

NOTE

Synthesis of Polypropylene–Clay Hybrid

INTRODUCTION

In our previous work, we successfully synthesized a nylon 6-clay hybrid (NCH) in which layers of clay mineral are uniformly dispersed in a nylon 6 matrix at the nano level.¹ NCH has good mechanical properties, heat resistance, and thermal stability even at a low loading of the clay mineral.² In addition, the NCH film has low gas permeability. Recently, other polymer–clay hybrids, such as polyimide,³ epoxy resin,⁴ polystyrene,⁵ polycaprolactone,⁶ and acrylic polymer,⁷ were reported. However, there is no report of a polyolefine–clay hybrid. It is considered that the silicate layers of clay mineral have polar hydroxyl groups and are incompatible with polyolefine. In this article, we studied whether polypropylene could be inserted into the clay gallery using clays modified with nonpolar organic molecules.

EXPERIMENTAL

Organophilic clay was obtained by a cation-exchange reaction between Na–montmorillonite (Na–Mt) and the distearyldimethylammonium ion, abbreviated DSDM–Mt, and its inorganic content was 52.8 wt %. A polyolefine oligomer with telechelic OH groups (polyolefine diol, carbon number = 150–200, Mitsubishi Chemical) was dissolved in toluene, and equal quantities of DSDM–Mt was added to the solution. Then, toluene was evaporated. Polyolefine diol was intercalated into the clay gallery, abbreviated PODS–Mt, and its inorganic content was 24.7 wt %. PODS–Mt and homopolypropylene were mixed using a Labo-Plastomill (Toyo Seiki) at 220°C until the motor torque became constant (about 5 min). Homopolypropylene was mixed with DSDM–Mt or Na–Mt. The inorganic (clay) content of these composites was 5 wt %. To confirm the dis-

persion of clays in polypropylene, a TEM observation was done for the intersection of injection-molded samples by a Jeol-200CX TEM using an acceleration voltage of 200 kV.

RESULTS AND DISCUSSION

Figure 1 shows a TEM photograph of the molded sample of PODS–Mt/polypropylene. The dark lines in the figure correspond to the intersections of sheet layers with 1 nm thickness. Figure 2 shows the TEM photographs of DSDM–Mt/polypropylene and Na–Mt/polypropylene.

In the case of PODS–Mt/polypropylene, the silicate layers were exfoliated and dispersed uniformly in the polypropylene matrix at the nano level. In the case of DSDM–Mt/polypropylene, the scores of silicate layers were laminated and aggregated in the polypropylene matrix. Na–Mt was dispersed in the polypropylene matrix at the micron level.

We studied the degree of dispersion of DSDM–Mt in polyolefine diol. The mixing ratio of polyolefine diol to DSDM–Mt was changed from 0.5 to 10.0,



Figure 1 TEM photograph of PODS–Mt/Polypropylene.

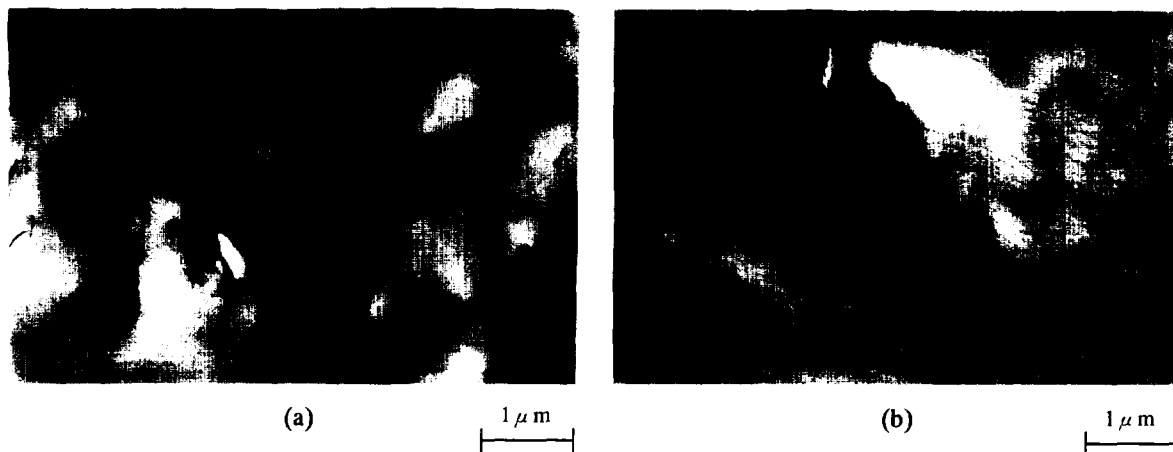


Figure 2 TEM photographs of DSDM-Mt/Polypropylene(a) and Na-Mt/Polypropylene(b).

and the basal spacing of these compounds were measured by the X-ray diffraction method.

These results are shown in Figure 3. The basal spacing of the intercalated compounds of polyole-

fine diol and DSDM-Mt increased as the mixing ratio increased. When the ratio exceeded 3, a clear diffraction peak was not observed (basal spacing > 8.8 nm). The basal spacing of mixture of poly-

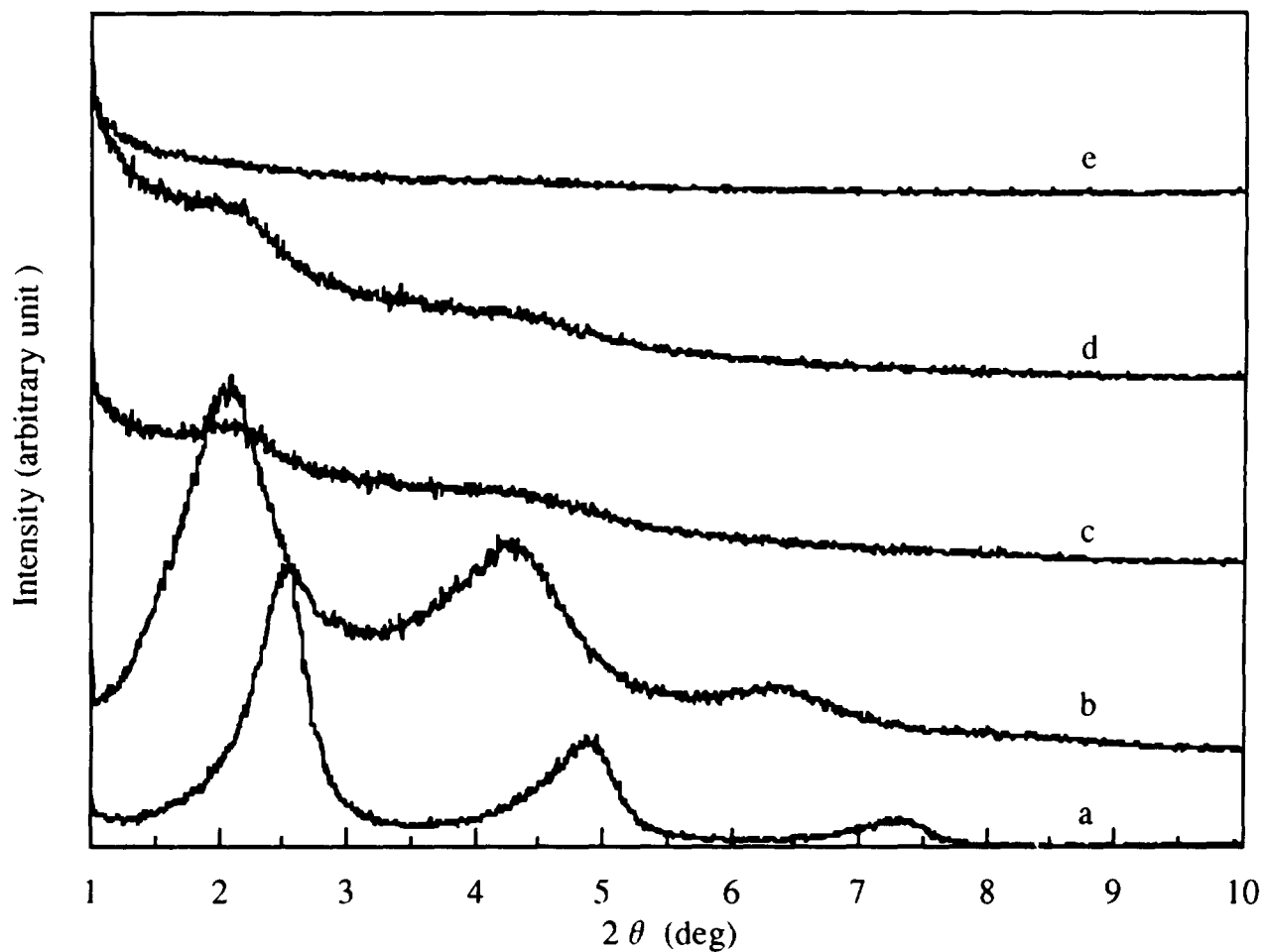


Figure 3 X-ray diffraction patterns of mixture of DSDM-Mt and polyolefine diol
 a: DSDM-Mt, b: polyolefine diol/DSDM-Mt=1 (PODS-Mt), c: polyolefine diol/DSDM-Mt=3,
 d: polyolefine diol/DSDM-Mt=5, e: polyolefine diol/DSDM-Mt=10.

olefine diol and Na-Mt was not changed from the pristine Na-Mt (basal spacing = 1.23 nm, data not shown).

Polyolefine and DSDM groups have good chemical affinity, so that polyolefine could be inserted into the clay gallery in the presence of toluene. After the toluene was evaporated, the telechelic OH groups interact with the silicate layer through hydrogen bonding. Polyolefine oligomer with telechelic OH remained in the clay gallery, and silicates of clay were exfoliated. In conclusion, we synthesized the polypropylene-clay hybrid using a polyolefine oligomer with telechelic OH groups.

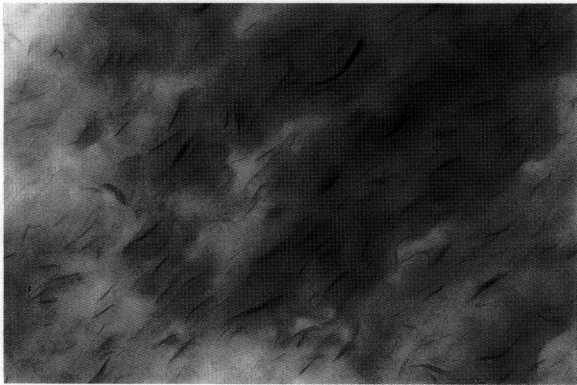
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1 μ m


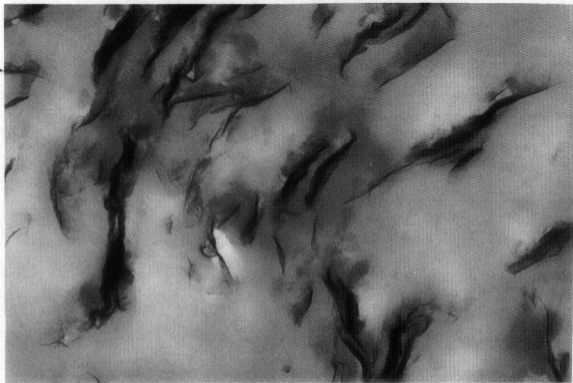
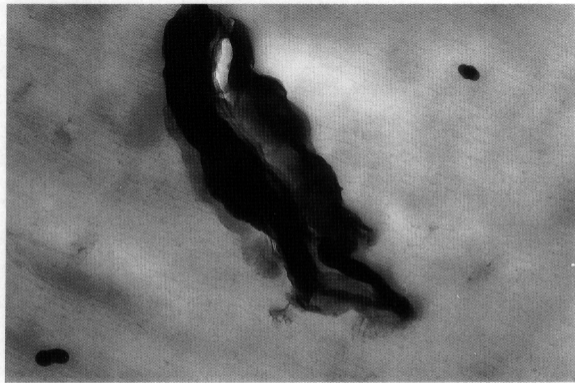
A horizontal scale bar with vertical end caps, indicating a length of 1 micrometer.

Figure 1 TEM photograph of PODS-Mt/Polypropylene.



(a)

1 μ m



(b)

1 μ m

Figure 2 TEM photographs of DSDM-Mt/Polypropylene(a) and Na-Mt/Polypropylene(b).