Abstract: α-Sulfonated fatty acid methyl ester salts (MES), which were made from vegetable sources, are attractive candidates for eco-friendly washing detergents because they have various special features like excellent detergency, favorable biodegradability, and high stability against enzymes. To overcome some disadvantages of powder-type detergents like caking, sorting, and dusting, we studied how temperature and humidity history, as a model for long-term storage conditions, can affect crystalline structures and reduce the brittleness of MES powder. We characterized the crystalline structure of MES grains using small-angle X-ray scattering, wide-angle X-ray scattering, differential scanning calorimetry, and Fourier transform infrared spectroscopy measurements and determined the yield values, which measure the brittleness of MES grains, in shear stress using dynamic viscoelasticity measurements. This study confirmed that MES crystals form three pseudo-polymorphs via thermal or humidity conditioning: metastable crystals (α subcell), anhydrous crystals (β subcell), and dihydrate crystals (β' subcell). Further, we found that the yield value increases upon phase transition from the β subcell to the β' subcell and from the β' subcell to the α subcell. Therefore, controlling the thermal and humidity conditioning of MES grains is an effective way to decrease the brittleness of MES powders and can be used to overcome the above mentioned disadvantages of powder-type detergents in the absence of co-surfactants.

Key words: α-sulfonated fatty acid methyl ester salts, crystal, subcell structure, pseudo-polymorph, brittleness, yield value

1 INTRODUCTION

α-Sulfonated fatty acid methyl ester salts (MES), which are made from vegetable sources, such as palm oils, are considered attractive candidates for sustainable surfactants, and their various physicochemical properties have been studied. Fujiwara et al. constructed a concentration-temperature phase diagram in a water-MES system and revealed aggregation states. Investigating low-concentration regions, they carried out thermodynamic analysis of micelle formation, solubilization of oleic acids as a model of sebum, and stability in hard water. In the case of oleic acids, they showed that the solubilization ability of the MES was 1.6–1.9 times higher than that of linear alkylbenzene sulfonate sodium salts (LAS), a common anionic surfactant. By using static and dynamic light scattering they revealed that the number of MES micelles was slightly lower than that of LAS micelles, whereas the solubilization ability of MES micelles was approximately 2.4 times higher than that of LAS micelles, owing to easier coalescence of MES micelles than LAS micelles. Regarding stability in hard water, it has been shown that MES performs better than LAS and alkyl sulfonate sodium salts (AS), which precipitate in hard water as divalent metallic salts. In addition, MES have other special features like excellent detergency, favorable biodegradability, and high stability against enzymes, and therefore, MES have been used as eco-friendly washing detergents.

There are two main types of washing detergents, powder and liquid, where the solid state of surfactants in powder detergents is primarily crystalline. The surfactant crystals are categorized into three types of repeating structural elements, monolayer, bilayer, and interdigitated structures.
The bilayer structure, which is lamellar with alternating head-to-head or tail-to-tail arrangement, is most commonly found in surfactant crystals. A few surfactants have the monolayer and the interdigitated structure, in which the head of one molecule is adjacent to the tail of the next one within the structural layer of the crystal. In addition, some surfactants have pseudo-polymorphs which are transformed hydrated states affected by temperature and humidity conditioning. For example, sodium dodecyl sulfate, which has a bilayer structure, forms 1/8 hydrate and hemi-hydrate crystals. In the case of MES, Abe et al. have revealed by analysis of single-crystal X-ray diffraction that MES crystals have an interdigitated structure, and MES form some hydrate crystals.

For powder detergents, investigating the mechanical characteristics is important. Crystal grains in powder detergents, for example, can be reduced in size due to impact during transportation if crystal brittleness is high. This affects the performance of powder detergents in terms of solubility, dissolution speed, caking, and dusting. On the other hand, crystals with low brittleness are disadvantageous during manufacturing processes because enormous amounts of energy are required to convert them. However, the mechanical characteristics of powder detergents are known only empirically, and the effect of the crystalline structure of surfactants on the mechanical characteristics is not clear. In this paper, we report the effect of the crystalline structures of MES, induced by temperature and humidity history, on the mechanical characteristics of MES grains.

There are several parameters for evaluating mechanical characteristics, for instance, yield value, tensile strength, bending strength, abrasion resistance, indentation hardness, and thermal tolerance. We used the yield value to evaluate brittleness of MES crystals in this study. We also performed X-ray scattering, differential scanning calorimetry (DSC), and Fourier transform infrared spectroscopy (FT-IR) experiments. In addition, we performed thermal treatment for MES as a model of long-term storage.

### Table 1  Sample preparation conditions and moisture contents of samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>The moisture contents of samples / wt%</th>
<th>Preparation conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>3.5</td>
<td>The number of cooling process from 80°C to 20°C / times 1</td>
</tr>
<tr>
<td>B</td>
<td>3.5</td>
<td>The number of temperature history / times 5</td>
</tr>
<tr>
<td>C</td>
<td>0.2</td>
<td>0</td>
</tr>
<tr>
<td>D</td>
<td>3.5</td>
<td>0</td>
</tr>
<tr>
<td>E</td>
<td>6.1</td>
<td>0</td>
</tr>
<tr>
<td>F</td>
<td>8.8</td>
<td>0</td>
</tr>
</tbody>
</table>
2.2 Methods

2.2.1 Differential scanning calorimetry (DSC) measurements

Approximately 10 mg of sample was sealed in silver cells. DSC measurements were carried out using an EXSTAR 6000 differential scanning calorimeter (Seiko Instruments Inc., Ltd.) with the temperature increasing at a rate of 2°C/min from −20 to 140°C.

2.2.2 Small- and wide-angle X-ray scattering (SAXS and WAXS) measurements

Observation of liquid crystal states was carried out using a SAXSess (Anton Paar Co., Ltd.). A sample was enclosed in a vacuum-tight thin quartz capillary and measured at 80°C with Cu-Kα (wavelength = 0.154 nm) radiation for 1 min. Observation of solid crystal states was carried out using an X’Pert-ProMPD (PANalytical Co., Ltd.). A few milligrams of sample was enclosed in an X-ray-transmitting film and measured at 20°C with Cu-Kα (wavelength = 0.154 nm) radiation using the transmission method.

2.2.3 Fourier transform infrared spectroscopy (FT-IR) measurements

FT-IR measurements were carried out using a Spectrum 400 (Perkin Elmer Co., Ltd.) using the attenuated total reflection method with ZnSe crystal at 20°C.

2.2.4 Elasticity measurements

Elasticity measurements were carried out using a Rheo Stress 6000 (Thermo Scientific Co., Ltd.). After stirring at 80°C for 2 h, the sample pastes were tucked between two serrated parallel plates (diameter = 20 mm, normal force = 0.1 N), and the temperature history was recorded with the temperature cycling five times from 40 to 50°C at 0.2°C/min. Then, the samples were measured in constant frequency mode (frequency = 1.0 Hz) at 20°C.

Additional elasticity measurements were performed on pelletized samples. Pellets were prepared by pressing approximately 10 mg of sample grains, with diameters ranging from 150 to 250 μm, using a Masada Jack (Masada Seisakusho Co., Ltd.) at 2000 N. Pellet elasticity was again measured in constant frequency mode (frequency = 1.0 Hz) at 20°C.

3 RESULTS AND DISCUSSION

3.1 Effect of temperature history on yield value of MES crystals

There are various methods to manufacture raw materials for surfactants. High-active-ingredient solids like MES can be manufactured using the following methods: evaporating water at high temperatures, condensing to a predefined concentration, and solidifying by cooling. Sample A was a model of the state after manufacturing, and sample B was a model of the state after storing.

Figure 1 shows the elasticity-shear stress plots for samples A and B. The elasticity of sample A was constant up to approximately $6 \times 10^5$ Pa, which is called a yield value, after which the elasticity reduced drastically. The yield value of sample B was approximately $1.5 \times 10^5$ Pa, which is lower than that of sample A, indicating that sample B was more brittle than sample A. Furthermore, the elasticity of sample A below the yield value was higher than that of sample B.

Figure 2 shows the DSC results of samples A and B. Sample A gave a single endothermic peak at 47.4°C, whereas sample B gave a weaker endothermic peak at 46.3°C and broad endothermic peaks at higher temperatures. It is known that temperature history has an influence on fat crystalline structures. Akita et al. reported that triacylglycerol, for example, had approximately three crystal polymorphs, and these crystal polymorphs were transformed rapidly by thermal treatment around the phase transition temperature owing to melt-mediated crystallization. In this study, sample B was prepared by using a process that included thermal treatment near the phase transition temperature, suggesting transformation of crystalline structures for sample B.
3.2 Effect of temperature history on crystalline structures of MES

Figure 3 shows the SAXS and WAXS patterns of sample A at 80°C. Sample A at 80°C shows three sharp peaks, 2θ = 2.79°, 5.88°, and 8.38°, in the SAXS region, which indicated a lamellar structure with 3.17 nm of long spacing. Furthermore, there was a broad peak at approximately 2θ = 19° in the WAXS region, which indicated chain melting. Fujiiwara et al. revealed that C16MES, which has 3.5 wt% moisture content, formed lamellar liquid crystals at 80°C. Additionally, sample A at 80°C showed flow ability and birefringence. Hence, sample A at 80°C was a lamellar liquid crystal.

Figure 4 shows the SAXS and WAXS patterns of samples A and B at 20°C. The SAXS peak is the second peak of the lamellar structure. Sample A at 20°C shows a peak at 2θ = 6.10° in the SAXS region and a peak at 2θ = 21.2° in the WAXS region. This means that the length of the long spacing of sample A at 20°C was 2.90 nm and that of the short spacing was 0.419 nm, indicating the α-type crystalline subcell structure, which has a hexagonal lattice. On the other hand, sample B exhibits a number of small peaks in the SAXS and WAXS regions. It is known that lattice spacing of triacylglycerol is affected by temperature history, and the crystalline states before transformation are called metastable crystals. Therefore, the temperature history changed the crystalline structure of MES, and sample A was composed of metastable crystals. We will discuss the detailed structure of sample B in the next section.

3.3 Effect of humidity history on crystalline structures of MES

We prepared samples C, D, E, and F by leaving the MES with 0.2 wt% moisture content in an atmosphere with 80% relative humidity at 30°C. The moisture content of MES during the above process is shown in Fig. 5. The moisture content increased rapidly with time at the beginning of the process and became constant at 8.8 wt% after approximately 1000 min, which corresponds to two hydrated water molecules per MES molecule. Therefore, samples C and F were composed of anhydrous crystals and dihydrate crystals, respectively.

Figure 6 shows the DSC thermograms of samples C, D, E, and F. Sample C shows a wide endothermic peak at approximately 90°C. With an increase in moisture content, the endothermic enthalpy change was reduced and the endothermic peak was shifted to a lower temperature. Simultaneously, a new endothermic peak at approximately 55°C appeared and evolved with an increase in moisture content. Finally, sample F exhibits an endothermic peak at approximately 55°C. The endothermic enthalpy changes of samples C and F were 19.2 and 54.6 mJ/mol, respectively. The endothermic enthalpy change of sample C was higher than that of sample F owing to hydrogen bonds. DSC analysis for C16MES has been reported previously. The moisture content of anhydrous crystals of C16MES was 0.2 wt%, and the phase transition temperature and endothermic enthalpy change were 112°C and 22.1 mJ/mol, respectively.
Effects of temperature and humidity history on brittleness of MES

**Figure 6** DSC thermograms of samples C, D, E, and F.

The moisture content of the dihydrate crystals of C16MES was 8.6 wt%, and the phase transition temperature and endothermic enthalpy change were 73°C and 67.5 mJ/mol, respectively. The phase transition temperatures and endothermic enthalpy changes of samples C and F were lower than those of the anhydrous and dihydrate crystals of C16MES, which indicated formation of a eutectic mixture in the present C16/C18MES system.

**Figure 7** shows the SAXS and WAXS patterns of samples C, D, E, and F at 20°C. A SAXS peak for 1.39 nm was observed in the SAXS pattern of sample C. Since this SAXS peak indicated the second peak of a lamellar structure, the long spacing of the lamellar structure is estimated to be 2.78 nm. Moreover, there were three peaks for short spacings of 0.471, 0.418, and 0.409 nm in the WAXS region. The intensity of the SAXS peak of sample C decreased, and a new peak at approximately 2θ = 5.7° was evolved with an increase in moisture content, corresponding to a long spacing of 3.10 nm in sample F. In the WAXS region, with an increase in moisture content, the intensity of the peaks at approximately 2θ = 18.8° and 21.7° decreased. Furthermore, a new peak at approximately 2θ = 23.3° was evolved, and the peak at approximately 2θ = 21.3° was shifted to a lower angle and evolved. There were two peaks for short spacings of 0.420 and 0.381 nm in sample F. Therefore, samples C and F had different crystal structures, and samples D and E were mixtures of them. The long spacings of samples C and F were slightly longer than those of the anhydrous and dihydrate crystals of C16MES because of the formation of a eutectic mixture.

**Figure 8** shows the FT-IR spectra of samples A, C, and F at 20°C. Samples A and C had a single peak at 1468 cm⁻¹, and sample F had two peaks at 1472 and 1464 cm⁻¹. It is known that differences in subcell structure affect FT-IR spectra, especially the CH₂ scissoring band. In general, hexagonal (H, or α) subcells and triclinic parallel (T, or β1) subcells have a peak at approximately 1468 and 1470 cm⁻¹, respectively, and orthorhombic perpendicular (O, or β2) subcells have peaks at approximately 1473 and 1462 cm⁻¹. Therefore, sample F was confirmed as a β₂ subcell. As shown in Fig. 4 and Fig. 7, sample A exhibits a single WAXS peak and sample C shows two WAXS peaks. By using information from both the FT-IR spectra and WAXS patterns, we can conclude that sample A had an α subcell and sample C had a β subcell, as shown in Fig. 9.

**Figure 10** shows the elasticity-stress plots for samples A, C, and F. Measurements were performed on pelletized powder samples because, as demonstrated, crystalline structures can be changed by temperature history. The yield values of samples A, C, and F were approximately 3.5 × 10⁴, 1.2 × 10⁴, and 2.5 × 10⁴ Pa, respectively, which indi-
cated that samples C and F were more brittle than sample A. From calculations of endothermic peak areas of each crystal of sample B in Fig. 2, it was found that sample B consisted of approximately 40 wt% metastable crystals, 35 wt% anhydrous crystals, 15 wt% dihydrate crystals, and 10 wt% amorphous states. Hence, the yield value of sample B was lower than that of sample A because of the mixing of more brittle crystals.

4 CONCLUSION

We investigated the effect of the crystalline structure of MES, induced by temperature and humidity history, on the brittleness of grains. Upon thermal treatment around the phase transition temperature, the yield value of MES decreased. Simultaneously, the crystalline structure of MES was transformed from metastable crystal (α subcell) to a mixture of anhydrous crystals (β subcell) and dihydrate crystals (β subcell) owing to melt-mediated crystallization. Because the brittleness of MES crystals increased on going from an α to a β to a β subcell, we found that the decrease in the yield value of MES was caused by transformation into more brittle crystals. Our findings suggest that it is important to understand the crystalline structures for the development of powder detergents. In particular, controlling the thermal and humidity conditioning of surfactant crystals is an effective way to manage the brittleness of surfactant grains, and might be used to overcome some disadvantages of powder-type detergents like caking, sorting, and dusting in the absence of co-surfactants.

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