

# Mechanical Properties and Applications for Floor Tiles of a Composite from Clay and Maleated Polyethylene

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**ABSTRACT:** New composites were prepared from dried waste mud containing clay (Clay) and maleated polyethylene (MPE) by melt mixing. Scanning electron microscopy showed strong adhesion of MPE to Clay in the MPE–Clay composite, and this was probably due to the increased compatibility between MPE and Clay. With an increase in the Clay concentration to 60 wt %, the tensile strength of the

MPE–Clay composite increased. Furthermore, the smaller elongation of the MPE–Clay composite indicated effective transfer of the high tensile strength of Clay to the MPE matrix through the strong adhesion between Clay and MPE.

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**Key words:** clay; composites; polyethylene (PE)

## INTRODUCTION

The utilization of waste mud from oil drilling sites for novel composites has attracted growing interest because of its ecofriendly and renewable nature. The mud constituents from a drilling plant with the original mud constituents (see the appendix) are similar to the geological layer substances encountered during the progress of the operation. Accordingly, the waste mud contains many stratal substances [i.e., the constituents of the dried waste mud containing clay (Clay)]. We have already proposed a waste mud utilization system for an oil drilling plant, as shown in Figure 1, which is applicable to both land and offshore oil drilling plants. The waste to be treated has been estimated to be 40 m<sup>3</sup>/d high-concentration mud, 100 m<sup>3</sup>/d low-concentration mud, and 5 m<sup>3</sup>/d cuttings for an offshore drilling plant. This waste should be treated properly and used as an ecofriendly material for global environmental protection now.

The compatibility between the Clay constituents and the resin matrix can also be enhanced by the modification of the resin, to the surface of which hydrophilic or active groups are added.

Maleic anhydride (MA) has been reported to be an effective modifier for polyethylene (PE).

However, few studies have been reported on composite materials of clay (reagent-grade) and thermoplastic resins.<sup>1,2</sup>

A key problem exists in the method of preparation of a composite with good mechanical properties. Grafting MA onto PE is the most effective method for improving the interfacial adhesion of the Clay components and PE matrix because of the formation of covalent bonds through esterification between the MA groups and hydrophilic groups in Clay.

In this study, we investigated the compounding of maleated polyethylene (MPE) with Clay from a waste mud treatment plant under melt mixing to prepare composites of Clay and MPE with Clay concentrations of 0–60 wt %. The mechanical properties of the MPE–Clay composite are discussed with respect to the concentration of Clay of the composite.

The development of organic–inorganic hybrid materials suggests that the synergistic effects of organic and inorganic substances stimulate each property by compounding.

## EXPERIMENTAL

### Materials and preparation

Waste mud was taken from an oil drilling plant up to a depth of 2500 m in the Niigata prefecture of Japan, and a powdered mud sample (Clay) was prepared with a flash dryer.

MPE with MA was purchased from Mitsubishi Chemicals Co., Ltd. (Tokyo, Japan) and was mechan-

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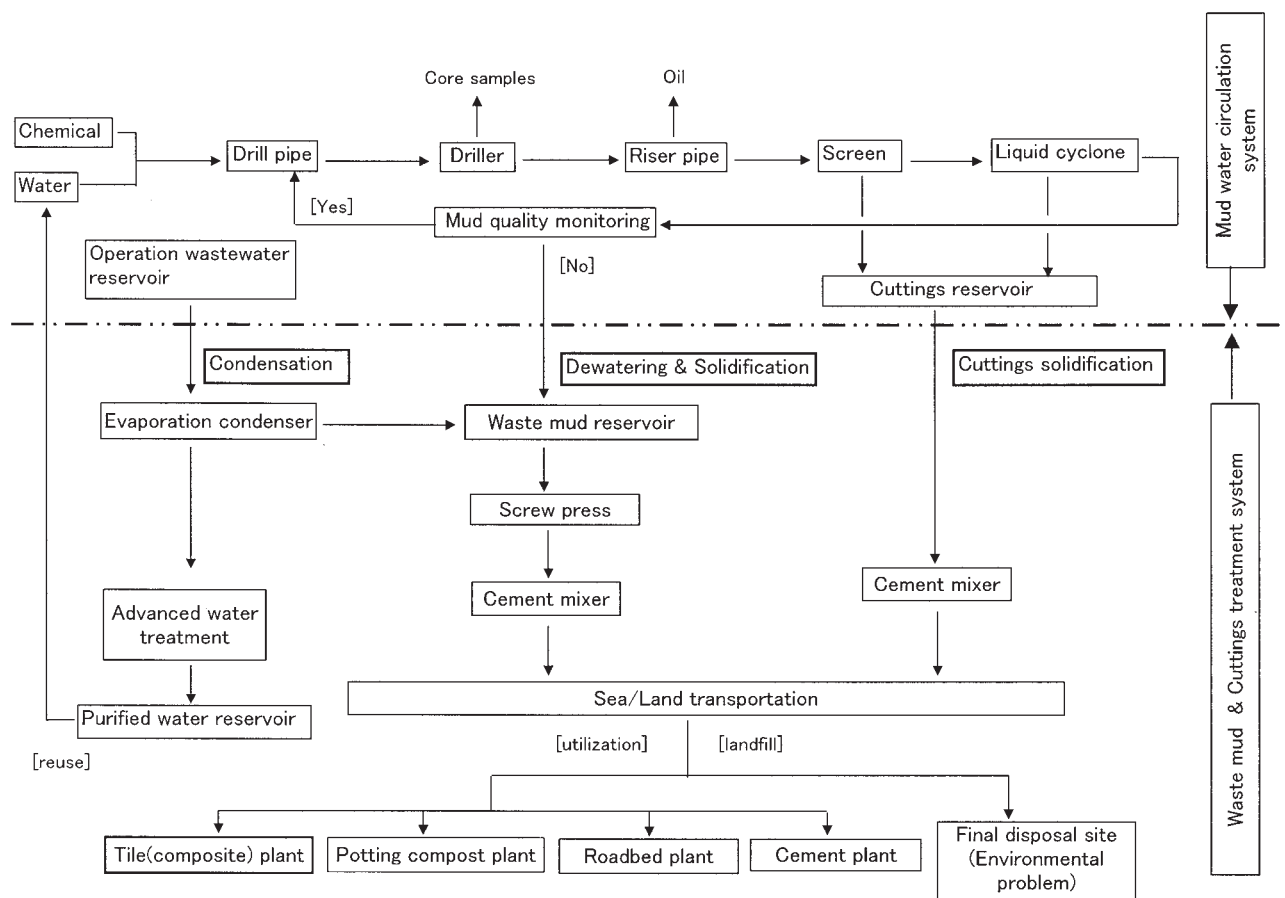


Figure 1 Waste mud utilization scheme in an oil drilling plant.

ically sieved into small flakes (ca. 2 mm) with a pulverizer (Pulverisette, Fritsch GmbH, Idar-Oberstein, Germany). The MA concentration was measured to be about 0.8 wt % by the chemical titration method.<sup>3</sup>

The MPE-Clay composites were prepared in a roller mixer (R60, Toyo Seiki Seisaku-syo Ltd., Tokyo, Japan), treated at 200°C for 20 min, and shaped into pellets (<2 mm). The sample sheets of the MPE-Clay composites were prepared by a heat compression molding. The pellets of the MPE-Clay composites were heat-pressurized at 200°C and 3–4 MPa for 3 min with a molding press (SFA-37, Shinto Metal Industries, Ltd., Osaka, Japan) with an automatic cycle of heating, pressurizing, and cooling. Teflon films were used to avoid direct contact between the MPE-Clay composites and the stainless surface of the mold.

The sample sheets were conditioned at 20°C and 65% relative humidity in a controlled-environment room for 24 h before the tensile strength and elongation were measured with a tensile tester (ASG-5kNG autograph, Shimadzu Co., Kyoto, Japan) in accordance with the test method for the tensile properties of plastics<sup>4</sup> at a strain speed of 50 mm/min.

The fractures of the composites after the tensile tests were coated with a thin gold-palladium layer and

observed with a scanning electron microscope (S-2460N, Hitachi Ltd., Osaka, Japan). Fourier transform infrared spectra of the MPE-Clay composites were obtained with a KBr-pellet method at a resolution of 4 cm<sup>-1</sup> (Spectrum 2000, PerkinElmer Cetus Instruments Inc., Norwalk, CT).

The chemical analyses of Clay were carried out according to gravimetric analysis for Si and Ba, according to flame spectrophotometry analysis for Na and K, and according to inductively coupled plasma atomic emission spectrometry analysis for heavy metals. The mineralogical analyses of Clay were carried out by an X-ray diffractometer (MXP3, MAC Science Co., Ltd., Yokohama, Japan) operated at 40 kV and 40 mA with Cu K $\alpha$  radiation. The samples were scanned at a speed of 2°/min at a diffraction angle ( $2\theta$ ) of 5–100°.

### Characterization methods

The characteristics of the composites as floor tiles were measured in accordance with test methods for resilient floor coverings<sup>5</sup> after the preparation of the samples (150 mm × 150 mm × 3 mm) with a compression-molding machine (KCK80-2-35VEX, Asada Iron Works Co., Ltd., Osaka, Japan) operated at a feeder

TABLE I  
Chemical Analysis of the Clay Sample from Waste Mud

Component	Concentration (mg/g)
SiO <sub>2</sub>	490
BaO	127
Al <sub>2</sub> O <sub>3</sub>	75
Fe <sub>2</sub> O <sub>3</sub>	32
K <sub>2</sub> O	32
CaO	13
MgO	9
Na <sub>2</sub> O	8
TiO <sub>2</sub>	3
P <sub>2</sub> O <sub>5</sub>	1
Ig-loss	161

Particle density = 2.80; mean particle diameter = 15 μm; Ig-loss = Ignition loss.

speed of 300 min<sup>-1</sup>, a screw speed of 43 min<sup>-1</sup>, and a temperature of 160–190°C and with an injection-molding machine (F-85, Klockner, Desma Werke AG, Fridingen, Germany) operated at an injection pressure of 100 MPa, a screw speed of 100 min<sup>-1</sup>, and a cylinder temperature of 180–200°C.

## RESULTS AND DISCUSSION

### Chemical constituents of the waste mud

Table I shows the results of the chemical analyses of Clay. The main components were quartz (SiO<sub>2</sub>) and

Al<sub>2</sub>O<sub>3</sub>; this was similar to general clay minerals. On the other hand, the barite (BaSO<sub>4</sub>) concentration was very high; this was characteristic of Clay because a large amount of BaSO<sub>4</sub> was added to the water by the drilling mud company to make the mud water much heavier against the earth pressure in the chute. BaSO<sub>4</sub> in Clay is a key point for waste mud being used to make useful materials.

Some typical clay minerals in the sample were identified as SiO<sub>2</sub>, cronstedtite [Fe(SiFe)<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>], and vaterite (CaCO<sub>3</sub>) by a comparison of the X-ray diffraction spectra of the standard minerals, as shown in Figure 2.

From the existence of SiO<sub>2</sub> in Clay, the structural OH groups seemed to be bonding on the particle surface and making the Clay surface more hydrophilic.<sup>6,7</sup>

### Interfacial adhesion and microstructure of the composite

Figure 3 shows the IR spectra of the MPE–Clay composite with Clay concentrations of 10, 20, 40, and 60 wt % and the IR spectra of 100 wt % MPE and 100 wt % Clay. The absorption bands at 2920, 2850, 1470, and 720 cm<sup>-1</sup> are due to the same backbone of PE. The typical absorption bands of SiO<sub>2</sub> at 1106 and 470 cm<sup>-1</sup> appear in part f.

The weak but clear absorption band at 3400 cm<sup>-1</sup> of Clay has been assigned to OH groups and seems to

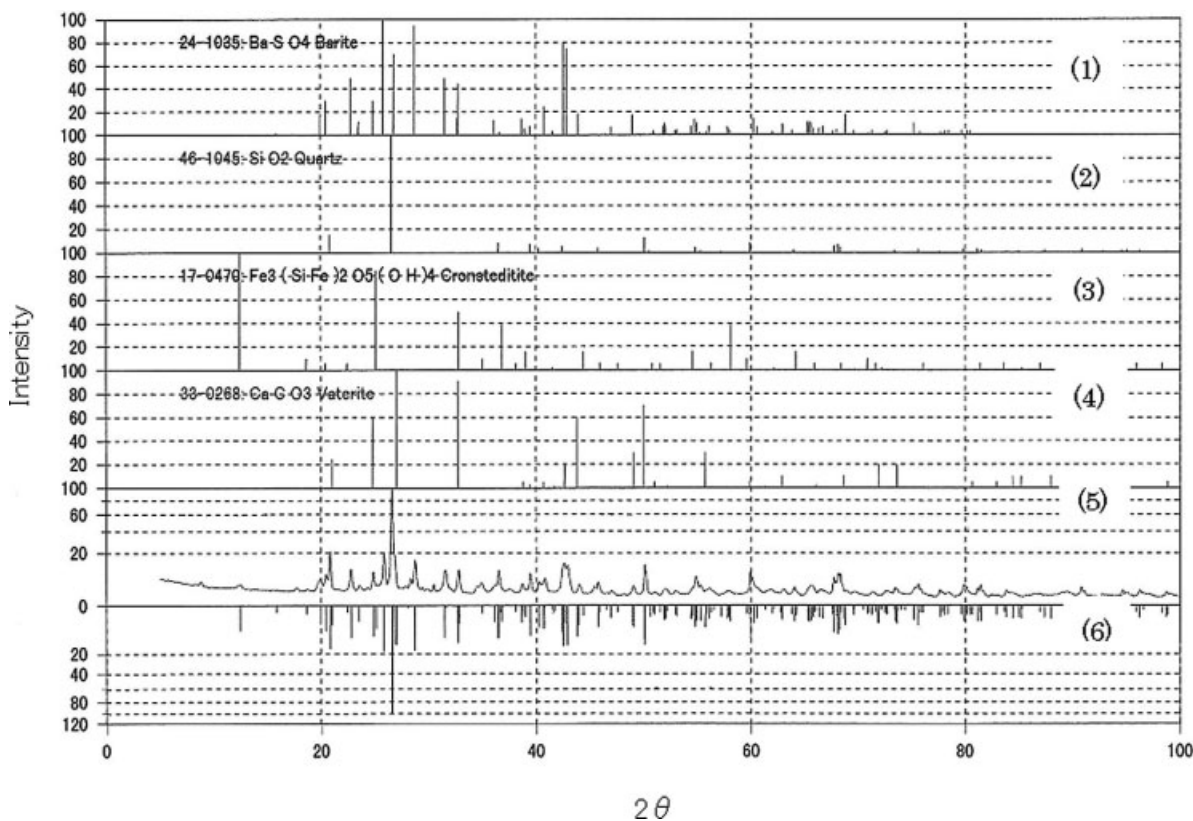
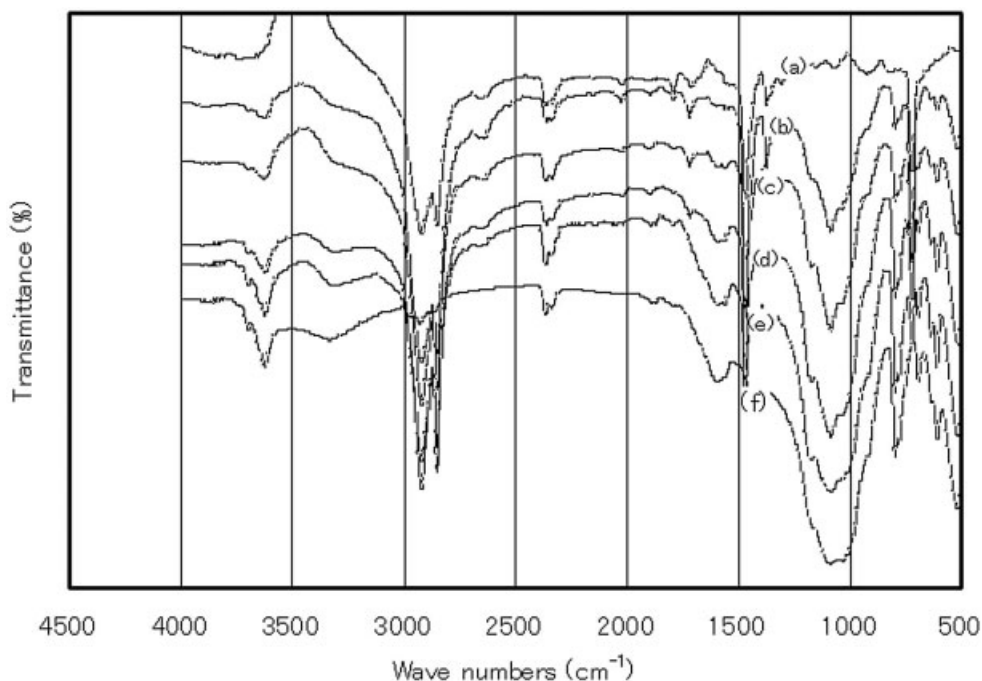
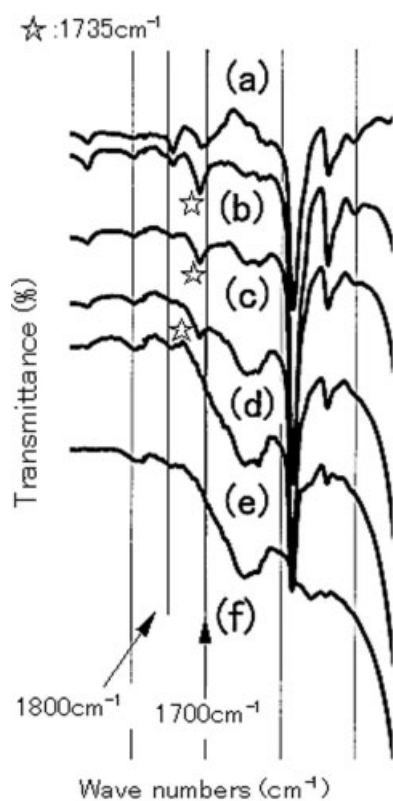


Figure 2 X-ray diffraction patterns of the Clay sample and standards: (1) BaSO<sub>4</sub> (JCPDS 24-1035), (2) SiO<sub>2</sub> (JCPDS 46-1045), (3) Fe(SiFe)<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub> (JCPDS 17-040), (4) CaCO<sub>3</sub> (JCPDS 33-0268), (5) sample spectrum data, and (6) sample peak data.



**Figure 3** IR spectra of MPE, Clay, and their composites: (a) 100 wt % MPE, (b) 90 wt % MPE and 10 wt % Clay, (c) 80 wt % MPE and 20 wt % Clay, (d) 60 wt % MPE and 40 wt % Clay, (e) 40 wt % MPE and 60 wt % Clay, and (f) 100 wt % Clay.



**Figure 4** IR spectra of MPE, Clay, and their composites at 1700–1800  $\text{cm}^{-1}$ : (a) 100 wt % MPE, (b) 90 wt % MPE and 10 wt % Clay, (c) 80 wt % MPE and 20 wt % Clay, (d) 60 wt % MPE and 40 wt % Clay, (e) 40 wt % MPE and 60 wt % Clay, and (f) 100 wt % Clay.

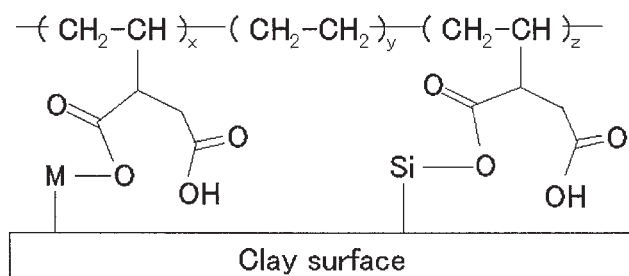
suggest the existence of a hydrophilic surface on the Clay particles.

Figure 3 shows that the MPE–Clay composite had a lower intensity of absorption at  $3400 \text{ cm}^{-1}$  than Clay. This suggested that some of the hydroxyl groups of Clay in the MPE–Clay composite took part in a reaction with MA groups grafted onto PE.

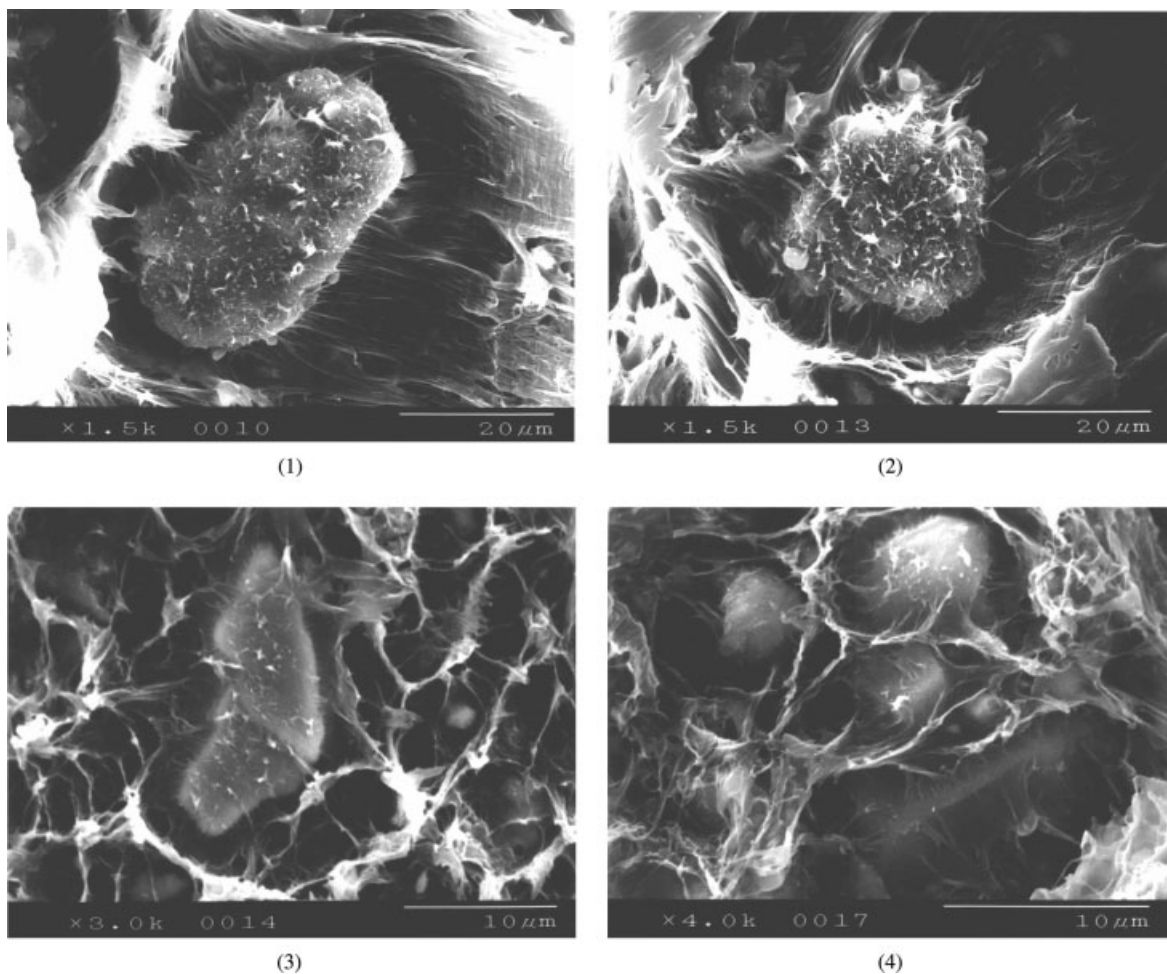
The magnified spectra of MPE between 1700 and  $1800 \text{ cm}^{-1}$  exhibited absorption bands due to saturated succinic anhydride and their hydrolysis derivatives at  $1792$  and  $1713 \text{ cm}^{-1}$ , respectively, as shown in Figure 4.

The disappearance of the band at  $1792 \text{ cm}^{-1}$  and the appearance of a new band at  $1735 \text{ cm}^{-1}$  suggested that, after MPE was compounded with Clay, esterification occurred between the OH groups of Clay and the succinic anhydride groups of MPE, as shown in Figure 4(b–d).<sup>8</sup>

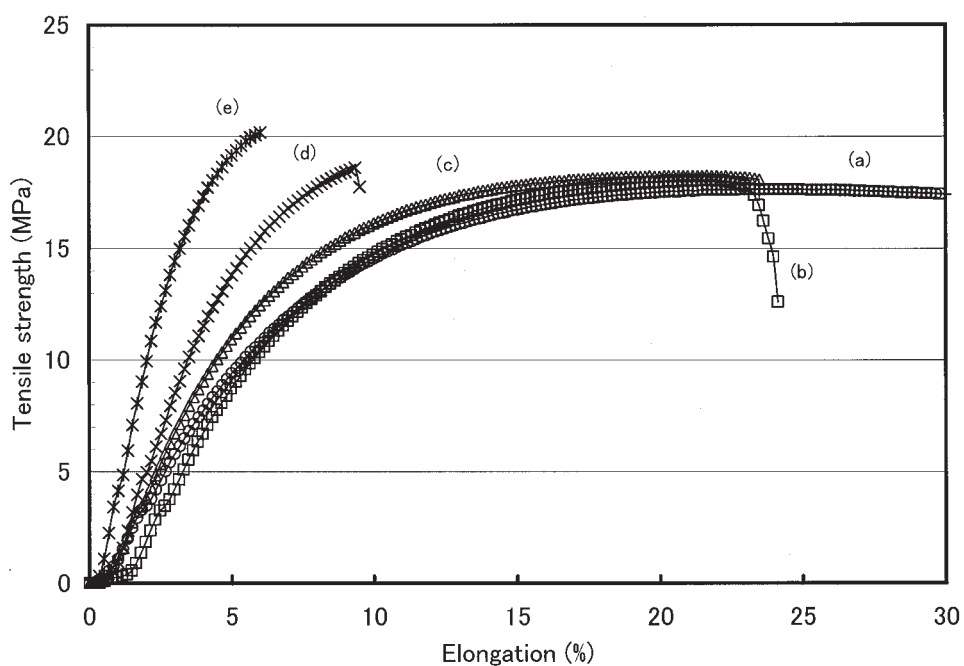
A proposed reaction mechanism for the formation of chemical bonds between MPE and Clay can be expressed as shown in Scheme 1.



**Scheme 1**



**Figure 5** SEM micrographs of the composites of MPE and Clay: (1) 90 wt % MPE and 10 wt % Clay, (2) 80 wt % MPE and 20 wt % Clay, (3) 60 wt % MPE and 40 wt % Clay, and (4) 40 wt % MPE and 60 wt % Clay.



**Figure 6** Tensile properties of the composites: (a) 100 wt % MPE, (b) 90 wt % MPE and 10 wt % Clay, (c) 80 wt % MPE and 20 wt % Clay, (d) 60 wt % MPE and 40 wt % Clay, and (e) 40 wt % MPE and 60 wt % Clay.



**Figure 7** Photographs of composite plate samples (150 mm  $\times$  150 mm  $\times$  3 mm): 100 wt % MPE (on the left) and 80 wt % MPE and 20 wt % Clay (on the right).

However, as there were adjacent groups of hydrolysis derivatives ( $1713\text{ cm}^{-1}$ ) in these areas, it was necessary to assign them carefully. It was not clear that the esterification between MPE and Clay had occurred in the composite samples with Clay concentrations of 40 and 60 wt % because of the laxness of the absorption at  $1735\text{ cm}^{-1}$ .

On the other hand, scanning electron microscopy (SEM) showed that a chemical reaction between MPE and Clay took place. The fractures of the MPE–Clay composite samples showed many ripped filamentous remains on the particle surfaces with Clay concentrations of 10, 20, 40, and 60 wt % (Fig. 5). All the composite samples revealed strong adhesion between the Clay particles and their surrounding MPE matrix in the composites.<sup>9</sup>

### Mechanical properties as floor tiles

Stress–strain curves of the MPE–Clay composites containing 10, 20, 40, and 60 wt % Clay are shown in

Figure 6. The elongation of the composites decreased significantly with an increase in the Clay concentration. The composites containing 10 or 20 wt % Clay [Fig. 6(b,c)] exhibited almost the same tensile strength as 100 wt % MPE but different elongations and toughnesses.

Increasing the Clay concentration above 20 wt % caused the tensile strength of the composite to increase more than that of the low-Clay-concentrations composites, but the difference was not remarkable. It was thought that a sufficient chance for adhesion might not have occurred with a high concentration of Clay and a shortage of maleated groups in MPE.

On the basis of laboratory experiments, larger composite samples were made as floor tiles with a compression-molding machine and an injection-molding machine. The sample size was 150 mm  $\times$  150 mm  $\times$  3 mm. The exterior appearance of the samples is shown in Figure 7. The left figure is a 100 wt % MPE tile with a white, smooth surface; the right figure is a dark-brown composite sample with 20 wt % Clay with a striping surface that was made during injection molding by the heterogeneous temperature distribution in the machine.

The characteristics of the MPE–Clay composites were measured according to test methods.<sup>5</sup> From a practical standpoint, the Japan Standard Society defines variables for floor-covering tiles: the dent, the rate of dent residual, the rate of length change after heating, the rate after water dipping, and the rate of weight decrease after heating.<sup>10</sup>

Table II shows the results for the samples from the injection-molding method, and Table III shows the results for the samples from the compression method.

The composites with Clay concentrations of 10, 20, and 40 wt % reached the standard, except for two variables: the dent at 23°C and the rate of length change after heating. These composites seemed to be a

**TABLE II**  
Characteristics of the MPE–Clay Composite as a Floor Tile: Injection-Molding Method

	Unit	Sample				Reference
		MPE 100	MPE 90/ Clay 10	MPE 80/ Clay 20	MPE 60/ Clay 40	
Dent at 23°C	mm	0.078	0.066	0.065	0.03	>0.15
Dent at 45°C	mm	0.163	0.096	0.103	0.13	<0.8
Rate of dent residual at 23°C	%	1.71	1.13	1.02	0.96	<8.0
Rate of length change after heating	%					
MD		0.30	0.21	0.42	0.51	<0.20
TD		0.33	0.05	0.18	0.30	
Rate of length change after water dipping	%					
MD		0.03	0.05	0.03	0.02	<0.20
TD		0.02	0.03	0.02	0.01	
Rate of weight decrease after heating	%	0.007	0.055	0.067	0.084	<0.5

Reference = JIS A 5705-1998, (Floorcovering—PVC), MD = resin-flow direction in the injection-molding machine; TD = direction 90° to MD.

**TABLE III**  
**Characteristics of the MPE—Clay Composite as a Floor Tile: Compression-Molding Method**

	Unit	MPE 100	MPE 90/ Clay 10	MPE 80/ Clay 20	Reference
Rate of length change after heating	%	0.73	0.62	0.71	<0.20
		0.75	0.52	0.74	

Reference = JIS A 5705-1998, (Floorcovering—PVC); upper: one direction; under: direction 90° to the other.

little harder at room temperature than at the floor-heating temperature in winter.

Also, anisotropic differences were observed for the rate of length change after heating. In Table II, MD is the machine direction, and TD is the transfer direction. When the injection-molding machine made the composite sample, anisotropic differences could occur. As shown in Table III, there were no differences between MD and TD when the compression-molding machine made the sample.

### CONCLUSIONS

The waste of drilling mud water, cuttings, and other wastewater, including rain water and floor-washing water, should be treated properly to protect the global environment. This is the responsibility of many oil-developing companies and even the organizations operating scientific ships drilling deep sea beds in the future.

Recently, much research has been conducted for developing new organic–inorganic complex materials, especially with polymers such as PE as organic substances and clay as an inorganic substance.

New composites with the advantages of both organics and inorganics have been developed through the mechanochemical surface modification of the materials.

In this study, we have demonstrated composites of MPE and Clay (waste from a drilling plant) and have proposed that these composites are applicable to floor tiles corresponding to Japanese standards.

The first aim of our experiments was to modify, from hydrophobic to hydrophilic, PE surfaces, even

partially, and to compound both materials mechano-chemically.

Furthermore, Clay, which we chose as an inorganic substance, has much BaSO<sub>4</sub> originally and seems to be applicable as a sound insulator because of its heavy weight. It is the next challenge for making new complex materials in the future.

### APPENDIX

The components of the typical mud (KCl lignate mud water) used for earth drilling and made by the mud company are as follows: tap water (100), KCl (7), KOH (0.3), bentonite (2), BaSO<sub>4</sub> (120), lignin sulfonic acid chromate (4), polymer (carboxy methyl cellulose, xanthan gum; 0.5), and Revdust (cuttings; 10; weight basis).

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