Characteristics of the Treated Ground Calcium Carbonate Powder with Stearic Acid Using the Dry Process Coating System

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This study examined the surface properties, fluidity, flowability and floodability of untreated ground calcium carbonate (GCC) powder and treated GCC powder with stearic acid (SA) using a dry process coating system. The surface of GCC powder is generally hydrophilic, but was changed to a hydrophobic surface when coated with SA. The contact angle of water on the coated GCC powder surface increased with increasing concentration of SA. The contact angle and hydrophobicity on the GCC powder treated with 1.0 mass% SA was 105° and 100%, respectively.

The dispersive component of the surface free energy, \(\gamma^D\), of the untreated GCC powder determined using inverse gas chromatography (IGC) was 103 mJ/m² at 100°C. However, that of the GCC powder treated with 1.0 mass% SA was 34.8 mJ/m². Kawakita’s equations were used to characterize the properties of the powder. The fluidity index was increased from 18.60 to 30.39 when the surface of GCC powder was modified with SA. On the other hand, the characterization based on the method suggested by Carr showed that the flowability and the floodability of the GCC powder treated with SA increased from 45 to 53 and from 30 to 69, respectively. Therefore, the flowability and floodability of the GCC powder treated with SA were superior to the untreated GCC powder. [doi:10.2320/matertrans.MRP2008351]

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1. Introduction

Ground calcium carbonate (GCC) is the most widely used filler in the plastics, rubber, paper, paint and ink industry.1) It is usually obtained by grinding natural white calcite (CaCO₃).

GCC powder is quite inexpensive and has superior whiteness, inertness and incombustibility as well as low oil-adsorbency and water adsorption compared with other inorganic powders.2,3) Accordingly, GCC powder is used widely in polymer composites to improve the physical properties, and allow various functionalities and improved workability. At the same time, the cost of the polymer composites can be decreased greatly by replacing the volume of expensive resin with a cheap GCC filler.4)

Smaller particles are needed to maximize effect of the filler in a polymer. However, the surface energy of the particles increases with decreasing particle size. In addition, the dispersibility of the filler failed due to the agglomeration of particles with high surface energy. Therefore, it is often necessary to treat the filler with surface-modifying agents to improve the dispersibility, water resistance, mechanical properties and reinforcement in a plastics system.5)

Fatty acid, surfactant, resin etc. are often used as surface modifying agents for calcium carbonate. An examination of the powder properties of a surface-modified filler is a very important factor in their effective use. Therefore, this study compared the surface properties, such as contact angle, hydrophobicity and dispersive component, as well as the physical properties, such as fluidity, adhesion, flowability and floodability of untreated and stearic acid (SA)-treated GCC powder.

2. Experimental

2.1 Materials

GCC powder was obtained by crushing and grinding natural calcite as shown in Fig. 1. Jaw and cone crushers were used for crushing and UD pulverizer (Braun Direct Driven Pulverizer, BICO, USA) was used for grinding of the first step. Finally, the GCC powder was subjected to grinding by jet mill (Fluidised-bed opposed jet mill,
Model 100 AFG, Alpine, Germany). Table 1 shows the chemical composition and physical properties of the untreated and SA-treated GCC powder. X-ray fluorescence spectrometry (XRF, MXF-2001, Shimatzu, Japan) was used for chemical composition analysis and particle analyzer (Model Master Sizer, Malvern, England) was used to measure particle size of the GCC powder. The CaO content in the powder was 54.6 mass%. The mean and maximum particle size of untreated GCC powder were 5.24 μm and 30.20 μm, respectively. On the other hand, the mean and maximum particle size of SA-treated GCC powder were 5.20 μm and 26.30 μm, respectively. The specific surface area of untreated and SA-treated GCC powder were 2.18 m²/g and 2.20 m²/g, respectively. Figure 2 shows the scanning electron microscope (SEM) photographs of the untreated and SA-treated GCC powder. Stearic acid (CH₃(CH₂)₁₆COOH) was used as the surface modifying agent, and distilled water was used to measure the contact angle. A homologous series of n-alkanes, hexane (C₆H₁₄), heptane (C₇H₁₆), octane (C₈H₁₈), nonane (C₉H₂₀) and decane (C₁₀H₂₂), were used as the non-polar probes for the IGC experiment.

### 2.2 Adsorption experiment

Molten SA was adsorbed onto the surface of GCC powder using the dry process coating system of a direct melting spray method. Figure 3 shows a schematic diagram of the dry process coating system.

In this system, the temperatures of the melting, transfer and spray parts of SA was maintained at 100 ± 10°C to allow melting and spraying. The amount of SA used in the adsorption experiment was 0.5, 1.0, 1.5 and 2.0 mass% of the GCC powder. The rotational frequency of the stud-mill for the adsorption of SA was 4,000 rpm. The stud-mill improves contact frequency and power between GCC powder and molten SA by strong turbulent flow induced from pins’ rotatory power in the mill. However, grinding effect of stud-mill was almost nothing in the adsorption experimental process because the particle size of the GCC powder used in this study was very small, as shown in Table 1 and Fig. 2.

This dry process coating system is a continuous system. Accordingly, the time for adsorption was insufficient because a stay time of GCC powder in the spray chamber and stud-mill for the adsorption of SA was short. In order to complement the above defect and achieve sufficient adsorption of SA, the treated GCC powder was subjected to stabilization for approximately 72 h.

### 2.3 Evaluation of powder properties

#### 2.3.1 Contact angle measurements and hydrophobicity experiment

The surface energies were readily evaluated on flat surfaces using classical liquid contact angle measurements. The determinations were also performed on powders compressed into discs. Moreover, for solids with high surface energy, it is preferable to used the two liquid technique. However, the exact determination of the surface energy using this method is difficult to apply to agglomerated or compressed GCC disc due to surface hysteresis. Hence, the contact angles only was used to illustrate roughly the significant changes in surface properties of GCC powder.

<table>
<thead>
<tr>
<th>Chemical composition (mass%)</th>
<th>CaO</th>
<th>MgO</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>K₂O</th>
<th>Na₂O</th>
<th>TiO₂</th>
<th>P₂O₅</th>
<th>Ig.loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated GCC</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Untreated GCC</td>
<td>54.61</td>
<td>0.40</td>
<td>0.38</td>
<td>0.12</td>
<td>0.05</td>
<td>0.07</td>
<td>0.38</td>
<td>0.02</td>
<td>0.01</td>
<td>43.32</td>
</tr>
<tr>
<td>Treated GCC with 1.0 mass% SA</td>
<td></td>
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</tr>
</tbody>
</table>

![auntreated GCC powder](auntreated-GCC.png)

![treated GCC powder with stearic acid of 1.0 mass%](treated-GCC-SA.png)

**Fig. 2** Scanning electron microscope (SEM) photographs of the untreated (a) and SA-treated (b) ground calcium carbonate powder.
when coated with SA. In practice, the discs were prepared by compression under controlled conditions: 100 mg of coated GCC powder and a pressure $10^9$ Pa, in a typical IR die. The contact angle measurements were carried out using a goniometric telescope (G-1 Contact Anglemeter, ERMA Inc., Japan) within 10 seconds after placing a drop of liquid on GCC disc.

The hydrophobicity experiment was carried out as follows: the coated GCC powder (10 g), distilled water (200 mL) were stirred at 600 rpm for one minute and left to stand for one hr. in order to allow the mixture to separate into a deposit and suspended particles. The separated deposit and suspended particles were weighed after drying.

2.3.2 Inverse gas chromatography (IGC)

The dispersive component of the surface free energy, $y^D$ was calculated from IGC experiment at the infinite dilution condition. In IGC under infinite dilution conditions, the retention volume $V_N$ can be calculated using the following equation (1):

$$V_N = (t_R - t_0)j D_C$$

where $t_R$ is the retention time of the probes, $t_0$ is the zero retention time measured with a nonadsorbing probe such as methane, $j$ is the compressibility factor depending on the pressure at the column inlet and outlet, and $D_C$ is the corrected flow rate. In practice, the retention time and retention volume, $V_N$ can be determined in a current chromatographic experiment: a larger $V_N$ will correspond to a higher affinity of a probe to the chromatographic support.

In eq. (1), $j$ was calculated using the following equation (2):

$$j = 1.5 \left[ \left( \frac{p_i}{p_o} \right)^2 - 1 \right] \left( \frac{p_i}{p_o} \right)^2 - 1$$

where $p_i$ is the inlet pressure of the carrier gas, and $p_o$ is the outlet pressure of the carrier gas, which usually equal to atmospheric pressure.

The IGC experimental conditions performed in this study is the following. Since the particle size of the GCC powder was too small to be used as a chromatographic support, GCC discs were prepared by compressing the powders in an IR die at a pressure of $10^9$ Pa. The discs were then hand-crushed and sieved to select the fraction of particles with sizes ranging from 250 to 425 µm. Particles of the correct size were introduced into a stainless steel column, which was 50 cm long and 3.17 mm in inner diameter. Approximately 1 g of each sample was used to fill the chromatographic column. Each column filled with the samples was attached to a gas chromatograph (HP 6890, Agilent Technologies, USA) equipped with a highly sensitive flame ionization detector (FID), and then conditioned at 200°C for 15 hours to remove any impurities. The carrier gas was nitrogen ($N_2$) and the flow rate was 20 mL/min. The temperature of the injector and detector was controlled at 220°C. Measurements were carried out at 100°C.

2.3.3 Packing properties, flowability and floodability

In this study, a powder integrative characteristic tester (Multi tester, MT-1000, Seisin, Japan) was used to measure the properties of the GCC powder according to the Japanese Industrial Standard (JIS).

The packing properties of a powder are a very important factor in the process of powder handling such as storage, portage and

Fig. 3 Schematic diagram of the dry process coating system.
transfer. R. L. Carr suggested a method for evaluating the flowability from his experience on the handling of various powders.\textsuperscript{10} The flowability was calculated using the sum of indices suggested by Carr for the angle of repose, angle of the spatula and compressibility. Floodability is an index that indicates the ease of the flushing phenomenon. Floodability was calculated using the sum of the indexation values of flowability, angle of crumble, angle of difference and degree of dispersion. Flowability and floodability are usually used to evaluate powder systems; larger values indicate better flowability and floodability.

3. Results and Discussion

3.1 Surface properties

Figure 4 shows the change in water contact angle on a coated GCC disc surface as a function of the amount of SA added. Table 2 shows the contact angle, hydrophobicity and dispersive component of the surface free energy of the untreated and treated GCC powder. The contact angle on the GCC powder treated with 0.5 mass% SA was 98 ± 3°. The contact angle increased with increasing amount of SA added, and was 105 ± 3° and 110 ± 3° for the GCC powder treated with 1.0 mass% and 1.5 mass% SA, respectively. Shafrin \textit{et al.} reported that the maximum contact angle was 103° for water when fatty acid was adsorbed as a complete monolayer.\textsuperscript{11} In this study, the contact angle for water reached the maximum value at 1.0 mass% SA. Therefore, it was estimated that the GCC powder was coated as a complete monolayer at 1.0 mass% and above.

Figure 5 shows the change in hydrophobicity of the coated GCC powder as a function of the amount of SA added. The hydrophobicity of the GCC powder treated with 0.5 mass% SA was 99.9%, and that of GCC powder treated with 1.0 mass% and above was 100%. From the above contact angle and hydrophobicity results, it was believed that optimal amount of SA to modify the GCC powder surface was 1.0 mass% because the contact angle and hydrophobicity of the GCC powder treated with 1.0 mass% SA was similar to those of the GCC powder surface coated with a complete monolayer. Therefore, the GCC powder treated with 1.0 mass% SA was used as the standard sample for the IGC experiment and measurement of the powder properties, and is herein referred to as the treated GCC powder.

The dispersive component of the surface free energy, $\gamma_S^D$, was obtained by injecting a homologous series of n-alkanes into the column and determining their retention characteristics. Dorris and Gray used the incremental amount of free energy of adsorption, which corresponds to the adsorption of a single CH$_2$ group, $\Delta G_A^{CH_2}$, to determine the value of $\gamma_S^D$:\textsuperscript{12}

\begin{equation}
\gamma_S^D = \frac{1}{4 \gamma_{CH_2}} \left[ \frac{\Delta G_A^{CH_2}}{N \cdot a_{CH_2}} \right]^{1/2}
\end{equation}

where $\gamma_{CH_2}$ is the surface energy of a solid composed solely of -CH$_2$- groups, i.e., a surface analogous to polyethylene, $N$ is the Avogadro’s number, and $a_{CH_2}$ is the cross sectional area of an adsorbed -CH$_2$- group (0.06 nm$^2$).\textsuperscript{12} The variation in $\gamma_{CH_2}$ with temperature is given by the following equation:

\begin{equation}
\gamma_{CH_2} = 35.6 + 0.058(293 - T) \text{ in mJ}\cdot\text{m}^{-2}
\end{equation}

where $T$ is the temperature in K.

Generally, the logarithm of $V_N$ varies linearly with the number of carbon atoms of the injected n-alkane. Therefore, it is possible to define the free energy of adsorption, $\Delta G_A^{CH_2}$,
of a single methylene group, which no longer depends on the arbitrary choice of a reference state:

\[
\Delta G^{\text{CH}_2} = -RT \ln \left( \frac{V_n^{n+1}}{V_n^n} \right) \tag{6}
\]

where \( R \) is the ideal gas constant, \( T \) is the absolute temperature, and \( V_n^{n+1} \) and \( V_n^n \) are the net retention volumes of \( n \)-alkanes with \( n + 1 \) and \( n \) carbon atoms, respectively.

Figure 6 shows the change in \([RT \ln V_n]\) at 100°C as a function of the carbon number of \( n \)-alkanes used to probe the surface properties of the untreated and treated GCC powder. In Fig. 6, \( \Delta G^{\text{CH}_2} \) is the slope of the line obtained from eq. (6). The \( \gamma_0^{D} \) values of the solid were calculated using eq. (4). Table 2 shows the calculated \( \gamma_0^{D} \) values of the untreated and treated GCC powder. The \( \gamma_0^{D} \) value of the treated GCC powder was 34.8 mJ·m⁻², whereas that of the untreated GCC powder was 93.3 mJ·m⁻² at 100°C. The \( \gamma_0^{D} \) value of treated GCC powder was similar to the reported \( \gamma_0^{D} \) value (approximately 30 mJ·m⁻²) for polyethylene composed solely of alkyl chains. Therefore, it is believed that the alkyl chains of SA shield the GCC powder surface. From the above results, it is clear that treating the GCC powder with SA will reduce the particle-particle interactions and allow the dispersion of filler in a polymer matrix.

### 3.2 Powder properties

Table 3 shows the packing properties of the untreated and treated GCC powder measured using the method suggested by Kawakita. The apparent density and fluidity of the GCC powder was increased by the surface treatment but the adhesion decreased. This means that the critical void of the powder decreased, and amount of packing increased because the surface of the GCC powder was more stabilized. In addition, the surface energy decreased when their surface modified with SA.

Table 4 shows the flowability (\( F_W \)) of the untreated and treated GCC powder calculated using the angle of repose, angle of spatula and compressibility according to powder evaluation method suggested by Carr. The angle of repose, angle of spatula and compressibility of the treated GCC powder were the lower than those of the untreated GCC powder. The \( F_W \) of the treated GCC powder was 53 whereas that of the untreated GCC powder was 45. This means that the flowability was improved with surface treatment.

Table 5 shows the floodability (\( F_D \)) of the untreated and treated GCC powder calculated using the flowability (\( F_W \)), angle of crumble, angle of difference and degree of dispersion introduced from Carr’s index. The angle of crumble of the GCC powder decreased with the surface treatment whereas the angle of difference increased, which is the differences between the angle of repose and the angle of crumble. Degree of dispersion of the treated GCC powder was greatly improved. The \( F_D \) of the treated GCC powder was 69, whereas that of the untreated GCC powder was 30.

#### Table 3  Packing properties of the untreated and stearic acid-treated ground calcium carbonate.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Sample</th>
<th>Loose bulk density (g/cm³)</th>
<th>Packed bulk density (g/cm³)</th>
<th>Initial porosity (ε₀) (%)</th>
<th>Final porosity (ε₀) (%)</th>
<th>Fluidity Index (a)</th>
<th>Adhesion Index (1/b)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Untreated GCC</td>
<td>0.42</td>
<td>0.99</td>
<td>0.84</td>
<td>0.63</td>
<td>0.59</td>
<td>18.60</td>
</tr>
<tr>
<td></td>
<td>Treated GCC with 1.0 mass% SA</td>
<td>0.63</td>
<td>1.47</td>
<td>0.77</td>
<td>0.45</td>
<td>0.46</td>
<td>30.39</td>
</tr>
</tbody>
</table>

Fluidity Index (a): The smaller (a) is, the larger fluidity is. Adhesion Index (1/b): The larger (1/b) is, the smaller adhesion is.

#### Table 4  A flowability of the untreated and stearic acid-treated ground calcium carbonate.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Sample</th>
<th>Angle of repose (°)</th>
<th>Angle of spatula (°)</th>
<th>Compressibility</th>
<th>Flowability</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Untreated GCC</td>
<td>60°</td>
<td>7.0</td>
<td>15.0</td>
<td>49.3</td>
</tr>
<tr>
<td></td>
<td>Treated GCC with 1.0 mass% SA</td>
<td>57°</td>
<td>9.5</td>
<td>16.0</td>
<td>37.5</td>
</tr>
</tbody>
</table>

Flowability \( F_W \): The larger \( F_W \) is, the larger flowability is.
This means that the floodability of the powder was improved remarkably with surface treatment. These powder properties can be applied as essential data to the design of a powder handling system, such as evaluation, transfer, storage etc.

4. Conclusions

Ground calcium carbonate (GCC) powder was subjected to a surface treatment with stearic acid (SA), using the dry process coating system designed by this study.

The contact angle and hydrophobicity of the GCC powder treated with 1.0 mass% SA were 105° and 100%, respectively, whereas those of the untreated GCC powder were 0° and 0%, respectively. The dispersive component of the surface free energy, $\gamma_S^D$, of the GCC powder treated with 1.0 mass% SA was 34.8 mJ-m⁻² at 100°C, which is considerably lower than that of the untreated GCC powder ($\gamma_S^D = 93.3$ mJ-m⁻² at 100°C). Treating GCC powder with SA will reduce the particle-particle interactions and allow the dispersion of filler in a polymer matrix.

The fluidity of the GCC powder increased after the surface treatment but the adhesion decreased. In the case of the index suggested by Carr, the flowability and floodability of the GCC powder were improved greatly with surface treatment. It is believed that these results can be applied to almost all process of powder handling.

Acknowledgement

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REFERENCES