Preparation of New Polymer Nanocomposites with High Aspect Ratio Nanolayers by Use of Nonexpandable Fluoromica

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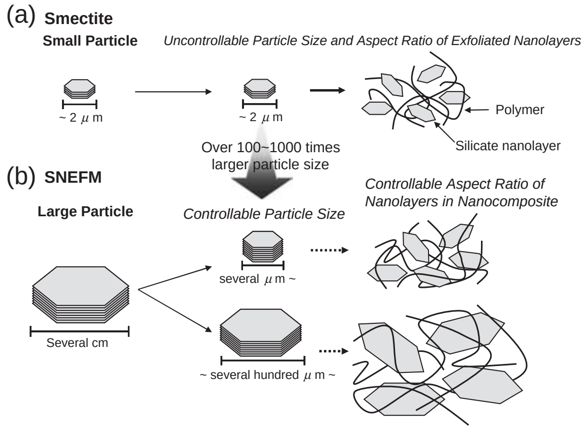
Dodecylammonium ions (DDA^+) were successfully intercalated in a synthetic nonexpandable potassium fluoromica (SNEFM) by replacing K^+ ions slowly in an aqueous solution of high DDA^+ concentrations at 70 °C. The resulting intercalated compound showed exfoliation in the polyamide 6 (PA6) matrix to form polymer nanocomposites. The materials had silicate nanolayers with aspect ratio as high as several dozen to hundreds times greater than that of conventional exfoliated clay–polymer nanocomposites.

Intercalation between inorganic layered materials and organic substances is attracting increasing interest from both scientific and industrial perspectives. Among various possible layered materials capable of accommodating guest species, the smectite group of layered clay minerals and expandable synthetic layered silicates have been widely investigated owing to their expandability and ion-exchange properties. One application using such hybrid materials is an exfoliated clay–polymer nanocomposite.[1] In the "exfoliated clay–polymer nanocomposite," the component layers composed of clay are individually dispersed in the polymer matrix. The resulting nanocomposite exhibits high tensile strength, modulus, heat distortion temperature, and excellent barrier properties at low clay content. Numerous reports have identified the aspect ratio (lateral length/thickness ratio) of the dispersed clay as a key factor for such improvements.[2]

Potassium fluorophlogopite (a mica mineral), which is prepared by a melting method, is an example of a manufactured synthetic layered silicate. The highly negative layer charge in the fluorophlogopite layers is ideally balanced by interlayer K^+ ions. Generally micas have the highest negative layer charge in the layered silicate group; the ideal charge is 1.0 equiv/half unit cell, whereas smectites are in the range of 0.2 to 0.6. The interlayer K^+ ions are believed to be nonexchangeable because they are strongly bound to the interlayer surfaces (in the form of inner-sphere complexes).[3] For this reason, despite its high crystallinity and large particle size (over several hundred–thousand times that of smectite clays), potassium fluorophlogopite has never been used in nanocomposites. If the mica were to be fully exfoliated, the aspect ratio of the individual layers would greatly exceed that of the smectite clays and can be controlled easily by setting the mica particle size using an industrial mill (Scheme 1). Recently, an exfoliated natural micaceous clay mineral (sericite)–epoxy nanocomposite was successfully prepared for the first time using a conventional polymer process.[4] In this study, in order to avoid problems such as the qualitative and quantitative differences in impurities and the inconsistent quality stemming from natural samples, we have investigated the intercalation properties and exfoliation behavior in a polymer matrix of synthetic nonexpandable fluoromica (SNEFM), the chemical compositions and particle sizes of which can be easily controlled.



Scheme 1. Comparing the dimensions of silicate nanolayers derived from (a) smectite and (b) synthetic nonexpandable fluoromica (SNEFM).

The SNEFM (a synthetic potassium fluorophlogopite obtained from Topy Industries) used was characterized as follows: the composition was $[(K_{0.89}Mg_{0.02}Al_{0.03})Mg_{3.00}(Si_{2.97}Al_{1.03})(O_{10}F_2)]$, the layer charge was 1.0 equiv/half unit cell, and median particle size was 24.5 μm.[5] Organically modified SNEFM was prepared by an ion-exchange reaction between SNEFM and dodecylamine hydrochloride (DDA, Wako Pure Chemical Industries) solution with various initial concentrations (DDA/K mole ratio = 1, 3, and 8).[5]

Typical XRD patterns of SNEFM and DDA-treated SNEFM (DDA-SNEFM) are shown in Figure 1. Each XRD profile has peaks at 2.3, 1.1, and 1.0 nm. In the case of DDA/K = 1, the peak at 2.3 nm gradually increased over time (Figure 1a). In

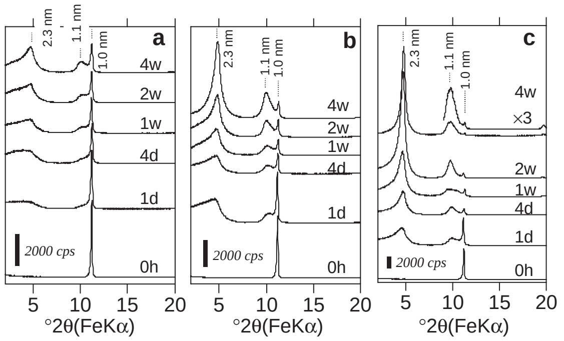


Figure 1. XRD patterns of SNEFM and DDA-SNEFM prepared by ion exchange with different DDA concentrations. (a) DDA/K = 1, (b) 3, and (c) 8 at 70 °C for various duration times.

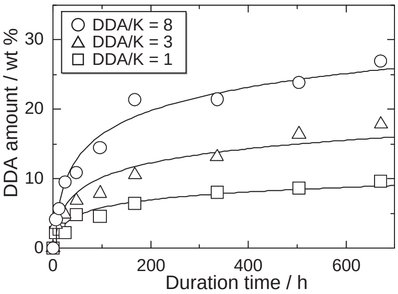


Figure 2. Relationship between exchange rate of DDA (wt %) and duration time.

the case of DDA/K = 3, the peak at 2.3 nm became sharper at a significantly higher rate than in the case of DDA/K = 1. In DDA/K = 8, the peak intensity of the 1.0 nm peak decreased relatively quickly over time compared to the other two initial DDA concentrations, and it was barely observed after four weeks of treatment. These intercalated compounds possess a slower reaction (i.e., the direct ion-exchange reaction between K^+ and DDA^+) rate than those mentioned in the previous work.[4]

The expanded phase has a d_{001} peak at 2.3 nm from the arrangement of interpenetrating monolayers of DDA ions attached to opposite silicate surfaces that is dependent on the large layer charge density of SNEFM.[6] The enhancement of the 2.3 nm peak with an increasing DDA/K mole ratio suggests that the intercalation is directly influenced by the concentration of the alkylammonium solution. This is further reinforced by the decrease in the XRD peak intensity for the unexpanded phase ($d_{001} = 1.0$ nm) with increasing the DDA^+ concentration (Figures 1a–1c).

The amount of intercalated DDA^+ was determined from the residual weight difference between DDA–SNEFM and pristine SNEFM at 1000 °C using thermogravimetric analysis (Figure 2). The amount of intercalated DDA^+ rapidly increased over a period of 48 h. The exchange rate between DDA^+ and K^+ ions increased with increasing DDA/K mole ratio. Although the intercalation rate of the DDA^+ decreased after 48 h, it slowly continued for at least four weeks. After four weeks, the amounts of intercalated DDA^+ present in DDA/K = 1, 3, and 8 were 10 (22), 18 (41), and 27 (60) wt %, respectively (the values in the parentheses indicate the DDA mol % based on the initial total amount of interlayer cations). These results indicate that the amount of intercalated DDA^+ was strongly dependent on the initial DDA/K ratio, which is consistent with the XRD results. Since the amount of intercalated DDA^+ for the DDA/K = 8 case continued to gradually increase after four weeks, the intercalation reaction clearly did not attain an equilibrium state. Compared to Na^+-montmorillonite, this is an extremely slow rate for the exchange reaction. Furthermore, natural nonexpandable sericite with an average particle size of 13 μm and average layer charge of 0.8 reached an ion-exchange equilibrium after two days of treatment.[4] These differences are due to the differences in the particle size and/or the electronic interactions resulting from differences in the layer charge.

To prepare the nanocomposites, a mixture of PA6 pellets and DDA–SNEFM (DDA/K = 8, 4w) were extruded using a twin-screw kneader at 260 °C.[5] Figures 3a and 3b show TEM images of DDA–SNEFM/PA6 and conventional DDA–montmorillonite/PA6 nanocomposites (silicate content: 2.5 wt %), respectively. Both layered silicates were exfoliated and well dispersed in the PA6 matrix. The length of the cross section of the exfoliated silicate nanolayers (dark line) in the DDA–SNEFM/PA6 is significantly longer than that in the DDA–montmorillonite/PA6. These results indicate that DDA–SNEFM can also be used for the development of high-performance polymer–inorganic hybrid materials. Here high performance means that the nanocomposite described above could be used to improve barrier properties, modulus and the heat distortion temperature. The particle size of SNEFM is easily controlled using standard industrial crushing methods, whereas it is very difficult to promote crystal growth using smectite, and it is also difficult to control the size of the smectite platelets. Therefore, if organized SNEFMs with different particle sizes are prepared using our reported method, it will be possible to develop polymer-exfoliated silicate nanolayers in the nanocomposites that have controllable aspect ratios.

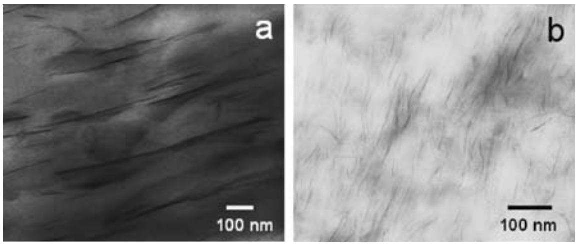


Figure 3. TEM images of (a) DDA–SNEFM/PA6 and (b) DDA–montmorillonite/PA6 nanocomposites.

In summary, a polymer nanocomposite with a dispersion of nanolayers having a large aspect ratio was successfully prepared using a high quality nonexpandable layered silicate. This opens the way to control the aspect ratio of dispersed layers in polymer nanocomposite technology. More importantly, this new composite system could extend the field of high-performance materials beyond traditional applications to encompass new unexpected functions.

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References and Notes

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