Neutron Reflectometry & Simultaneous Measurements of Rheology and Small Angle Neutron Scattering Studies for Polyether Modified Silicone Vesicle Systems

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Abstract: Polyethyleneglycol 12 mol / polydimethylsiloxane co-polymer (PEG-12 dimethicone) is a type of polyether modified silicone (PEMS), which can form a lamellar liquid crystalline phase, and is widely used in cosmetics. The structural changes of PEG-12 dimethicone caused by water contents as well as shear flow were evaluated using simultaneous measurements of rheology and small angle neutron scattering (Rheo-SANS) and neutron reflectometry (NR). At high PEG-12 dimethicone concentrations (≥ 36 wt%), a reorientation of plate-like lamellar structures were observed and the neutral orientation was the most favorable. However, lamella-to-vesicle transitions were hardly observed. PEG-12 dimethicone turned out to form a bi-layer on a hydrophilized Si-wafer in a similar manner to that in bulk though the structure had a certain level of roughness.

Key words: Rheo-SANS, NR, polyether modified silicone, vesicle

1 Introduction

In pharmaceuticals and cosmetics, and industrial lubricants, it is essential to understand the changes of self-assembled structures of surfactants or polymers caused by the evaporation of water as well as the shear flow. Furthermore, it is also important to clarify adsorbed film structures on a substrate such as a skin, as these phenomena are key factors to control the product functions and tactile feelings in cosmetics\(^1\)\(^-\)\(^2\). These phenomena take place during and after the application of a product.

The shear-induced lamellar-to-onion transition is surely one of the most striking phenomena among the effects of shear flow on the self-assembled structures of surfactants. This phenomenon was found for the first time in 1990s by Roux et al. in ionic surfactants using electron microscopy and rheology concurrent with small angle X-ray scattering (Rheo-SAXS)\(^3\)\(^-\)\(^12\). According to their work, the shear flow induces transformation of the lamellar structure into multilamellar vesicles (onions) of polyhedral shape, which fill space without excess water. They characterized and showed three different principal orientation states of a lamellar phase, which are parallel to the vorticity (perpendicular, neutral), parallel to the velocity (transverse, flow), and the parallel to the velocity gradient (parallel, gradient), respectively. Kato et al. have reported for the first time the lamellar-to-onion transition with increasing temperature under a constant shear rate in polyethyleneglycol-type (PEG) nonionic surfactant systems by using rheology concurrent with small angle light scattering (Rheo-SALS) and Rheo-SAXS\(^13\)\(^-\)\(^15\). Medronho et al. have proposed that the simultaneous measurement of rheological and nuclear magnetic resonance parameters (Rheo-NMR) is an alternative method of measuring the multilamellar vesicles (MLVs) dimensions in sheared lamellar systems composed of nonionic surfactants\(^16\). Moreover, simultaneous measurements of rheology and small angle neutron scattering (SANS), so-called Rheo-SANS, have been also performed for such systems\(^17\)\(^-\)\(^19\).

For the adsorption process of surfactants or polymers on substrates, interactions between them have a substantial
effect on the self-assembly which are surely related to the bulk structure but often differ strongly from the bulk situation\textsuperscript{20–22}. Warr \textit{et al.} has reported that polyoxyethylene 9 mol lauryl ether forms a micellar (discontinuous) cubic phase in bulk, but forms a hemicylinders on graphite due to a strong interaction with the substrate\textsuperscript{23}. Also, Inoue \textit{et al.} reported the processes of dynamic aggregation transformations of micelles at a mica surface by using atomic force microscopy (AFM)\textsuperscript{22}. Therefore, information on aggregation structures in bulk is insufficient to gain insights into interfacial structures. The adsorbed layer on a substrate can be clarified by quartz crystal microbalance with dissipation (QCM-D), ellipsometry, or AFM, which yield information on the adsorbed amount or thickness, but yield no information about its mesoscopic structure. X-ray reflectometry is limited in analyzing surfactant/water-based layers, because of the low contrast in the light elements. In contrast, neutron reflectometry (NR) can offer unique structural information on such layers as contrast conditions can be controlled and detailed information on the layer structure can be obtained by using deuterated materials\textsuperscript{23–25}. In this study, we focused on PEG 12 mol polydimethylsiloxane co-polymer (PEG-12 dimethicone, as shown in Fig. 1), one type of polyether modified silicone (PEMS) polymer, as it can form lamellar liquid crystals and is widely used in cosmetics. Yan \textit{et al.} investigated the effects of glycerol on vesicle formation of PEG-polydimethylsiloxane-PEG tri-block co-polymer with transmission electron microscopy and pulse-field gradient nuclear magnetic resonance\textsuperscript{26}. Watanabe \textit{et al.} have improved the stability of PEG-12 dimethicone vesicles by complexing them with anionic surfactant micelles\textsuperscript{27}. To the best of our knowledge, there is no comprehensive report focusing on the effects of shear flow and water evaporation on the self-assembly on substrates as well as in bulk, though such information is essential to develop novel and functional cosmetics. Though we wanted to perform experiments with the evaporation of water, it was impossible due to the machine restrictions. Therefore, we prepared samples that imitate the drying process by changing water contents. In this paper, we discuss the self-assembled structures of PEG-12 dimethicone based on Rheo-SANS and NR results.

2 Experimental

2.1 Materials

Except for the neutron scattering/reflectivity experiments, deionized MilliQ water (>18.2 MΩ cm\textsuperscript{-1}) was used. PEG-12 dimethicone was provided by Dow Toray Co., Ltd. (Tokyo, Japan). According to the supplier, the lipophilic and hydrophilic balance (HLB) of PEG-12 dimethicone which was used in this study is about 8.0. Heavy water (D\textsubscript{2}O) employed in neutron experiments and 3-aminopropyltriethoxysilane were purchased from Fujifilm Wako Pure Chemical Corporation (Osaka, Japan). Dipropylene glycol (DPG) was purchased from Nacalai tesque, Inc. (Kyoto, Japan). One-side polished 3-inch Si wafer with a thickness of 8 mm was obtained from Matsuzaki Seisakusyo Co., Ltd. (Shimane, Japan).

2.2 Sample preparation

Adequate amounts of PEG-12 dimethicone were dispersed in water or water/DPG mixed solution at room temperature. Prepared samples are described in terms of mass ratios for H\textsubscript{2}O/DPG/PEG-12 dimethicone, where the use of D\textsubscript{2}O (neutron experiments) was recalculated in terms of the corresponding H\textsubscript{2}O samples, i.e. they then possess an identical molecular composition.

2.3 Rheo-SANS

SANS experiments were carried out using a TAIKAN instrument installed on the BL15 beamline at Materials and Life Science Experimental Facility (MLF), J-PARC (Tokai, Japan)\textsuperscript{28–30}. Using large-area detector banks (small, middle, high, backward) and white neutron beams in the wavelength (λ) range of 0.07 – 0.78 nm together with the time-of-flight (TOF) method, TAIKAN the instrument can simultaneously cover a Q-range of 0.05 – 170 nm\textsuperscript{-1}, where the magnitude of the scattering vector Q is defined as $Q = 4\pi \sin(\theta/2)/\lambda$ (θ representing the scattering angle). For the Rheo-SANS measurement, only the small-angle detector bank located at 5.65 m from the sample position was used, covering the Q-range of 0.05 – 15 nm\textsuperscript{-1}. Rheo-SANS was performed using a stress-controlled rheometer, Anton Paar MCR302 (Anton Paar, Graz, Austria). A double-cylindrical cell made of quartz glass with an inner-bob diameter of 48 mm and a gap of 1 mm was used as shown in Figs. 2a and 2b. The sample temperature was maintained at 30°C by flowing air heated by a temperature-controlled electric heater. Two scattering configurations were used: one is the so-called radial configuration where the neutron beam is directed through the center of the cell (along the velocity gradient direction), and the other is the tangential configu-
ration where the beam is directed through the end of the cell (along the flow direction) as shown in Fig. 2c. The optical path length is 2 mm, the slit size of the upstream is $23 \times 23$ mm$^2$, the sample beam size is 10 mm$\phi$ for the radial beam, whereas the optical path length is about 10 mm, the slit size of upstream is $8 \times 23$ mm$^2$, the sample beam size is $0.5 \times 10$ mm$^2$ for the tangential beam. Both radial and tangential measurements were performed on each of the same samples. For the radial observation, with a logarithmically increasing shear rate ($\dot{\gamma}$) that increased from $10^{-3}$ s$^{-1}$ to $10^{3}$ s$^{-1}$, both SANS and the corresponding viscosity were measured. The obtained TOF spectra were corrected for sample transmission, incident neutron intensity distribution, and detector efficiency according to the standard procedures for TAIKAN. Finally, we converted the scattering intensity to the absolute intensity with units of cm$^{-1}$ using a secondary standard of 1 mm thick glassy carbon.

SANS data fitting was carried out using NCNR software, which is a SANS data reduction and analysis software provided by national institute of standards and technology (NIST), for Igor Pro 7.

### 2.4 NR

The NR experiments were conducted using a SOFIA reflectometer installed on the BL16 beamline at MLF, J-PARC, (Tokai, Japan). Sample holders provided by the instrument for solid-liquid interface observation were used for the experiments. As a substrate, we used a Si wafer hydrophilized by oxygen plasma treatment and subsequently silanized with 3-aminopropyltriethoxysilane. First, the hydrophilized Si substrate was placed on a stainless plate. Secondly, an O-ring made of Viton rubber was sandwiched between the substrate and a tubing made of titanium with a space of $32 \times 52$ mm$^2$ and fixed with the stainless plate and screws to prevent solution leakage. Finally, sample solutions were injected through the aperture on the backside of the tubing, and the apertures were capped with sets of a screw and Viton O-ring. For the NR experiments, all the sample holders were kept 2 hours before measurements to complete PEG-12 dimethicone adsorption.

The interface between the substrate and solution of 30 mm$\times$50 mm was illuminated with pulsed neutrons with the wavelength $\lambda$, of 0.2 nm to 0.88 nm at the repetition rate of 25 Hz, in which the $\lambda$ of each neutron was evaluated from the velocity using the TOF method. The neutrons were introduced through the substrate by changing the incident angle, $\theta$, to be 0.2, 0.4, 0.8, and 1.6º, and the distribution of $\theta$ due to beam divergence was corrected by the reflection angle of neutrons under the assumption of the specular reflection condition. All the NR measurements were conducted around 25°C. The reflection intensity at each angle was normalized by the direct beam, and the reflectivity profile depending on the momentum transfer normal to the substrate, $Q = 4\pi\sin(\theta/2)/\lambda$, was obtained by taking the $\lambda$ and $\theta$ of each neutron into consideration. The reflectivity profiles were combined into one reflectivity profile to cover the $Q$ range from 0.05 nm$^{-1}$ to 1.5 nm$^{-1}$, and the merged data was analyzed by the least-squares fitting with the reflectivity based on Parratt’s recursive formula. NR data fitting was carried out using Motofit for Igor Pro.
3 Results and Discussion

3.1 Phase behavior

Figure 3 shows the ternary phase diagram of water/DPG/PEG-12 dimethicone system at 30°C expressed as a weight ratio. The phases shown are the aqueous micellar solution (Wm), normal hexagonal (H1), non-dispersed lamellar (La), and dispersed lamellar (vesicles, La') phases. Open red circles show the measurement samples for Rheo-SANS and NR. Dashed red arrow shows the dilution line.

3.2 Rheo-SANS experiments

Viscosities as a function of shear rate for four water/DPG/PEG-12 dimethicone systems were shown in Fig. 4. Basically, the higher the PEG-12 dimethicone concentration was, the higher the viscosity became, though the viscosities between the water/DPG/PEG-12 dimethicone 80/2/18 (black open diamond), 60/4/36 (green cross), 40/6/54 (blue open circle), and 20/8/72 (red open triangle) systems.

Figures 5–8 show the shear rate dependence of the sector-averaged SANS profiles for water/DPG/PEG-12 dimethicone systems at 30°C for various ratios of 80/2/18, 60/4/36, 40/6/54, and 20/8/72, respectively. In this system, PEG-12 dimethicone is considered to transformed from MLVs to a non-dispersed lamellar phase based on the phase diagram as shown in Fig. 3. The one-dimensional SANS profiles were obtained by sector averaging perpendicular and parallel to the flow direction at azimuthal angles of ±15°. For water/DPG/PEG-12 dimethicone = 80/2/18, the SANS pattern for the radial directions at 0.01 s⁻¹ (Figs. 5a and 5b) indicated the existence of spherical dispersions having multimamellar structures. Broad peak profiles were observed in the Q-range of Q ~ 0.3–0.7 nm⁻¹. However, the peak position was unclear. Therefore, we performed a model-fitting analysis. Table 1 shows the chemical formula, density, and the scattering length density (SLD) of each.
Fig. 5  Shear rate dependence of the sector-averaged SANS profiles for water/DPG/PEG-12 dimethicone = 80/2/18 system at 30°C for (a) flow, (b) radial neutral, (c) gradient, and (d) tangential neutral. Profiles are shifted by a factor of ×5 for the purpose of clarity.

Fig. 6  Shear rate dependence of the sector-averaged SANS profiles for water/DPG/PEG-12 dimethicone = 60/4/36 system at 30°C for (a) flow, (b) radial neutral, (c) gradient, and (d) tangential neutral. Profiles are shifted by a factor of ×10 for the purpose of clarity.
Fig. 7 Shear rate dependence of the sector-averaged SANS profiles for water/DPG/PEG-12 dimethicone = 40/6/54 system at 30°C for (a) flow, (b) radial neutral, (c) gradient, and (d) tangential neutral. Profiles are shifted by a factor of ×30 for the purpose of clarity.

Fig. 8 Shear rate dependence of the sector-averaged SANS profiles for water/DPG/PEG-12 dimethicone = 20/8/72 system at 30°C for (a) flow, (b) radial neutral, (c) gradient, and (d) tangential neutral. Profiles are shifted by a factor of (a) ×30, (b) ×30, (c) ×300, (d) ×300 for the purpose of clarity.
material which was used. Though the precise chemical formula of PEG-12 dimethicone has not been disclosed, we estimated its formula and calculated its SLD value. As shown in Table 2, the volume fraction of PEG-12 dimethicone is 0.175. Then we divided the PEG-12 dimethicone into PEG-12 and dimethicone parts and estimated the volume of each fraction to be 0.078 and 0.097, respectively. Since the SANS result is on an absolute scale, the scale corresponds to the volume fraction of the lamellar components. Then, the scale value, and the SLD of the layer formed by the dimethicone were fixed to be 0.097, 0.063, respectively, as shown in Table 3. Figure 9 shows the SANS profiles of the experimental data and the fitting curve. Based on the obtained fitting parameters, the MLV model was depicted in Fig. 10. A deviation of the fitting curve from the experimental curve around \( q = 2 \text{ nm}^{-1} \) was observed. We attributed it to simplifying the model. We considered the scattering length density in the membrane as constant, however, there should be a deviation from the average value. Furthermore, the thickness of the membrane should have certain deviation. Nonetheless, we think it does not affect the fitting results so much. According to the SANS fitting, the \( d \) spacing was suggested to be 12.8 nm. SANS patterns seemed to be almost constant regardless of the shear rate. To quantitatively evaluate the degree of orientation of the bi-layers, we estimated an alignment

| Material             | Chemical formula | Density \( \text{g/cm}^3 \) | SLD \( \times 10^{-4}/\text{nm}^2 \) |
|----------------------|------------------|-----------------------------|-----------------------------------|
| Heavy water          | \( \text{D}_2\text{O} \) | 1.107                       | 6.36                              |
| DPG                  | \( \text{C}_6\text{H}_{14}\text{O}_3 \) | 1.022                       | 0.226                             |
| PEG-12 dimethicone   | -                | 1.034                       | 0.269                             |
| PEG-12 dimethicone   | \( \text{C}_{34}\text{H}_{49}\text{O}_{13} \) | 1.130                       | 0.645                             |
| dimethicone          | \( \text{C}_2\text{H}_6\text{OSi} \) | 0.965                       | 0.063                             |
| 1-propyl amine       | \( \text{C}_3\text{H}_7\text{N} \) | 0.719                       | –0.320                            |

Table 1: Chemical formula, density, and scattering length density (SLD) values of each material.

| Volume fraction and SLD values of the mixture and the solvent for the water/DPG/PEG-12 dimethicone = 80/2/18 system. |
|---------------------------------------------------------------|
| \begin{tabular}{|c|c|c|c|c|c|} 
| Weight / g & 88 & 2 & 18 & 88 & 2 \\
| Volume / \( \text{cm}^3 \) & 80.0 & 1.96 & 17.4 & 80.0 & 1.96 \\
| Volume fraction & 0.805 & 0.0197 & 0.175 & 0.976 & 0.0234 \\
| \( \text{SLD}_o \) / \( \times 10^{-4}/\text{nm}^2 \) & 6.21 & 5.17 \\
| \( \text{SLD}_m \) / \( \times 10^{-4}/\text{nm}^2 \) & \\
| \end{tabular} |

Table 2: Volume fraction and SLD values of the mixture and the solvent for the water/DPG/PEG-12 dimethicone = 80/2/18 system.

| SANS fitting parameters for the water/DPG/PEG-12 dimethicone = 80/2/18 system for NCNR in Igor Pro 7. Values without standard errors are fixed ones. Values with standard errors are obtained ones by fitting. |
|---------------------------------------------------------------|
| \begin{tabular}{|c|c|c|c|c|c|} 
| Scale & 0.097 \\
| Lamellar thickness & 5.6 ± 1.1 \\
| Number of layers & 80 ± 13 \\
| Layer spacing / nm & 12.8 ± 0.5 \\
| polydispersity of spacing & 0.42 ± 0.04 \\
| SLD of layer / \( \times 10^{-4}/\text{nm}^2 \) & 0.063 \\
| SLD of solvent / \( \times 10^{-4}/\text{nm}^2 \) & 2.4 ± 0.1 \\
| Incoherent Background & 0.0003 \\
| \end{tabular} |

Table 3: SANS fitting parameters for the water/DPG/PEG-12 dimethicone = 80/2/18 system for NCNR in Igor Pro 7. Values without standard errors are fixed ones. Values with standard errors are obtained ones by fitting.

Fig. 9: SANS profiles of experimental data (open circle) and fitting curve (solid line) for water/DPG/PEG-12 dimethicone = 80/2/18 system at 30°C.
factor \( \langle A_f \rangle \) given by the following equation \(^{41} \):

\[
A_f = \frac{\int_{Q_{\min}}^{Q_{\max}} I_{\text{gradient,flow}}(Q) dq - \int_{Q_{\min}}^{Q_{\max}} I_{\text{neutral}}(Q) dq}{\int_{Q_{\min}}^{Q_{\max}} I_{\text{gradient,flow}}(Q) dq}
\]

where \( I_{\text{gradient,flow}}(Q) \) and \( I_{\text{neutral}}(Q) \) are the SANS intensities of the gradient (or flow) and tangential neutral (or radial neutral), respectively. Using \( Q_{\min} = 0.2 \text{ nm}^{-1} \) and \( Q_{\max} = 2.0 \text{ nm}^{-1} \), \( A_f \) values were estimated. Figures 11a – 11d show the evaluated \( A_f \) values of all the systems. All the values were close to zero \( (A_f = 0) \), indicating that MLVs of this system were always roughly distributed at random, regardless of the shear rate. However, when we have a close look at the values, those for both the flow and tangential were
seemed to slightly approach zero with an increase in shear rate, indicating a rearrangement and more random distribution of MLVs in a sample solution.

For the water/DPG/PEG-12 dimethicone = 60/4/36 system, PEG-12 dimethicone is considered to form MLVs from the phase diagram as shown in Fig. 3. SANS patterns were almost constant regardless of shear rate as shown in Fig. 6. Peak positions were around $Q = 0.551 \text{nm}^{-1}$. Since the interplanar distance, $d$, given by $d = 2\pi/Q$, the $d$ spacing can be calculated as 11.4 nm. Figure 11b shows evaluated $A_1$ values of this system. All values were approximately zero independent of the shear rate, but the $A_1$ values for flow direction continuously decreased and became negative ($A_1 = 0.014 \rightarrow -0.027$) with an increasing shear rate. In contrast, those for the gradient were almost constant and negative. This indicated that neutral is the most favorable orientation against the shear flow for this system at least within the measurement shear rate range. If the globular MLVs are the only structure in the solution, there should be no favorable orientation. Therefore, this result indicated that a sliced plate-like lamellar structure co-existed in the system. As shown in Fig. 4, an exponential decrease in viscosity from $2.66 \times 10^4 (\gamma = 10^{-2} \text{s}^{-1})$ to $1.18 \times 10^2 (\gamma = 10^2 \text{s}^{-1}) \text{mPa} \cdot \text{s}$ resulting from the shear thinning was observed.

In the system of water/DPG/PEG-12 dimethicone = 40/65/34, PEG-12 dimethicone is considered to form MLVs from the phase diagram as shown in Fig. 3. However, as above mentioned, sliced plate-like lamellar structures, as well as globular MLVs, are thought to exist in this system since the system is located on the border with a non-dispersed lamellar phase, as shown in Fig. 3. Although peak positions were constant ($Q = 0.641 \text{nm}^{-1}, d$ spacing = 9.80 nm) as shown in Fig. 7, the shear rate dependence of SANS patterns was clearly observed. The peak intensities for flow especially became less pronounced with an increased shear rate (Fig. 7a). The evaluated $A_1$ values (Fig. 11c) were no longer close to zero, indicating that dispersed plate-like lamellar structures were dominant compared to MLVs in this system and their orientations depend on the shear rate. The $A_1$ values for the flow continuously decreased and became negative from 0.239 to $-1.208$ with an increased shear rate, while those for the gradient have a local minimum ($A_1 = -0.399$). This indicated that neutral is the most favorable orientation against the shear flow for this system, at least within the measurement shear rate range. However, since the $A_1$ values for the gradient have a local minimum, a transition of the orientation from neutral to gradient might occur at a higher shear rate ($\gamma > 10^3 \text{s}^{-1}$). As shown in Fig. 4, an exponential decrease in viscosity from $1.22 \times 10^3 (\gamma = 10^{-3} \text{s}^{-1})$ to $1.73 \times 10^2 (\gamma = 10^2 \text{s}^{-1}) \text{mPa} \cdot \text{s}$ due to the shear thinning was observed.

For the water/DPG/PEG-12 dimethicone = 20/8/72 system, PEG-12 dimethicone is considered to form non-dispersed plate-like lamellar structures from the phase diagram as shown in Fig. 3. SANS patterns were greatly affected by shear rate, though peak positions were constant ($Q = 0.783 \text{nm}^{-1}, d$ spacing = 8.02 nm) as shown in Fig. 8. The peak intensities for flow especially became less pronounced with an increase in shear rate (Fig. 8a). The evaluated $A_1$ values (Fig. 11d) were drastically changed by shear rate. Those for both flow and gradient continuously decreased and became negative ($A_1 = 0.369 \rightarrow -10.797$ for flow and $A_1 = 0.884 \rightarrow -2.030$ for gradient, respectively) with an increased shear rate. This indicated that neutral is the most favorable orientation against the shear flow for this system at least within the measured shear rate range. The reason why the $A_1$ values were positive at first (at a low shear rate) is that the vertical shear stress works when the inner cell moves down to a predetermined position on the rheometer. We waited for 30 minutes for a cancellation of orientations after setting the rheometer. However, orientations might not be fully cancelled. As shown in Fig. 4, an exponential decrease in viscosity from $1.35 \times 10^3 (\gamma = 10^{-3} \text{s}^{-1})$ to $2.11 \times 10^2 (\gamma = 10^3 \text{s}^{-1}) \text{mPa} \cdot \text{s}$ due to the shear thinning was observed.

According to Roux et al., lamellar structures were more or less oriented parallel to the velocity gradient (gradient) at a very low shear rate. An isotropic state composed of MLVs was observed at an intermediate shear rate by breaking the membranes into pieces due to the flow, with lamellar structures fully oriented parallel to the velocity gradient at a high shear rate$^{10,12}$. However, such an isotropic state at an intermediate shear rate was not observed in our system. In other words, no lamellar-to-onion transition could be seen. More surprisingly, the neutral orientation was the most favorable in our system, which differed from Roux’s report. Roux et al. also stated that no vesicle transition was observed in some binary systems, probably because of an insufficient bending flexibility of the membranes$^{4,47}$. However, polydimethylsiloxane is generally much more flexible than hydrocarbon chains. We assumed that the transition of orientations from flow (or gradient) to neutral occurs so quickly that no vesicle transition can be observed in the PEG-12 dimethicone system. However, future work is needed to explain why a neutral orientation is more favorable than a gradient orientation.

3.3 NR experiments

NR experiments were done to understand the static adsorption of PEG-12 dimethicone on a hydrophilized solid silicon substrate. Figure 12a shows the neutron reflectometry data of $D_2O/DPG/PEG-12$ dimethicone solutions at an ambient temperature (approximately 25°C). We confirmed that there is no clear difference in the phase behaviour between 25 and 30°C. With the increase in PEG-12 dimethicone concentration, the Bragg peaks of the lamellae became more pronounced, indicating that the amount of
deposited material on the hydrophilized Si-wafer and its degree of ordering were becoming higher. At the same time, the peak position shifted to a higher q. In order to compare the d spacing between the SANS and NR curves, we fitted the NR data of water/DPG/PEG-12 dimethicone = 80/2/18 system using Motofit for Igor Pro 7. NR fitting analysis was also done with more concentrated systems. However, probably due to unevenness or roughness, we could not obtain satisfactory results (data not shown). According to McDermott et al., PEG-6 monododecyl ether molecules adsorb onto Si/SiO2 substrate as a bilayer, its hydrophilic PEG moiety facing the substrate. Thus, we assumed that the PEG moiety, the hydrophilic group of PEG-12 dimethicone, is also facing the substrate. Figure 12b shows the fitting result with the two-layer model, in which we assumed that a propyl amine layer was on the Si substrate and PEG-12 dimethicone layer was on top of that. In the fitting, the SLDs of the Si substrate and solution were fixed to be the value calculated with the bulk density and composition of the mixture (see Tables 1, 2, and 4 for detail). As this simple model with minimal layers could adequately reproduce the main features of the NR profile, we adopted it without any further modification to make the further discussion as simple as possible.

Figure 12c shows the SLD profile obtained with the fitting parameters shown in Table 4. From the obtained SLD values, we can evaluate the amount of water in each layer. As the SLD value of the propyl amine layer was identical to that of the bulk, the D2O/DPG mixture was found to hardly exist in the propyl amine layer. On the other hand, the SLD value of the PEG-12 dimethicone layer was slightly different from that of the bulk one. The volume fractions of PEG-12 dimethicone and D2O/DPG were calculated to be 0.379 ± 0.05, and 0.621 ± 0.05, respectively, under the assumption that DPG is homogenously mixed with D2O and that they localize evenly in the PEG-12 dimethicone layer. This indicates that a large amount of solvent distributes in the layer and that PEG-12 dimethicone does not fully cover the surface as shown in Fig. 13. McDermott et al. also reported that the coverage of polyoxyethylene 6 mol lauryl ether on the Si/SiO2 surface was only about 60%48. The thickness of this layer turned out to be 13.8 nm from the fitting, which was close to the d spacing in the SANS experiment. This indicates that the structural dimensions of the self-assembled structures of PEG-12 dimethicone molecules are quite similar in bulk and on a Si wafer. Interestingly, the number of layers of MLVs was 80 as shown in Table 3. However, there was a single bi-layer on the hydrophilized Si wafer surface.

4 Conclusion
In this study, the impact of shear stress, water contents,
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Table 4  NR fitting parameters for the water/DPG/PEG-12 dimethicone = 80/2/18 system for Motofit in Igor Pro 7. Values without standard errors are fixed ones. Values with standard errors are obtained ones by fitting.

| layer       | thickness / nm | SLD /10^{-4}nm^{-2} | solvent | roughness |
|-------------|----------------|----------------------|---------|-----------|
| fronting    | Infinite       | 2.07                 | -       | -         |
| 1           | 4.1 ± 0.2      | -0.2 ± 0.1           | 0       | 14 ± 1    |
| 2           | 13.8 ± 0.1     | 3.96 ± 0.03          | 0       | 1 ± 3     |
| backing     | Infinite       | 5.22                 | -       | 19.9 ± 0.7|

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