ABSTRACT

X-ray diffraction has been utilized to characterize basal plane spacing changes in Laponite RDS, a synthetic smectite-type clay, due to insertion of polymer species between the clay silicate sheets. To establish the effect of polymer intercalation on the basal plane spacing of Laponite RDS, two clay-polymer composite case studies are described: Laponite RDS and a polyester ionomer AQ55D, and Laponite RDS and a biopolymer gelatin. With polymer addition, Laponite RDS basal plane spacings ranged from 12.4 to ~40 Å depending upon the polymer, polymer weight fraction, and ambient humidity.

INTRODUCTION

Clay-polymer nanoparticulate composite (NPC) materials are of interest as a result of their wide range of novel physical properties [1, 2]. For example, researchers at Toyota have patented clay/nylon composites with greatly improved tensile strength, tensile modulus, and heat distortion temperature when compared to neat nylon [3-5]. In these composites, the layered clay material is exfoliated in the polymer matrix, and the improvement in the physical properties was brought about with only 5% of clay incorporation. Clay found in nature is generally inexpensive to purchase. However, these clays typically are not phase pure, which makes natural clay undesirable in some industrial applications. Synthetic clay is identified as an inexpensive, transparent, environmentally benign, nanoparticulate material with unique electrical, mechanical, and rheological properties, which are of interest to a number of industries. An added benefit of synthetic clay is that it can be produced at a high enough purity for critical manufacturing applications.

The clay material used in this work is a synthetic smectite, Laponite, that closely resembles the natural clay mineral hectorite in both structure and composition [6]. Laponite is a 2:1 layered hydrous magnesium lithium silicate consisting of two tetrahedral silica sheets sandwiching a central octahedral magnesia sheet, with the formula reported as Na_{0.35}[Mg_{2.77}Li_{0.13}]Si_{4}O_{10}(OH)_{2}\cdot nH_{2}O [7]. The (001) basal plane spacing of the clay is defined as the distance from a certain plane in one layer to the corresponding plane in another parallel layer of the crystal and, thus, includes the features of the geometry of stacking of layers, as well as any material present between layers.

The dispersion of clay in a polymer matrix can result in any of the following three general types of morphology [8]. (1) Conventional composites may contain clay with the layers unintercalated in a face-to-face aggregation; here, the clay platelet aggregates are simply
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dispersed with macroscopic segregation. (2) Intercalated clay composites are intercalation compounds of definite structure formed by the insertion of one or more molecular layers of the organic compound into the clay host galleries. (3) Exfoliated clay composites where singular clay platelets are dispersed in a continuous organic phase. These three types of morphology can be conveniently monitored by X-ray diffraction (XRD). With face-to-face aggregation of clay platelets, the basal plane spacing is very similar to that of “as received” clay powder. With intercalation of organic compounds in the clay gallery, an increase in the basal plane spacing can be detected by XRD. When completely exfoliated, the clay diffraction peaks disappear because the crystallographic order is lost.

The purpose of this paper is to discuss some general aspects of clay chemistry, particularly its interaction with different polymers, which will dictate its successful formulation and incorporation in industrial products. Emphasis is placed on X-ray diffraction analysis of clay-polymer composites. XRD revealed significant information about the morphology of these composites, which, in turn, determines their physical performance.

EXPERIMENTAL

The synthetic commercial clay used in this work is known as Laponite RDS, a peptized version of Laponite, supplied by Southern Clay Products, a division of Laporte Industries Ltd. of U.K. The peptizer, Na₅P₂O₇, modifies the surface of the clay platelet, increasing its stability in aqueous dispersions. The polymers in this study were a polyester ionomer, AQ55D (Eastman Chemical), or a biopolymer, gelatin (Eastman Kodak Company).

Composite materials were prepared by first dispersing Laponite RDS clay powder in deionized water using a high-shear mixer to form a clay sol. An aqueous solution, or dispersion of the polymer, was then added to this clay sol in various weight ratios to obtain the clay/polymer mixture in its final aqueous form. The total solids content was maintained at 4% by weight.

Samples for XRD were prepared by placing ~10 drops of the clay/polymer aqueous mixture onto microscope slides and dried in ambient to form a thin film of the sample. All XRD data were collected using a Rigaku RU-300 Bragg-Brentano diffractometer coupled to a copper rotating anode X-ray source. The diffractometer was equipped with a diffracted beam flat graphite monochromator, tuned to CuKα radiation, and a scintillation detector. Diffraction patterns were collected in reflection mode geometry from 2-40° 2θ at a rate of 2° 2θ/min.

RESULTS AND DISCUSSION

Laponite RDS

The diffraction pattern for Laponite RDS clay powder is shown in Figure 1 (a). The pattern is consistent with a hectorite-type powder pattern showing some disorder in the clay. In addition, several sharp diffraction peaks due to Na₅P₂O₇ are also present. When Laponite RDS is dispersed
in water and prepared for XRD analysis, the clay platelets form a film with the (00L) basal plane oriented parallel to the substrate surface. This film results in a diffraction pattern with highly oriented (00L) diffraction peaks, as seen in Figure 1 (b). The degree of orientation will be influenced by platelet size and sample matrix. The high-intensity diffraction peak at $2\theta = 6.64^\circ$ corresponds to an interplanar d-spacing of 13.3 Å and is often referred to as the basal plane spacing. It is important to note that the exact position of this peak will vary as a function of relative humidity (RH). In this work, the basal plane spacing for Laponite RDS has been observed to range from 12.4 to 13.6 Å, depending upon RH (higher RH results in a larger d-spacing value because of incorporation of water in the clay gallery).

![Figure 1](image_url)

Figure 1. (a) X-ray diffraction pattern for Laponite RDS powder, (b) X-ray diffraction pattern for Laponite RDS dispersed in water and dried as a film.

The basal plane crystallite size was determined for Laponite RDS by the Scherrer technique [9], using the full width at half maximum (FWHM) of a specified diffraction peak. The sample FWHM was corrected for instrumental broadening. Using the diffraction pattern generated for a Laponite RDS film, the average (00L) crystallite size was found to be 25 Å. Lateral plane (a-b axis) crystallite size is a more difficult determination for montmorillonite clays, since many of the diffraction peaks are broad as a result of multiple lattice plane overlap. In an as-received powder sample of Laponite RDS, a diffraction peak for the (060) lattice plane (observed at $\sim 61^\circ 2\theta$) was used for a Scherrer technique calculation. The average (0K0) crystallite size was found to be 80 Å. TEM data indicate that the lateral dimension of the clay platelets varied from about 200 to 400 Å. Based on the X-ray crystallite size estimate, the clay particles are generally comprised of $\sim 2\text{-}5$ crystallites.
Laponite RDS in AQ55D

Laponite RDS:AQ55D samples with ratios of 100:0 to 10:90 (wt:wt) were formulated for XRD measurement. The diffraction patterns from some of these samples are plotted in Figure 2, showing the basal plane diffraction peak shift to higher d-spacing caused by increasing concentration of AQ55D.

Figure 2. Low angle X-ray diffraction patterns of Laponite RDS:AQ55D composite samples.

The (001) basal plane spacing corresponding to different clay:polymer ratios, as measured at 47% RH, is listed in Table 1 for the Laponite RDS:AQ55D system.

<table>
<thead>
<tr>
<th>Laponite RDS:AQ55D weight ratio</th>
<th>(001) basal plane spacing (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100:0</td>
<td>13.4</td>
</tr>
<tr>
<td>90:10</td>
<td>14.2</td>
</tr>
<tr>
<td>80:20</td>
<td>15.5</td>
</tr>
<tr>
<td>70:30</td>
<td>16.9</td>
</tr>
<tr>
<td>60:40</td>
<td>18.5</td>
</tr>
<tr>
<td>10:90</td>
<td>not observed</td>
</tr>
</tbody>
</table>

As the AQ55D concentration increases, an increase in the basal plane spacing up to 40% AQ55D is observed. This increase in spacing is nearly linear with AQ55D composition. At much higher levels of AQ55D (greater than 70%) the (001) diffraction peak was not observed, indicating that the clay had become exfoliated. This exfoliated state is believed to be due to a loss of plane-to-plane ordering in the clay. Although the insertion of AQ55D in between basal planes
causes lattice expansion, there is a limit to an ordered expansion. Once this limit is reached, the clay integrity is lost and the basal plane spacing is no longer observed. In the case of AQ55D, the apparent threshold for Laponite RDS clay exfoliation appears to be at 70% of polymer content.

**Laponite RDS in Gelatin**

Laponite RDS:gelatin samples were prepared and analyzed in a manner similar to the previous case, and the diffraction patterns are plotted in Figure 3. The effect of gelatin on Laponite lattice expansion can be clearly detected as the (001) basal plane peak shifted to lower 2θ with increasing concentration of gelatin.

![Diagram](image)

**Figure 3.** Low-angle X-ray diffraction patterns of Laponite RDS:gelatin composite samples.

The (001) basal plane spacing corresponding to different clay:gelatin ratios, as measured at 30% RHI, is listed in Table 2 for the Laponite RDS:gelatin system. (Note that the 100% Laponite RDS basal plane spacing is smaller in Table 2 than observed in Table 1. This reduction in spacing is due to the lower RH at the time of data collection for the clay:gelatin experiments, an important point to remember when stating basal plane spacing values.)

The principal basal plane spacing increases with the gelatin concentration, up to 70% gelatin level. However, at this concentration the clay peak is poorly defined indicating significant lattice disorder. In general, the (001) peaks in Figure 3 are quite broad, suggesting a distribution in the basal plane spacing for a given composition, which might be due to nonuniform inclusion of gelatin in the lattice, effects of differing gelatin chain lengths (varying molecular weight), and/or variations of water content in the clay-gelatin film matrix. No (001) diffraction peak is
observed at 85% gelatin level, indicating clay exfoliation. The (100) gelatin peak at 2θ ~8° begins to emerge at this level of gelatin concentration.

Table 2 - Laponite RDS basal plane spacing for a specified Laponite RDS:gelatin ratio

<table>
<thead>
<tr>
<th>Laponite RDS:gelatin weight ratio</th>
<th>(001) basal plane spacing (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100:0</td>
<td>12.4</td>
</tr>
<tr>
<td>85:15</td>
<td>14.8</td>
</tr>
<tr>
<td>70:30</td>
<td>16.3</td>
</tr>
<tr>
<td>55:45</td>
<td>26.8</td>
</tr>
<tr>
<td>45:55</td>
<td>33.1</td>
</tr>
<tr>
<td>30:70</td>
<td>39.8</td>
</tr>
<tr>
<td>15:85</td>
<td>not observed</td>
</tr>
<tr>
<td>5:95</td>
<td>not observed</td>
</tr>
<tr>
<td>0:100</td>
<td>not observed, gelatin pattern only</td>
</tr>
</tbody>
</table>

The observed increase in the clay basal plane spacing with increasing amount of organic component is similar to that found in the AQ55D study. However, the magnitude of the increase due to gelatin is larger compared to that due to AQ55D. At a gelatin concentration of 70%, a spacing of ~40 Å is observed, which is more than three times the spacing of the unintercalated Laponite RDS. Such a large spacing is indicative of the high propensity for lattice expansion for this particular clay in an appropriate matrix.

As an illustration of the effect of NPC generation on a material's properties, Figure 4 shows the change in viscosity for a gelatin solution at 40 °C as clay is added to the gelatin matrix (total solids 2%). At a 40:60 Laponite RDS:gelatin ratio, the viscosity increases four orders of magnitude relative to neat gelatin indicating that the intercalation of gelatin into the clay lattice has a significant thickening effect.

Figure 4. Change in gelatin solution viscosity due to the addition of Laponite RDS.
By controlling the Laponite RDS:gelatin ratio, parameters such as mixing rate, coating speed, and drying rate can be tailored to a specific manufacturing application. Understanding the state of the clay, unintercalated, intercalated, or exfoliated, allows for the understanding of changes in NPC properties.

**SUMMARY**

Laponite RDS:polymer systems have been studied using XRD. The (001) basal plane spacing provided useful information regarding intercalation and exfoliation of clay in the presence of different polymers. Both intercalation and exfoliation appeared to be dependent on the polymer type and clay:polymer ratio. These results should be useful in the selection of suitable polymeric binders for clay formulations to generate optimum material performance.

**REFERENCES**