Clay Film Formabilities of Montmorillonites with Different Interlayer Cations

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Abstract: Self-standing-film-formability was evaluated by using montmorillonite clay samples with different interlayer cations such as Na\(^{+}\), Li\(^{+}\), Mg\(^{2+}\), and Ca\(^{2+}\). These montmorillonite samples provide self-standing films without any binder. Films of the montmorillonite samples with monovalent interlayer cations had smooth film surfaces. The clay platelets in the film were connected each other like one sheet, and deep waved structures were observed in the cross-section SEM photographs of the samples. On the other hand, montmorillonite samples with divalent interlayer cations showed gentle wave structures. These film structures affected film properties. Na- and Li-montmorillonite films were more flexible than Mg- and Ca-montmorillonite films. As a consequence, surface morphology and layer stacking morphology and flexibility of prepared self-standing films were different by interlayer cation species. It may be owing to interlayer cation species affecting a swelling which is considered as an important factor on the film formability.

Keywords: Self-standing film, Film formability, Interlayer cation, Swelling, Montmorillonite

1. INTRODUCTION

Recently, a flexible transparent clay-based film with low polymer loading has been bought much attention because of its great heat durability, high gas barrier property, transparency retained even at 350 °C [1]. These heat durability and gas barrier property increase with the ratio of clay in the nanocomposite. To prepare self-standing films with high clay content, film formability of clay itself becomes an important factor.

We have investigated film formability of various natural and synthetic clays. As a result, it was confirmed that swelling is a principle property for the self-standing-film-formation [2]. Swelling is affected by some parameters such as layer charge, interlayer cations, pH, etc. [3-6]. In particular, interlayer cations affect a swelling by having influence on an interlayer space, hydration energy, etc [7-9].

Montmorillonite is a clay used to prepare in clay films. In the nature, there are many kinds of natural montmorillonites with different interlayer cations. If influences of interlayer cations on film formability is defined, we can select montmorillonite adequating for clay-based film preparation. In this study, we investigate about an influence of interlayer cations on the self-standing-film-formability by using montmorillonites with exchanged interlayer cations from Na\(^{+}\) to other cations (Li\(^{+}\), Mg\(^{2+}\), and Ca\(^{2+}\)).

2. EXPERIMENTS

2.1 Exchange of interlayer cations

Interlayer cation of purified montmorillonite (Tsukinuno, Japan, purified montmorillonite, Kunimine Industries Co. Ltd., Japan) was exchanged to Li\(^{+}\), Mg\(^{2+}\), and Ca\(^{2+}\). The exchange was carried out by dispersing the clay by 0.1 N chloride salt aqueous solutions followed by the solid-liquid separation. It was repeated 3 times. The treated clay samples were then washed by water until any chlorine is undetected.

2.2 Self-standing film preparation.

The clay films were prepared from aqueous dispersions of the clays without any binder. The aqueous dispersions of the clays were dried at 60°C in polypropylene trays. And then, the dried dispersion was peeled off from the tray by hand.

2.3 Characterization

Interlayer cations of the original clay (Na-montmorillonite) and ion-exchanged clays were measured by using ICP (SPS 1500R; Seiko Instruments).

The film formations were evaluated to elucidate whether the film can be a self-standing film or not. Surfaces and fractured cross sections of prepared self-standing films were observed by SEM (S-800; Hitachi Ltd.). Flexibilities of films were measured by bend test with cylindrical mandrels (BD2000, Thermimport Quality Control).

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Table 1. Interlayer cations of original and ion-exchanged montmorillonites.

<table>
<thead>
<tr>
<th></th>
<th>Interlayer cations (ppm)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Na&lt;sup&gt;+&lt;/sup&gt;</td>
<td>Li&lt;sup&gt;+&lt;/sup&gt;</td>
<td>Mg&lt;sup&gt;2+&lt;/sup&gt;</td>
</tr>
<tr>
<td>Na-Mt</td>
<td>346.0</td>
<td>0.3</td>
<td>4.5</td>
</tr>
<tr>
<td>Li-Mt</td>
<td>11.6</td>
<td>77.9</td>
<td>4.9</td>
</tr>
<tr>
<td>Mg-Mt</td>
<td>2.4</td>
<td>0.3</td>
<td>142.6</td>
</tr>
<tr>
<td>Ca-Mt</td>
<td>2.1</td>
<td>0.3</td>
<td>4.2</td>
</tr>
</tbody>
</table>

Mt: montmorillonite

Figure 1. Surface and fractured cross sections of self-standing films analyzed by SEM.

<table>
<thead>
<tr>
<th></th>
<th>Surface</th>
<th>Fractured-cross-section</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na-Mt</td>
<td><img src="image1" alt="Surface of Na-Mt" /></td>
<td><img src="image2" alt="Fractured-cross-section of Na-Mt" /></td>
</tr>
<tr>
<td>Li-Mt</td>
<td><img src="image3" alt="Surface of Li-Mt" /></td>
<td><img src="image4" alt="Fractured-cross-section of Li-Mt" /></td>
</tr>
<tr>
<td>Mg-Mt</td>
<td><img src="image5" alt="Surface of Mg-Mt" /></td>
<td><img src="image6" alt="Fractured-cross-section of Mg-Mt" /></td>
</tr>
<tr>
<td>Ca-Mt</td>
<td><img src="image7" alt="Surface of Ca-Mt" /></td>
<td><img src="image8" alt="Fractured-cross-section of Ca-Mt" /></td>
</tr>
</tbody>
</table>

(Mt: montmorillonite)

3. RESULTS AND DISCUSSION

Table 1 shows interlayer cations of original and ion-exchanged montmorillonite measured by ICP. Table 1 indicates that interlayer cation Na<sup>+</sup> of the original clay was exchanged to aimed cations well.

All of the obtained montmorillonite samples were found to form self-standing films whose thickness of 70 ~ 120 µm. Na-montmorillonite formed a brownish gray film.

Table 2. Bending test with cylindrical mandrels of original and ion-exchanged montmorillonite film.

<table>
<thead>
<tr>
<th></th>
<th>Diameter of mandrel /mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na-Mt</td>
<td>2</td>
</tr>
<tr>
<td>Li-Mt</td>
<td>16</td>
</tr>
<tr>
<td>Mg-Mt</td>
<td>25</td>
</tr>
<tr>
<td>Ca-Mt</td>
<td>32</td>
</tr>
</tbody>
</table>

Mt: montmorillonite

Li-montmorillonite film was similar to Na-montmorillonite film but a little bright, while Mg- and Ca-montmorillonite films were yellowish brown.

Figure 1 presents surface and fractured cross section images of the self-standing films. The surface morphology was different depending upon the valance of interlayer cations. Na- and Li-montmorillonites showed continuous film surfaces like one sheet. On the other hand, Mg- and Ca-montmorillonite films presented laminate surfaces with small thin particles. This means the montmorillonite samples with divalent interlayer cations are not sufficiently swell like those with monovalent ones. It has been reported that ion exchanged clays with divalent cations such as Ca<sup>2+</sup> poorly swell compared with those with monovalent cations [10].

On the other hand, Na- and Li-montmorillonite films have deeply waved structure while Mg- and Ca-montmorillonite films showed gentle waves. It is considered that the film structure was affected by the swelling. Na- and Li-montmorillonites were sufficiently swelled and, as a result, provide deeply waved structure. Mg- and Ca-montmorillonites form small waves by aggregation of clay particles.

Table 2 summarizes flexibility of the films in terms of the diameter of the mandrels in order to measure the flexibility of the films. The diameters were 2, 16, 25, and 32 mm for the films of Na-, Li-, Mg-, and Ca-montmorillonite, respectively. Na- and Li-montmorillonite films were more flexible than the Mg- and Ca-montmorillonite films. This result suggests that film structures influence the flexibility of the films.

From above results, it was confirmed that monovalent interlayer cations are advantageous for preparing a highly flexible self-standing film.

4. CONCLUSIONS

Interlayer cation of the purified montmorillonite was exchanged to Li<sup>+</sup>, Mg<sup>2+</sup>, and Ca<sup>2+</sup>. These ion-exchanged-montmorillonite samples form self-standing films with ordered laminated structure. However, detailed surface and cross section structures of the films were different depending upon the interlayer cation species. Montmorillonite with monovalent interlayer cations form more flexible films compared with those with divalent ones.
5. REFERENCES