ensure that the elastomer is not absorbed by rock pores during the delivery. Secondly, the encapsulation will ensure that no reaction is taking place, and that the activation can take place later, e.g. upon heating above the glass transition temperature of the shell material. Finally, the reactive groups on the surface of the microspheres only need to react partly before a relative strong elastomer is obtained.

## THEORY

### Hinze-Kolmogorov Theory

Many industrial processes involve liquid-liquid dispersion in stirred vessels and knowledge of the resulting drop size distribution characteristics with changes in external mechanical energy input. Much work has been done to investigate the mean diameter and size distribution in turbulent liquid-liquid dispersions subjected to mechanical stirring, and most of these investigate the concept of turbulent energy cascades to predict the mean diameter of the droplets, referring to the Hinze-Kolmogorov theory.<sup>[14]</sup> This theory presents a decreasing power law for the dependence of the diameter on average turbulent energy dissipation. Applying this approach, similar equations have been derived for systems where viscous energy dissipation occurs.<sup>[9,10,15-17]</sup> A recent version of the resulting formula is;<sup>[15-17]</sup>

$$\frac{D_{32}}{D} = k \cdot We^{-0.6} (1 + a \cdot Vi (\frac{D_{32}}{D})^{\frac{1}{3}})^{0.6} (1 + b \cdot \varphi) \quad (1)$$

where  $We$  is the Weber number, given by Equation (2), and  $Vi$  is the viscosity number, given by Equation (3).

$$We = \frac{\rho \cdot \omega^2 \cdot D^3}{\sigma} \quad (2)$$

$$Vi = \frac{\mu_d \cdot \omega \cdot D}{\sigma} \quad (3)$$

where  $D_{32}$  is the Sauter mean diameter,  $D$  is the impeller diameter,  $k$  is an empirical constant,  $a$  is a proportionality factor,  $b$  is an empirical system-dependent constant,  $\rho$  is the density of the continuous phase,  $\varphi$  is the volume fraction of the dispersed phase,  $\mu_d$  is the viscosity of the continuous phases,  $\omega$  is the rotational speed of the impeller, and  $\sigma$  is the surface tension of the aqueous solution.

### Size Distribution in Turbulent Systems

Particle size distribution has been predicted in turbulent systems using many methods. Amongst these, the population balance model, Monte Carlo simulation, and maximum entropy formalism are most commonly used. The population balance model deals with systems containing particles in a continuous phase. In this model, the basic assumption is that there exists a number density of particles in a continuous phase.<sup>[18]</sup> By coupling conservation equations with this assumption, the population balance model is used to depict the number density and size distribution of particles at given conditions. The population balance model has been applied in various studies, in which the number density and particle distribution play an important role.<sup>[19]</sup> For instance, this model has successfully predicted the size distribution of droplets in water-in-oil systems<sup>[20,21]</sup> and oil-in-water systems.<sup>[22,23]</sup> As the population balance model is concerned about the particle size distribution on a macroscopic level, the Monte Carlo simulation has also been used for describing the particle size distribution by means of statistics.<sup>[24]</sup> Compared to the other methods, the Monte Carlo simulation describes the particles with various degrees of freedom, such as temperature, pressure, and density. Also, the simulation can provide a realistic way to understand a system in a dynamic way. For instance, Monte Carlo simulation has been used to predict the particle size distribution by combining the behaviour of individual particles in the system.<sup>[25]</sup> While the Monte Carlo simulation describes the particle size distribution in a dynamic way, maximum entropy formalism depicts the particle size distribution in a thermodynamic way.<sup>[26]</sup> The maximum entropy formalism suggests the least biased solution in the prediction of the particle size distribution, given that the statistical entropy in the system is maximized. For instance, the drop size distribution in a spraying process has been successfully predicted by this formalism.<sup>[27]</sup> In the present study, the population balance model and the maximum entropy formalism will be used to describe the size distribution of the PDMS microspheres.

### *Population balance model*

Consider a suspension that contains a large number of clusters, each consisting of a number of primary particles. Due to high-speed mechanical stirring in the vessel, there is a high possibility that the clusters will collide with each other and form larger clusters in the suspension; but it is also possible that the clusters will break and divide into smaller clusters or primary particles due to the mechanical stirring, until a dynamic equilibrium is established.<sup>[15,28]</sup> Given that the fragmentation and aggregation processes occur randomly and independently, the maximum entropy assumption can be used to predict the particle size distribution in the equilibrium system. For maximum entropy derivation from the combination of primary particles, see Supplementary Information 3. The final expression is the Poisson-type size-distribution probability function.<sup>[29]</sup>

$$p(i) = \exp(-Z) \frac{Z^i}{i!} \quad (4)$$

where  $Z$  is the characteristic parameter of  $N_0$ , and it satisfies the following equation:

$$N_0 = Z \exp Z \quad (5)$$

where  $N_0$  is the number of primary particles in the system. The primary particle size is denoted  $d_{min}$  to describe the relation between drop size distribution and cluster size using the mathematical definition of  $D_{32}$ .<sup>[11,30]</sup>

$$\frac{\sum_{i=1}^{N_0} i \cdot p(i)}{\sum_{i=1}^{N_0} i^{2/3} \cdot p(i)} = \frac{D_{32}}{d_{min}} \quad (6)$$

### *Maximum entropy formalism*

In the prediction of particle size distribution in a turbulent system, an alternative method is to use Shannon's entropy function.<sup>[31]</sup> For the derivation maximizing Shannon's entropy function, see Supplementary Information 4. The final expression for volume-based distribution can be written based on the assumption that Shannon's entropy function is maximized:

$$f_v(D_p) = q^{\frac{q-4}{q}} \frac{D_p^3}{D_{q0}^4 \Gamma(4/q)} \exp\left(-\frac{D_p^q}{q D_{q0}^q}\right) \quad (7)$$

where  $f_v(D_p)$  is volume-based distribution, the parameter  $q$  equals the distribution parameter of the Rosin-Rammler distribution,  $D_p$  is the particle diameter,  $D_{q0}$  is mean diameters, and  $\Gamma$  is the Gamma function.

### *Normal distribution*

In order to compare the size distributions predicted by the population balance model and the maximum entropy formalism, normal distribution is introduced. Several studies <sup>[10,32,33]</sup> have shown that the normal distribution fits the experimental size distribution in the turbulent system well:

$$f(D) = \frac{1}{\sqrt{2\pi}\sigma_d} \exp\left[-\frac{(D-D_{32})^2}{2\sigma_d^2}\right] \quad (8)$$

where  $f(D)$  is the particle size distribution,  $D_{32}$  is the mean diameter, and  $\sigma_d$  is the standard deviation.

## EXPERIMENTAL

### **Materials**

Sylgard 184 consisted of vinyl functional PDMS (Batch A) and curing agent (Batch B) (RTV silicone elastomer, Dow Corning), 25–35 % (methylhydrosiloxane) with 65–70 % (dimethylsiloxane) copolymer (HMS-301) (Mw = 2000 g/mol 8-functional cross-linker, Gelest), platinum-cyclovinylmethylsiloxane complex (SIP6832.2 catalyst) (Gelest), poly(vinyl alcohol) (PVA) (Mw = 22 000 g/mol, Fluka), poly(methyl methacrylate) (PMMA) (Mw = 15 000 g/mol, Aldrich), dimethyl formamide (DMF) (> 99 %, Aldrich), sodium dodecyl sulphate (SDS) (> 99 %, BDH), non-reactive silicone oil (20 cSt, Dow Corning), and deionized water.



## **Experimental Procedure**

**PDMS microsphere preparation:** 8 g Sylgard 184 vinyl functional PDMS and an appropriate amount of curing agent were mixed in a polystyrene cup in a ratio of 10:1 or 20:1 at 1000 rpm for 2 min to yield a mixture. 7 g of this mixture was then poured into a conical flask with 200 g of aqueous surfactant solution. The choice of geometry is discussed in Supplementary Info 1. A 2.0 cm diameter impeller with two inclined blades was used to stir for 2 min at 2000 rpm to produce an emulsion. After the emulsion was formed, the system was placed in an oven at 80 °C for 2 h to cure the PDMS microspheres. The system was then filtered using a vacuum filter and washed with deionized water several times to remove residual surfactant. The PDMS microspheres were then dried in an oven at 80 °C for 2 h, and weighed to calculate the microsphere yield.

**PDMS microsphere coated with PMMA:** 0.4 g PDMS microspheres with a ratio of vinyl functional PDMS to curing agent of 20:1 were added to a watch glass (radius 22 mm). PMMA was dissolved in DMF to yield solutions with 10 %, 20 % and 50 % of PMMA, respectively, by weight, which were dropped into the watch glass with a syringe. The watch glass was then placed in the spin coater. Spin coating was performed at 5000 rpm for 1 min, with an acceleration of 1000 rpm/s from 0 to 5000 rpm. After coating, the coated PDMS microspheres were placed in an oven at 80 °C to remove the residual DMF. Agglomeration of particles after the application of centrifugal force was minimal, since the PMMA is not sticky and most of the agglomerated particles could simply be separated by use of a spatula.

## **Apparatus**

PDMS microsphere size distribution was measured with a Mastersizer (Malvern, UK) in a jar tester. In this measurement, PDMS microspheres in aqueous solution were pumped through transparent

tubing with an internal diameter of 5 mm by a peristaltic pump at a flow rate of 10 mL/min, and then back to the conical flask. The instrument was equipped with a laser with a wavelength of 633 nm, and the size range is 1–1000  $\mu\text{m}$  in the measurement.

The surface tension was measured using the Nelder-Mead simplex method with a Data Physics OCA20 tension meter. The sample was loaded into a syringe mounted to a stepper motor, which was used to control the rate of the advancing and receding drop front. 10  $\mu\text{L}$  samples were dispensed at a rate of 2  $\mu\text{L/s}$  using a needle with a diameter of 1.67 mm. The pendant drop was illuminated from behind by a white-light projector. A CCD camera was used to capture the images for analysis.

The viscosity of the PDMS emulsion was measured using an AR-2000 Rheometer (TA Instruments, USA) at room temperature using a conical tank. 100 mL of the PDMS emulsion was tested at shear rates ranging from 100–0.1  $\text{s}^{-1}$ .

Spin coating was performed using a Spin150 (SPS coating, Netherland). 0.4 g PDMS microspheres on a watch glass were subjected to spin-coating with different concentrations of PMMA solution in DMF for 1 min at 5000 rpm.

The thermogravimetric behaviour of coated PDMS microspheres was analyzed using a TGA Q500 (TA Instruments, USA). Typically a 20~50 mg sample was used. The measurement was made from 30–800  $^{\circ}\text{C}$  in nitrogen at a heating rate of 10  $^{\circ}\text{C}/\text{min}$ .

The rheological behaviour of coated and uncoated PDMS microspheres was investigated using an AR-2000 with a time sweep procedure. 0.4 g of PDMS microspheres were mixed with 0.01 g hydride 8-functional cross-linker (HMS-301) and 0.1 g non-reactive silicone oil. Measurements were made using a parallel plate geometry consisting of a pair of 25 mm plates at 50  $^{\circ}\text{C}$  with a strain rate of 2 % (within the linear viscoelastic region), while the normal force was around 9 N.

## MODELLING

The mean diameter of PDMS microspheres can be calculated from Equations (1–3) with the following parameters:

$k$  is an empirical number equal to 0.100 for systems with a viscosity ranging from 0.005–4 Pa·s,<sup>[15,28]</sup>  $a = 11.5$  for the silicone oil-water system,<sup>[10,16]</sup> and  $b$  is an empirical number equal to 4.47 for systems with concentrations between 1.5–5 %.<sup>[10,28]</sup> The values of  $k$ ,  $a$ , and  $b$  are from the literatures, while the following parameters are determined from the measurements:  $D$  is the impeller diameter ( $D = 0.02$  m);  $\rho$  is the density of the continuous phase (993 kg/m<sup>3</sup>);  $\varphi$  is the volume fraction of PDMS mixture,  $\varphi \approx 3.5$  % as 7 g PDMS mixture (6.8 mL) is dispersed in 200 g solution (194 mL);  $\omega$  is the rotational speed of the impeller (2000 rpm);  $\mu_d$  is the viscosity of the continuous phase ( $\mu_d = 0.00528$  Pa·s, measured by AR-2000); and  $\sigma$  is the surface tension of the aqueous surfactant solution ( $\sigma = 36.2$  mN·m<sup>-1</sup>).<sup>[34]</sup>

For the population balance model, the size distribution of PDMS microspheres can be calculated from Equation (6). The primary particle size ( $d_{min}$ ) is measured by using a Mastersizer 2000 in the experiment. After substituting the values of  $D_{32}$  and  $d_{min}$ , the particle size distribution can be obtained.

For maximum entropy formalism, the size distribution of PDMS microspheres can be calculated from Equation (7). The parameter  $q$  is estimated from a plot of  $\ln(1-Q_i)^{-1}$  versus  $d_i/Y$ .

For normal distribution, the size distribution of PDMS microspheres can be calculated from Equation (8). Similar to the population balance model, the standard deviation ( $\sigma_d$ ) is equal to the primary particle size ( $d_{min}$ ).

## RESULTS AND DISCUSSION

## PDMS Microsphere Size Distribution from Experiment

In order to investigate PDMS microsphere size distribution with respect to the diameter and yield of PDMS microspheres, eight samples were prepared by mixing Sylgard 184 in a recommended ratio of 10:1 with different surfactant concentrations. Sample ID, surfactant concentration, mean diameter, and microsphere yield are listed in Table 1. The Sample ID indicates the surfactant concentration, e.g. S3P1 means that 3 % SDS and 1 % PVA are added to the aqueous solution.

The yield of PDMS microspheres is calculated from Equation (9). As shown in Table 1, the yield ranges from 25.3–71.4 %, and a maximum yield of 71.4 % is obtained in Sample S5P1. Meanwhile, the yield depends on the surfactant concentration in the solution, which is in line with the yield of poly(divinylbenzene) microspheres in surfactant solutions,<sup>[35]</sup> indicating that the yield of PDMS microspheres not only depends on the external mechanical energy input to the turbulent system, but also to the surfactant concentration in the solution.<sup>[36]</sup>

$$Y_{PM} = \frac{m_{PM}}{m_{tot}} \cdot 100\% \quad (9)$$

where  $Y_{PM}$  is the yield of PDMS microspheres,  $m_{PM}$  is the mass of PDMS microspheres, and  $m_{tot}$  is the mass of vinyl functional PDMS and curing agent.

Table 1. PDMS microsphere mean size and yield from varying surfactant concentrations

Sample ID	SDS ( g/g)	PVA ( g/g)	$\sigma$ (mN/m)	$D_{32}$ ( $\mu$ m)	$Y_{PM}$ ( g/g)
S0P0	0	0	72.9	/	0
S1P0	1	0	37.3	120	41.6
S3P0	3	0	32.3	104	47.4
S5P0	5	0	32.0	102	54.4
S0P1	0	1	52.4	/	0

S1P1	1	1	37.9	105	25.3
S3P1	3	1	36.2	107	69.4
S5P1	5	1	36.1	89	71.3

Figures 1 and 2 show the volume frequency and the accumulated volume frequency of the PDMS microsphere in different surfactant solutions. As shown in Figure 1, the PDMS microsphere diameter falls between 30–300  $\mu\text{m}$ , and the mean diameter is  $\sim 100 \mu\text{m}$ . The mean diameter of PDMS microspheres is similar to what is reported in literature, where diameter ranged from 100  $\mu\text{m}$  to 1 mm.<sup>[37,38]</sup> The high polydispersity of PDMS microspheres demonstrates that the size distribution of the cross-linked PDMS microspheres is different from the narrow size distribution of silicone oil droplets in the water emulsion.<sup>[23]</sup>

Among the samples in the present study, the samples with PVA exhibit a narrower size distribution than those without, indicating that the emulsions created from mechanical stirring are more stable in the presence of PVA. This is in agreement with findings that emulsion stability can be increased by using PVA as an assistant surfactant.<sup>[39]</sup> On the other hand, Sample SOP1 shows that no PDMS microspheres can be obtained, meaning that PVA cannot be solely used in the preparation of PDMS microspheres, and should be added to the solution as assistant surfactant.

Figure 1. Experimental relative volume fraction versus microsphere diameter for different surfactant concentrations.

Figure 2. Experimental accumulated volume fraction versus microsphere diameter for different surfactant concentrations.

## Comparison of Theoretical Predictions with Experimental Results

### *Comparison of population balance model simulation with experimental results*

As discussed in previously the theoretical mean diameter of the PDMS microsphere can be calculated from Equation (1). By substituting the parameters from the measurements and literature, the theoretical mean diameter of the PDMS microspheres can be obtained. Table 2 shows the experimental as well as theoretical mean diameters of the PDMS microsphere. As can be seen, the experimental mean diameter varies from 89–120  $\mu\text{m}$ , while the predicted mean diameter is around 99  $\mu\text{m}$ . The maximum deviation between the experimental value and the theoretical value is 20  $\mu\text{m}$ , and the average deviation is around 7  $\mu\text{m}$ , indicating that the theoretical values fit the experimental results quite closely. However, the theoretical prediction cannot distinguish between microspheres obtained from different surfactant systems, but captures the mean diameter satisfactorily.

Table 2. Comparison between the experimental and theoretical mean diameters of PDMS microspheres in different surfactant solutions

Sample ID	S1P0	S3P0	S5P0	S1P1	S3P1	S5P1
Exp. mean diameter ( $\mu\text{m}$ )	120	104	102	105	107	89
Theo. mean diameter ( $\mu\text{m}$ )	98.1	99.5	99.6	97.9	98.4	98.4
Deviation between exp. and theo. ( $\mu\text{m}$ )	21.9	4.5	2.4	7.1	8.6	9.4

The population balance model introduced earlier is used to describe the size distribution of the PDMS microspheres based on Equation (6). Normal distribution is introduced in order to compare this with the size distribution predicted by the population balance model. Table 3 shows the volume frequency of the most probable distribution from the experiment, the population balance model, and the normal distribution. It can be seen that the deviation of the most probable distribution between the experiment and the population balance model is around 5 %, while the deviation between the

experiment and the normal distribution is substantial, indicating that the population balance model provides a realistic solution to the prediction of the volume frequency of the most probable distribution.

Table 3. Comparison of volume frequency for PDMS microspheres in different surfactant solutions

Sample ID	S1P0	S3P0	S5P0	S1P1	S3P1	S5P1
Exp. most probable distribution (%)	6.3	6.9	8.4	7.6	9.4	10.0
Theo. most probable distribution (%)	8.3	11.0	11.0	6.6	11.0	11.0
Normal distribution (%)	36.4	36.4	36.4	36.4	36.4	36.4

The PDMS microsphere size distribution between the experiment, the population balance model, and the normal distribution are compared and shown in Figure 3. It can be seen that the size distribution obtained from the population balance model is similar to that of the experiment. Meanwhile, the experimental distribution indicated that there is a small possibility of primary particles forming clusters smaller than 30  $\mu\text{m}$  or larger than 300  $\mu\text{m}$ , which cannot be predicted by the population balance model.

Figure 3. Comparison between experimental, population balance model simulation, and normal distribution of the PDMS microsphere. Size distribution -- solid circle: experiments, open circle: population balance model, open triangle: normal distribution. Cumulative distribution -- solid line: experiments, dotted lines: population balance model, dashed lines: normal distribution.

Close agreement between the experimental and modelling values is observed, with the theoretical predictions being within +/- 20 % of the experimental data. This demonstrates that the Hinze-Kolmogorov theory and population balance model based on dilute systems provide acceptable values for the mean diameter and size distribution of the PDMS microspheres. Many

experiments and simulations based on the Hinze-Kolmogorov theory have been reported;<sup>[15,16,28]</sup> however, to the best of our knowledge, none of them involve chemical reactions and irreversible cross-linking in the system. The close agreement between the experimental and theoretical values shows that the applicability of the Hinze-Kolmogorov theory for determining mean diameter can be fairly broadened.

*Comparison of maximum entropy formalism simulation with experimental results*

As described previously, the mean diameter and size distribution of PDMS microspheres can also be predicted by the maximum entropy formalism using Equation (7). The mean diameter obtained from the simulation is compared with the experimental values, and shown in Table 4. As shown, the mean diameter deviation between the experiment and the simulation is around 20  $\mu\text{m}$ , meaning that the agreement between the experiment and the simulation is reasonably close.

Table 4. Comparison of different characteristics of microspheres from different surfactant solutions

	S1P0	S3P0	S5P0	S1P1	S3P1	S5P1
Exp. mean diameter ( $\mu\text{m}$ )	120	104	102	105	107	89
Theo. mean diameter ( $\mu\text{m}$ )	118	120	121	120	138	122
Deviation between exp. and theo. ( $\mu\text{m}$ )	2	16	19	15	29	33

In Equation (7), the size distribution predicted by the maximum entropy formalism is relevant to the distribution parameter  $q$ . In some studies, the value of  $q$  is arbitrarily set to 1, providing the size distribution in terms of linear mean diameter.<sup>[27,40]</sup> Meanwhile, the value of  $q$  can also be determined using Equation (11) from Supplementary Information 4, where  $q$  is equal to the slope of  $\ln(1-Q_i)^{-1}$  versus  $d_i/Y$ .<sup>[26,41]</sup> The value of the size parameter  $Y$  and the distribution parameter  $q$  are shown in Table 5.



In order to compare these results with the maximum entropy formalism model, the normal distribution is also introduced. Table 5 shows the volume frequency of the most probable distributions of the PDMS microsphere from the experiment, the maximum entropy formalism, and the normal distribution in different surfactant solutions. It can be seen that the deviation of the volume frequency of the most probable distribution between the experiment and the maximum entropy formalism is around 5 %, while the deviation between the experiment and the normal distribution is quite large, demonstrating that the maximum entropy formalism provides a fairly realistic solution for the prediction of the volume frequency of the most probable distribution.

Table 5. Comparison of different characteristics of microspheres from different surfactant solutions

	S1P0	S3P0	S5P0	S1P1	S3P1	S5P1
Exp. most probable distribution ( % )	6.3	6.9	8.4	7.6	9.4	10.0
Theo. most probable distribution ( % )	11.4	9.7	8.4	8.4	10.8	8.4
Normal distribution ( % )	36.4	36.4	36.4	36.4	36.4	36.4
Y value (size below 63.2 %) ( $\mu\text{m}$ )	152	158	135	184	124	113
$q$ (slope of $\ln(1-Qi)^{-1}$ versus $d_i/Y$ )	1.1	0.8	0.6	2.7	1.0	0.6

Figure 4 shows the PDMS microsphere size distributions from the experiment, the maximum entropy formalism, and the normal distribution. It can be seen that the normal distribution shows a remarkable difference in distribution trend, and thus is not suitable to describe the experimental data. Meanwhile, the size distribution predicted by the maximum entropy formalism can describe the distribution trend of the experimental data, as well showing a difference in the peak. This demonstrates that the entropy in the experimental systems is not maximized, resulting in the deviation between the predicted and experimental values.

Figure 4. Comparison between experimental, maximum entropy formalism simulation, and normal distribution of PDMS microspheres. Size distribution -- solid circle: experiments, open circle: maximum entropy formalism, open triangle: normal distribution. Cumulative distribution -- solid line: experiments, dotted lines: maximum entropy formalism simulation, dashed lines: normal distribution.

### **PMMA-Coated PDMS Microsphere Characterization**

#### *Thermogravimetric analysis*

In order to investigate the content of PMMA in the coated PDMS microspheres, four samples were coated in the presence of various concentrations of PMMA. Sample ID, PMMA concentrations, and char yield at 800 °C are summarized in Table 6. The sample ID indicates the coating concentration of PMMA, e.g. ‘10PD’ means the coating solution is 10 % PMMA in DMF, while PM is the abbreviation of PDMS microsphere.

In the TGA measurements, the PDMS microsphere degrades simultaneously with the PMMA. Since PMMA degrades completely at 430 °C, the char yield at 800 °C depends only on the content of the PDMS microsphere. As shown in Table 6, the char yield of the coated PDMS microsphere decreases when a higher concentration of PMMA is used in the spin-coating process. This indicates that PMMA content in the coated PDMS microsphere increases with high concentrations of PMMA in the solution.

Table 6. Thermogravimetric analysis of PDMS microspheres coated with different concentrations of PMMA with spin coating

Sample ID	PMMA	non-coated PM	PM-10PD	PM-20PD	PM-50PD

PMMA concentration in solution (%)	/	0	10	20	50
Char yield at 800°C (g/100g)	0	37.7	27.5	18.3	11.4

Figure 5. TGA thermograms in a N<sub>2</sub> atmosphere of PDMS microspheres coated with PMMA, and non-coated sample.

As a commercially available technique, spin-coating has been used for decades to produce thin films on a planar substrate. However, it has not been reported that spin-coating can be used to produce coated microspheres. There is no conclusive evidence to prove that PMMA can be coated perfectly onto PDMS microspheres, and further studies (e.g. rheology) are required.

#### *Rheological measurement*

In the preparation of PDMS microspheres, excess vinyl-terminated PDMS is added to the mixture to obtain vinyl-functional PDMS microspheres. The vinyl groups on the surface of PDMS microspheres are able to react with the cross-linker in the presence of catalyst. The reaction between the PDMS microsphere and the cross-linker will increase the cross-linking density of the system, resulting in an increase of the storage modulus.

The objective of the rheological measurement is to investigate the quality of the coated PMMA layer, namely whether the coated PMMA is sufficient to prevent the vinyl-functional PDMS microsphere from reacting with the cross-linker. If the PDMS microspheres are completely coated with PMMA, the cross-linker cannot penetrate the PMMA shell and the modulus will remain constant, and vice versa.

In the measurement, 0.4 g PMMA-coated vinyl-functional PDMS microsphere is mixed with 0.01 g HMS-301 cross-linker and 0.1 g non-reactive silicone oil. Uncoated PDMS

microspheres are used as a control sample. For details of the applied amount, see Supplementary Info 2. Meanwhile, the rheological measurements are made at 50 °C for two reasons: first, the measuring temperature is lower than the  $T_g$  of the PMMA, such that the coated PMMA remains rigid; secondly, the PDMS microspheres react with the cross-linker at a moderate rate if the cross-linking reaction occurs.

Figure 6 shows the rheological behaviour of the PDMS microspheres with and without coating over a period of 10 h. For the PDMS microspheres without coating, the storage modulus increases from 10 to 38 kPa, indicating that the PDMS microspheres undergo a cross-linking reaction with the cross-linker. The slope of the storage modulus curve is relatively steep during the first hour, showing a relatively high rate of the cross-linking reaction. Afterwards, the storage modulus levels out, meaning that the vinyl groups on the surface of the PDMS microspheres have been consumed. For the coated PDMS microspheres, the storage modulus increases slightly for the thinnest-coated microsphere (PM-10PD), demonstrating that the cross-linking reaction occurs to a small degree. The microspheres with thicker coatings (PM-20PD and PM-50PD) soften over time, indicating an equilibration of the rigid PMMA shell and silicone interface. In the comparison of the uncoated and coated PDMS microspheres, the difference in rheological behaviour suggests that the PMMA shell greatly hinders the cross-linking reaction.

Figure 6. Rheological behaviour of PDMS microspheres with and without PMMA coating in silicone oil at 50 °C.

## CONCLUSIONS

PDMS microspheres were prepared by mechanical stirring using a series of surfactant solutions. The size distribution of the microspheres was investigated, and it was found that the diameter of 90

% of PDMS microsphere falls between 30–300 $\mu\text{m}$ , while the mean diameter is around 100  $\mu\text{m}$  in all samples.

As the PDMS microsphere preparation process involves the dispersion of PDMS in the aqueous surfactant solution, the PDMS microsphere mean diameter was predicted with the Hinze-Kolmogorov theory. The agreement between the experimental and calculated values is acceptable, with theoretical predictions within +/- 20 % of the experimental data despite the unaccounted for reactive nature of the microspheres. This indicates that the applicability of the Hinze-Kolmogorov theory can be broadened in the prediction of the mean diameter of droplets in turbulent systems. Furthermore, the PDMS microsphere size distribution was described using the population balance model and maximum entropy formalism. Compared to experimental results, it is shown that both simulations provide accurate results.

The PDMS microspheres with residual vinyl groups on their surfaces were further coated by PMMA in a newly developed spin-coating procedure. The coated PDMS microspheres show very slow reaction rates compared to those without coating, indicating that the reaction is significantly hindered by the PMMA shell. Such properties may provide the potential for designing responsive materials.

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