An Organic/Inorganic Hybrid Layered Polymer: Methacrylate–Magnesium(Nickel) Phyllosilicate

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Reaction of a silicon trialkoxide with magnesium or nickel chloride leads to a new polymer in which organic side chains are linked to a phyllosilicate-like framework through Si–C covalent bonds.

SiO_4 tetrahedral sheets and $M(OH)_2O_4$ (M = Mg or Ni) form a phyllosilicate mineral similar to smectite or mica [Fig. 1(*a*)]. Increasing pH causes Mg^{2+} (or Ni^{2+}) gelation and formation of hydroxides. When a Si^{4+} cation or a silicon tetraalkoxide is combined with Mg^{2+} (or Ni^{2+}) Si–O–Mg(Ni) bonds were also formed besides Si–O–Si and Mg(Ni)–O–Mg(Ni) bonds under appropriate pH conditions.[1] A phyllosilicate, as smectite, mica or kaolin, was formed by gelation followed by hydrothermal treatment. It had been presumed that a silicon trialkoxide containing an organic chain with an Si–C bond could not generate a phyllosilicate structure due to an inadequacy of bonding sites around the Si. We however, found that a layered structure formed without formation of tetrahedral sheets by use of silicon trialkoxides.

We made a new layered polymer [Fig. 1(*b*)] composed of an inorganic framework controlled to form a lamellar structure, and organic chains with methacrylic groups arranged in a two-dimensional manner on the inorganic framework. The inorganic lamellar framework has a phyllosilicate structure similar to mica or smectite consisting of two sheets of SiO_4 tetrahedra and a sheet of magnesium or nickel octahedra between them; each silicon atom at the centre of a tetrahedron is linked to the organic chain by a Si–C covalent bond.

2.73 g of 3-methacryloxypropyltrimethoxysilane (MPTS); $H_2C{=}CHMe\text{-}CO\text{-}O(CH_2)_3Si(OMe)_3$ and magnesium chloride hexahydrate (1.68 g) or nickel chloride hexahydrate (1.96 g) were dissolved in 50 ml of methanol. This solution was mixed with 200 ml of 0.05 mol dm^{-3} sodium hydroxide to form a gel. The obtained suspension was aged for 24 h at room temp., then filtered and washed with distilled water and dried in vacuum at room temp. A white powder of methacrylate–magnesium phyllosilicate or a green powder of methacrylate–nickel phyllosilicate were obtained. The samples were studied by X-ray powder diffraction (XRD), infrared (IR) absorption spectroscopy and transmission electron micrography (TEM).

XRD patterns of the methacrylate–nickel phyllosilicate and the methacrylate–magnesium phyllosilicate are shown in Fig. 2. A typical pattern for the 2 : 1 nickel–phyllosilicate, which was synthesized under hydrothermal conditions[1] in the absence of an organic compound, is also shown in Fig. 2(*a*). Although peaks in patterns of the methacrylate phyllosilicates are broad due to non-hydrothermal treatment, they are similar to that of the 2 : 1 nickel–phyllosilicate. As listed in Table 1, peaks at *ca.* 60° were indexed as 06, 33 for a trioctahedral type smectite structure, and *d*-values of asymmetrical peaks at *ca.* $2\theta = 40°$ agree with those of 13, 20 for smectites.[2] Peaks at $2\theta \approx 7°$, indexed to 001, indicated a layered structure with 1.8 nm basal spacing. The basal spacing of 2 : 1 nickel–phyllosilicate is 1.0 nm. The larger value of the basal spacing indicates the existence of organic chains in the interlayer spaces. These facts suggested that methacrylate phyllosilicates have a smectite-like structure with incorporation of organic chains. Broad peaks observed at 20°, are considered to have their origin in both 13, 20

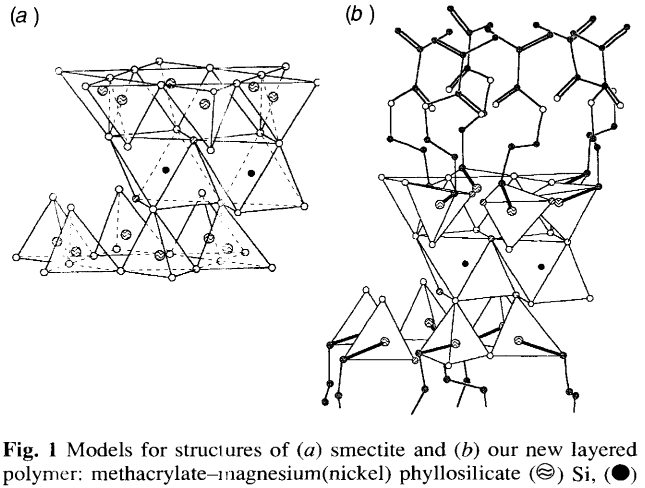

Fig. 1 Models for structures of (*a*) smectite and (*b*) our new layered polymer: methacrylate–magnesium(nickel) phyllosilicate (⊜) Si, (●) Mg (or Ni), (○) O, (▨) OH, (⊛) C

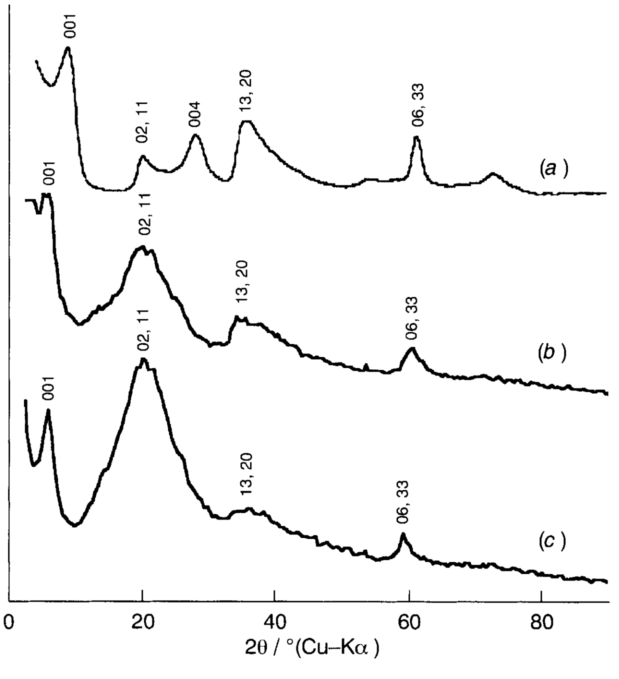

Fig. 2 X-Ray powder diffraction patterns (Cu-Kα) of (*a*) the 2 : 1 nickel–phyllosilicate, (*b*) methacrylate–nickel phyllosilicate and (*c*) methacrylate–magnesium phyllosilicate

Table 1 Non-basal diffractions from smectites[2] and methacrylate phyllosilicates; spacings in nm

hk indices	Saponite *d*	2 : 1 Ni–phyllosilicate *d*	Methacrylate–Ni phyllosilicate *d*	Methacrylate–Mg phyllosilicate *d*
02, 11	0.451	0.449	0.45	0.45
13, 20	0.258	0.258	0.26	0.26
06, 33	0.152	0.152	0.155	0.157

diffractions of a phyllosilicate and reflections from organic chains.

The IR spectra of MPTS (*a*) and methacrylate–magnesium phyllosilicate (*b*) are shown in Fig. 3. Absorption bands at 2950 (CH_2), 1720 (C=O), 1640 (C=C) and 1180 cm^{-1} (Si–C)[3] in the spectrum for methacrylate–magnesium phyllosilicate indicate that the methacrylic group in the organic chains linked to Si atoms were retained in the polymer without any chemical change during synthesis. Vibration bands of the $(Si_2O_5)_n$ layer in magnesium phyllosilicates[4] at 1040 and 1014 cm^{-1}, and a Mg–O vibration band[4] at 535 cm^{-1} which is observed for talc[5] indicates a magnesium phyllosilicate like structure in the hybrid polymer.

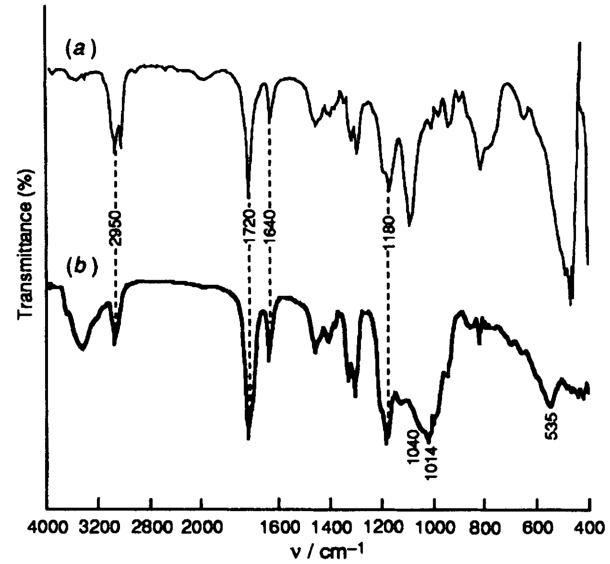

Fig. 3 An infrared spectrum of (*a*) 3-methacryloxypropyltrimethoxysilane (MPTS) and (*b*) the methacrylate–magnesium phyllosilicate

A transmission electron micrograph of the methacrylate–magnesium phyllosilicate also suggests a layered structure.

These results confirm that the new polymer has a smectite-like structure as shown in Fig. 1(*b*). However, Si–C bonds make the normal formation of SiO_4 tetrahedral networks in the sheets difficult. Therefore it is considered that the polymer had a well-ordered octahedral sheet and slightly disordered $-C-SiO_3$ tetrahedral sheets. This suggested that the formation of the tetrahedral sheets was not essential to growth of a smectite-type phyllosilicate crystal and that growth of the octahedral sheet dominated formation of the layered structure silicate. The arrangement of the organic groups caused by hydrophobic interactions might also promote the formation of their two-dimensional arrangement.

The new layered polymer is not only interesting as a material with a new structure, but also of use in the study of the defect structures in silicates and inorganic crystals growing under the influence of an organic substance.

Received, 3rd October 1994; Com. 4/06014H

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