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Three-Dimensional Observation of Structure and Morphology in Nylon-6/Clay Nanocomposite

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ABSTRACT

We previously synthesized new nanocomposites that have clays uniformly dispersed in a nylon-6 matrix. Observation under the transmission electron microscope showed these clays to be a 1-nm-thick, 100-nm-wide layered filler. Recently, we have succeeded in making a three-dimensional observation of the cross section of the nanocomposites subjected to oxygen plasma treatment, using a scanning electron microscope. The observation revealed a novel structure, in which the clay layers stood perpendicularly to the nylon surface, resemblin a vertical cliff. We named these layers a "nano wall".

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We have developed a nylon-6/clay hybrid (nanocomposite, abbreviated NCH) in which clay silicate monolayers are uniformly dispersed at a nano level in a nylon-6 matrix.[1,2] NCH is synthesized industrially using organophilic montmorillonite (a common kind of clay) and caprolactam (the monomer of nylon-6). Caprolactam is intercalated into the gallery of organophilic montmorillonite[3] and polymerized there. The space between the clay silicate layers becomes wider during the polymerization period. The features of NCH include good mechanical properties, heat resistance,[4] and low gas permeability.[5] Since then, other polymer-clay hybrids such as polyimide,[6] epoxy resin,[7] polystyrene,[8] polycaprolactone,[9] acrylic polymer,[10] polyolefins[11] are reported.

The clay silicate in these nanocomposites exhibited superior reinforced effect. For example, the tensile strength of NCH (97.2 MPa, clay content: 4.0 wt %) became 1.4 times higher than that of nylon 6 (68.6MPa). The flexural modulus of NCH (4.34 GPa) was 2.24 times higher than that of nylon 6 (1.94 GPa).

The permeability of hydrogen for NCH film (clay content: 1.85 wt %) decreased 30% as compared with nylon 6. In the NCH film, the planes of the silicate layers are arranged parallel to the surface of the film formed by the extrusion molding through a die. A transmission electron micrograph (TEM) of the NCH film is shown in Figure 1. The dark lines in the figure correspond to the intersections of the clay silicate layers with a thickness of 1 nm. The barrier effect of the gas is explainable by the arrangement of the silicate layers. However, the clay dispersion at the intersection surface could not be directly observed by transmission electron microscopy.

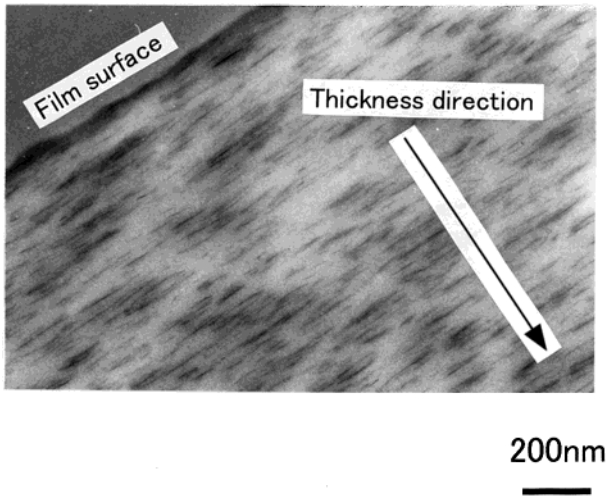

Figure 1. TEM photograph of NCH Film. The specimen has a thickness of 300 nm. The dark lines are the intersections of the clay silicate mono layers. The background is nylon 6 matrix.

This is the first time that we observed three-dimensional clay dispersion at the intersection of NCH to form a novel "nano wall" structure. The clay content in the NCH was 1.85 wt % (0.74 vol %).[12] A 60-μm-thick, 300-mm-wide NCH film was prepared from molten NCH pellets using an extruder with a T-die (300 $\times$ 0.4 mm) at a temperature about 250 °C, and only the center of the film was used for this study. The NCH film specimen was held in the epoxy resin. The cross section of film was treated with oxygen plasma (Yamato Inc., RF generator RFG-500, plasma chamber PC-103, power 120 W, oxygen flow 40 mL/min). The longitudinal section of the NCH film was treated with oxygen plasma at room temperature for 30 s. After carbon coating,

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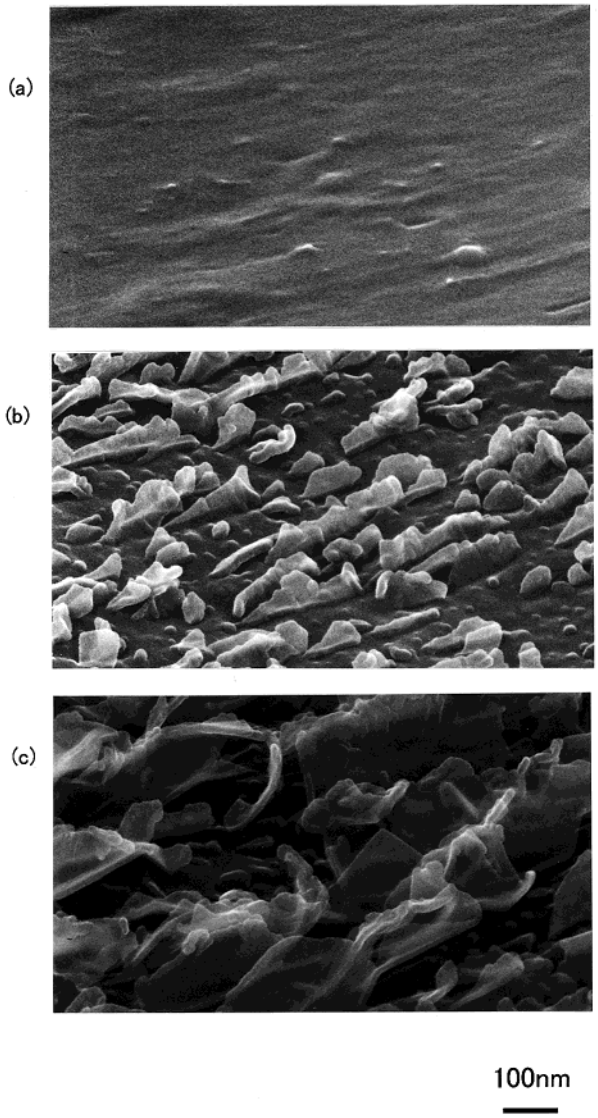

Figure 2. SEM photograph of NCH film. The actual length is equal to the square root of 2 times as long as the measured length in SEM photographs. This is because the specimen settled in the holder at an inclination of 45 degrees to the horizontal plane. (a) NCH surface before oxygen plasma treatment, (b) NCH surface after 30 s oxygen plasma treatment, (c) NCH surface after 60 s oxygen plasma treatment.

we observed the film under a scanning electron microscope (SEM, JEOL Inc., JSM-890). Figure 2 (b) shows a three-dimensional cross section of the NCH film. The clay layers (1-nm-thick) stand out in bold relief against nylon, which was etched by oxygen plasma treatment. These perpendicular clay layers against nylon surface resemble a vertical cliff. We named these layers a "nano wall".

The nano wall stood vertically when the film was subjected to oxygen plasma treatment for 20 to 50 s. However, it became inclined to the matrix when treated for 60 s. From an elemental analysis of this "wall" part using secondary electrons, Si, Al, Mg, and O were mainly detected. From the elemental composition of the wall, the wall was found to be the montmorillonite layer used for synthesizing NCH. The distance between clay minerals is defined as the basal spacing. The basal spacing in NCH varies with the clay content in nylon. Assuming that the clay layers are dispersed uniformly in nylon, the basal spacing is 135 nm[13] with 1.85 wt % (0.74 vol %) of clay content. The basal spacing measured using the SEM photographs of the clay layers was within the range of 85 nm to 150 nm. The average measured value was 125 nm, which is in close agreement with the calculated value, 135 nm. From these results, it was found that we are able to produce a nano wall at an arbitrary distance from the nano walls by changing the clay content in NCH. The distance between the walls could be 50 nm at a clay content of 5 wt %, and 25 nm at 10 wt %. These silicate layers are arranged in parallel, with the average separation distance caused by the stretching force of the extruder.

The observation method is effective in measuring the real distribution of the inorganic filler in an organic/inorganic nanocomposite. The nano wall can be further expected to find applications in nano size filters and nano sensing probes.

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(11) Kawasumi, M.; Hasegawa, N.; Kato, M.; Usuki, A.; Okada, A. *Macromolecules* **1997**, *30*, 6333−6338.
(12) This NCH was commercialized under the name of "1022C2" by UBE Ind., LTD Japan.
(13) The thickness of montmorillonite silicate layer is 1 nm. The content of clay in NCH is 0.74 vol %. From these data, the spacing between silicate layers is 100/0.74 = 135 nm. A number of silicate layers are arranged with separation distance 135 nm ideally.

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