

## Synthesis of a PET-Clay Hybrid Material

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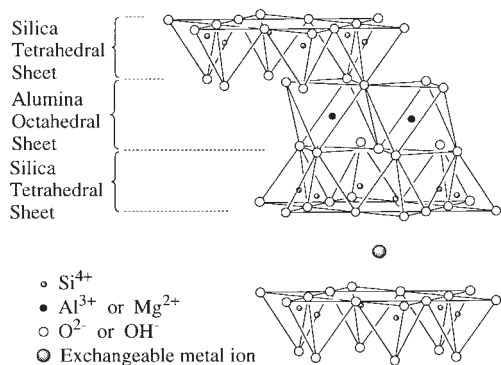
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The hybridization of poly(ethylene terephthalate) (PET) with montmorillonite (Mont) was investigated by using hydroxyethyl isonicotinamide (HENA) as an ionic anchor monomer capable of being adsorbed onto clay surfaces by a pyridinyl group ( $-C_5H_5N$ ). The hybrid films of HENA/Mont with bis(hydroxyethyl) terephthalate (BHET) exhibited favorable characteristics of being optically clear and transparent.

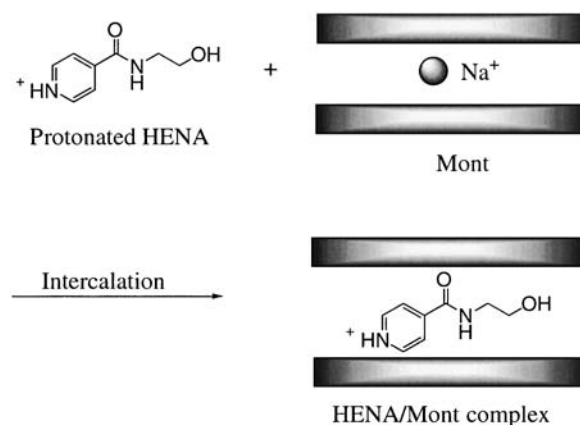
PET is one of the most widely used polymers due to its low cost and high performance, applied as synthetic fibers, films, filaments, bottles, and engineering plastics<sup>1-3</sup> with an overall production of more than 16 million tons a year worldwide.<sup>4,5</sup> Many papers concerning polymer-clay hybrids have been reported in the past decade<sup>6</sup> and the hybridization of organic polymers with inorganic clay minerals has been found to improve the properties of the polymer materials. For instance, NCH (nylon-clay-hybrid) was developed for practical use for its mechanical strength and thermal stability.<sup>7</sup> However, thus far, there have been few reports on the hybridization of PET with clay minerals. This is because PET-clay is difficult to prepare due to the lack of any interaction between the non-ionic polymer chain and the ionic surface of the clay minerals. In this communication, a new synthetic strategy for the preparation of PET-clay hybrid materials is introduced.

Layered structural clay minerals are typically suspended in aqueous solutions as fine particles with an average diameter of about several micrometers.<sup>8</sup> One typical clay mineral, montmorillonite (Mont), is composed of two silica tetrahedral sheets and an alumina octahedral sheet in which a part of  $Al^{3+}$  is replaced by  $Mg^{2+}$ , generating negative charges in the clay layers. Their intersheet layers include exchangeable metal ions (e.g.,  $Na^+$ ), neutralizing the net negative charges of the octahedral layers (Figure 1).<sup>9</sup> HENA, an ionically charged terminal monomer, was obtained by protonation of the pyridinyl group and intercalated



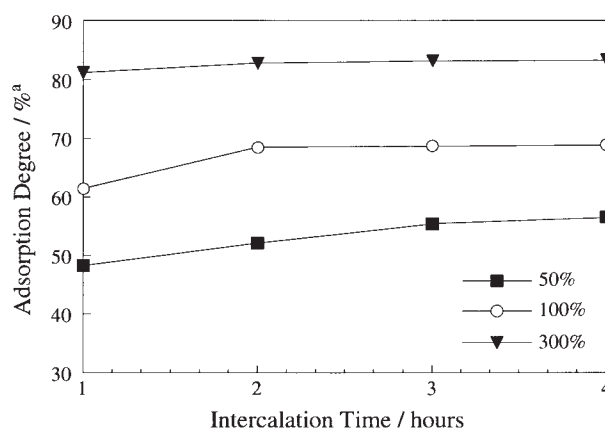
**Figure 1.** The laminating structure of montmorillonite clay.

very efficiently into the clay interlayers by exchanging the metal cations, as shown in Scheme 1.



**Scheme 1.** The exchange of the Mont interlayer cations.

The intercalation degrees of HENA against the cation exchange capacity (CEC) of Mont are shown in Figure 2. The intercalation, though not quantitative, was efficient under conditions of higher concentrations of HENA and, at the same time, the longer intercalation time resulted in a higher intercalation degree. By adding three equivalents of HENA on the basis of the CEC of the clay, HENA of more than 80 mol% was introduced into the HENA/Mont complex, as shown in Figure 2.



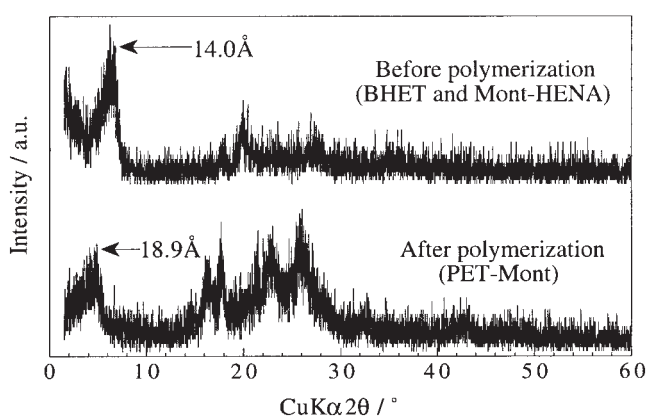
**Figure 2.** The adsorption degree of HENA cation into the montmorillonite clay interlayers. a) Adsorption degrees are expressed in % vs CEC (1.12 mmol/g).

It can be seen that the interlayer distance of the HENA/Mont complex increased when the intercalation degree was increased, as shown in Table 1, suggesting that the insertion of HENA molecules elongated the interlayer spaces of Mont.

**Table 1.** The interlayer distances of the HENA/Mont complexes.

[HENA]/mmol/dm <sup>3</sup> (% vs CEC)	Intercalation for 3 h Interlayer Distance/Å
0	12.5
2.5 (50)	13.2
5.0 (100)	13.4
7.5 (150)	13.5
15.0 (300)	14.0

The polymerization of BHET initiated by the HENA/Mont complex (intercalation of 300% CEC, 3 h) was carried out by condensation of a mixture of BHET and the HENA/Mont complex (2 : 1 in wt%) at 250 °C and 3 mmHg for 4 h to produce brown solid polymers. Figure 3 shows the XRD patterns of the hybrids before and after the polymerizations.

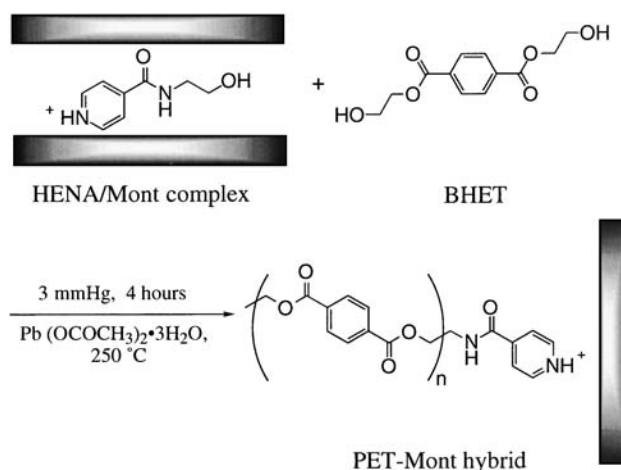
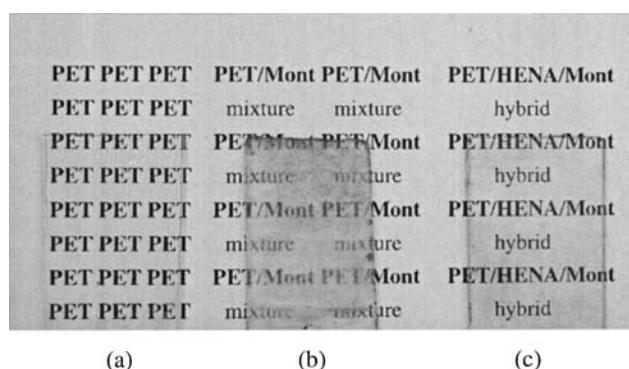
**Figure 3.** The XRD patterns of the PET-Mont hybrid materials.

Before polymerization, the XRD pattern of the reaction mixture was similar to that of Mont-HENA, indicating that the laminated structure of Mont clay is retained. After polymerization, however, the basal spaces of Mont was enlarged to 18.9 Å, accompanied by a decrease in the peak intensities. At the same time, new diffraction peaks, attributed to the PET polymers appeared at around 15–30° in the XRD spectrum of the reaction mixture. This copolymerization is depicted in Scheme 2.

HENA reacts with BHET as they both have hydroxyethyl substituents. Condensation occurs in the interlayers of Mont, and thus, induces exfoliation of the lamellar structure of the HENA/Mont complex and a dispersion into the polymer matrix of PET. Significantly, the PET/HENA-Mont hybrid films were found to be optically transparent, as shown in Figure 4. This figure shows photographs indicating the transparency of the PET-Mont hybrid containing HENA (picture c), the cloudiness when it is a mixture of PET with Mont (picture b), and also the pure PET polymer (picture a).

In conclusion, HENA intercalated into the interlayers of Mont, could be polymerized with BHET to form an effective PET-clay hybrid. Moreover, the melted films were found to be optically transparent and the clay layers were exfoliated and dispersed finely into the PET-clay hybrid.

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**Scheme 2.** The polymerization of BHET and HENA/Mont.**Figure 4.** Transparency of the melted films of: (a) PET, (b) a physical mixture of PET and Mont and; (c) the PET-Mont hybrid containing HENA. Samples b and c contain 10 wt% Mont; Samples a, b and c were polymerized at 290 °C, 1 mmHg for 4 h.

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