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Hybrid lamellar nanocomposites based on organically functionalized magnesium phyllosilicate clays with interlayer reactivity

Nicola T. Whilton, Sandra L. Burkett† and Stephen Mann*

Department of Chemistry, University of Bath, Bath, UK BA2 7AY

A series of layered magnesium phyllo(organo)silicate nanocomposites that contain covalently linked organic functionalities have been prepared by a one-step, direct synthesis procedure. Organoclays with allyl, epoxy, imidazole or ethylenediamino functionalities were synthesized and characterized by XRD, TEM, FTIR and solid state ^{29}Si and ^{13}C NMR spectroscopy. The epoxy-functionalized nanocomposite undergoes *in situ* cross-linking reactions with *m*-phenylenediamine to produce a polymer–inorganic lamellar hybrid, as well as ring-opening reactions with methyl thioglycolate to give a covalently linked hydroxysulfide derivative. The ethylenediamino-functionalized magnesium phyllo(organo)silicate showed good binding capacity for aqueous Co^{II}.

Recently, several reports have shown how ordered inorganic materials can be prepared under non-hydrothermal conditions by biomimetic template synthesis using self-organized assemblies of organic molecules.[1] Most notably, work utilizing liquid crystal and surfactant assemblies has been an active area of research.[2] By combining this templating approach with a reaction strategy based on co-condensation of tetraethoxysilanes and alkyltrialkoxysilanes, hexagonally ordered, covalently linked organo-silica-surfactant mesophases have been prepared.[3] Post-synthesis removal of the surfactant template afforded organo-functionalized materials with ordered mesoporosity.

Reports have recently illustrated how a similar approach using organotrialkoxysilanes can be employed to produce layered organoclay structures with organophilic functionalities occupying the interlayers.[4–6] It seems reasonable to propose that the use of organotrialkoxysilanes in this way could be of general use for the synthesis of chemically-functionalized organized inorganic matter provided that appropriate templates and directing agents can be established. We are currently investigating the one-step direct synthesis of ordered organo-functionalized magnesium clays with lamellar structures analogous to the 2 : 1 trioctahedral phyllosilicates (smectites). The parent inorganic structure, talc [$Si_8Mg_6O_{20}(OH)_4$], consists of 9.6 Å thick layers constructed from a central sheet of octahedrally coordinated magnesium oxide/hydroxide chains (brucite sheets) overlaid on both sides with a tetrahedrally coordinated silicate network (Fig. 1). It has been proposed that the brucite sheets, which form by two-dimensional condensation, act as incipient templates for the subsequent condensation of the silicate layers.[7] This seems feasible as there is good epitaxial matching at the brucite–silicate interface and appropriate chemical reactivity in the surface O/OH groups of the hydroxide framework. We therefore investigated the possibility of replacing the silicate sheets with a range of functionalized organosilicate moieties by co-assembling the brucite framework in the presence of organotrialkoxysilanes. In this system, the hydrophobic interactions between adjacent organic moieties and resulting microphase separation should also facilitate the formation of the lamellar structures.[5,8]

In this paper, we describe the synthesis, characterization and reactivity of a range of covalently linked inorganic–organic lamellar nanocomposites based on the magnesium phyllo(organo)silicate structure with approximate composition, $Si_8R_8Mg_6O_{16}(OH)_4$.The functionalized organoclays were synthesized at room temperature from ethanolic solutions containing $MgCl_2$ and organotrialkoxysilanes $(R^*O)_3Si{-}R$; R* = Me, Et) such as glycidylpropyltrimethoxysilane [$R = {-}(CH_2)_3OCH_2CH(O)CH_2$, epoxy, EPTMS], 3-(2-aminoethyl-3-aminopropyl)trimethoxysilane [$R = {-}(CH_2)_3NH(CH_2)_2NH_2$, ethylenediamino, EDTMS], 1-propenyltrimethoxysilane ($R = {-}CH_2CHCH_2$, allyl, ALTMS), and dihydrotriethoxysilylpropyl-1*H*-imidazole [$R = {-}(CH_2)_3$-$NCHNCH_2CH_2$, imidazole, ITES]. The resultant magnesium (organo)phyllosilicates are described with the prefix Mg- (*e.g.* Mg-EPTMS for the epoxide-containing organoclay).

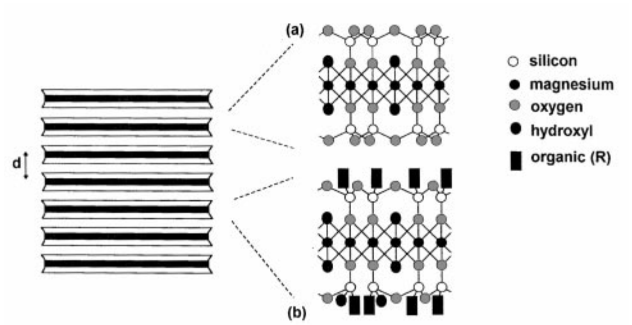

Fig. 1 Schematic representation of the layered structures of (a) 2 : 1 trioctahedral phyllosilicate (talc) [$Si_8Mg_6O_{20}(OH)_4$] and (b) magnesium phyllo(organo)silicates [$Si_8R_8Mg_6O_{16-x/2}(OH)_{4+x}$]; in this example, $x = 2$ to illustrate that not all of the organosiloxane centers are completely condensed

Experimental

Synthesis of magnesium phyllo(organo)silicates

ALTMS, ITES, EPTMS and EDTMS were obtained from Apollo Sci. Ltd. All compounds were used as received. The organotrialkoxysilane (11.1 mmol) was added to a stirred solution of $MgCl_2 \cdot 6H_2O$ (1.68 g, 8.3 mmol) in ethanol (50 ml). Sodium hydroxide solution (200 ml, 0.05 M, 10 mmol) was added quickly and the white suspension stirred for 24 h at room temperature. The precipitated white solid was isolated by centrifugation, washed with water (3 × 50 ml) and ethanol (1 × 50 ml) and dried at 65 °C in air.

An ethylenediamino-functionalized magnesium phyllo (organo)silicate clay was also prepared in ethanol at neutral pH without the addition of NaOH. 3-(2-Aminoethyl-3-amino-

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†Current address: Department of Materials Science, Massachusetts Institute of Technology, Cambridge, MA 02139, USA

propyl)trimethoxysilane (11.1 mmol) was added to a stirred solution of $MgCl_2 \cdot 6H_2O$ (1.68 g, 8.3 mmol) in ethanol (50 ml). The resultant light-yellow suspension was stirred at room temperature for 24 h before isolation of the product by repeated centrifugation with washing (3 × 50 ml) and drying at 65 °C in air. The pH of the reaction mixture remained around 7.6 for the duration of the reaction period.

Crosslinking reactions in epoxy-functionalized clays

Mg-EPTMS (0.3 g, 0.15 g epoxide residues) was ground with *m*-phenylenediamine (*m*-PDA) (0.02 g, ≈14 wt.% of clay organics) and stirred for 30 min. Under vacuum the mixture was heated at 70 °C for 30 min before raising the temperature to 125 °C for 4 h. The clay product was isolated by thorough washing with ethanol (3 × 10 ml) and H_2O (3 × 10 ml).

Reaction of epoxy-functionalities with methyl thioglycolate

Dry THF (18 ml) was added to a nitrogen-purged flask charged with Mg-EPTMS (0.22 g, *ca.* 1.0 mmol epoxy residues) and anhydrous K_2CO_3 (0.69 g, 5.0 mmol). Methyl thioglycolate (0.4 ml, 4.0 mmol) was added with stirring under nitrogen and the resultant mixture refluxed at 70 °C for 24 h. The clay component was isolated by washing with THF (2 × 50 ml) and H_2O (3 × 20 ml), and dried under nitrogen at 50 °C.

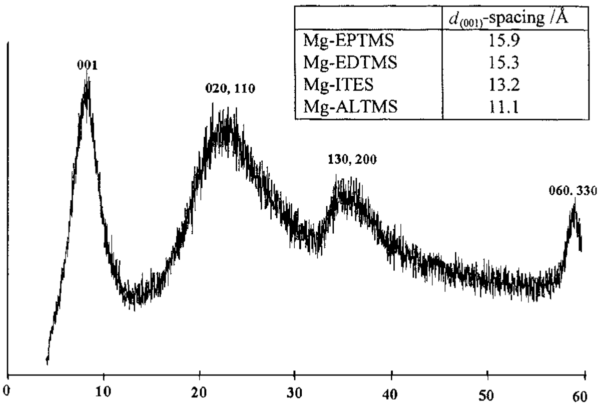
Characterization

X-Ray powder diffraction (XRD) data were collected on a Phillips PW1130 diffractometer using Cu-Kα radiation ($\lambda = 1.5405$ Å). FTIR spectra were recorded on samples pressed into KBr discs using a Nicolet 51OP FTIR spectrophotometer. Electron microscopy and EDX analysis was performed on ground samples, dispersed by sonication in ethanol or water, using a JEOL 1200EX microscope with attached scanning imaging device. Thermal analyses of powdered samples up to temperatures of 1000 °C were carried out at a ramp rate of 10 °C min^{-1} in flowing N_2 using a Netzsch combined TGA/DSC analyser. Organic contents were calculated from the C:N ratio obtained from microanalyses of the samples performed on a Varian AA-275 Series spectrophotometer.

Solid state NMR studies were performed at ambient temperature using a Varian Unityplus 300 spectrophometer, fitted with a Doty Scientific MAS probe. Spectra were referenced to an external sample of tetramethylsilane (TMS). Deconvolution of the spectra was performed using Varian software. Typically, ^{29}Si MAS NMR spectra were recorded at 60 MHz, with a relaxation delay of 300 s, and for 300 cycles. Direct polarisation (DP) experiments were performed with a pulse angle of 90 degrees and a spin rate of approximately 4.5 kHz. For ^{13}C MAS NMR studies, a frequency of 75.4 MHz with a relaxation delay of 1–2 s and CP time of 1 ms, were used. Non-quaternary suppression experiments were employed with the insertion of a dephasing pulse (typically 40 μs) during which the decoupler was turned off prior to acquisition.

Results and Discussion

Although the carbon, hydrogen and nitrogen analyses of the epoxy-(Mg-EPTMS) and allyl-functionalized (Mg-ALTMS) organoclays correlated closely with the idealized 2:1 trioctahedral phyllosilicate structural composition [$Si_8R_8Mg_6O_{16}(OH)_4$], organic contents for the imidazole-(Mg-ITES) and ethylenediamino-containing (Mg-EDTMS) materials were lower than expected, suggesting an increased number of defects in these structures.[9] The powder X-ray diffraction patterns of the synthesized magnesium organosilicates exhibited a broad basal peak and three broad higher angle in-plane reflections (Fig. 2). Each sample showed an in-plane reflection at $2\theta = 59°$ ($d = 1.56$ Å) that was characteristic of the (060) reflection in smectites.[10,11] Together, the data were consistent with a 2:1 trioctahedral phyllosilicate structure. In each case, the basal $d_{(001)}$ interlayer separation was expanded compared to the talc parent structure [$d_{(001)} = 9.34$ Å (ref. 12)], indicating that the organic functionalities were present within the interlayer spaces. Although the $d_{(001)}$ spacings were proportional to the length of the organic functionalities, they were too small to accommodate an ordered bilayer arrangement but consistent with an alternating or interdigitated monolayer between the inorganic sheets. The broadness of the in-plane peaks was consistent with either a disordered inorganic framework or a turbostratic arrangement of stacked crystalline plates, or both.



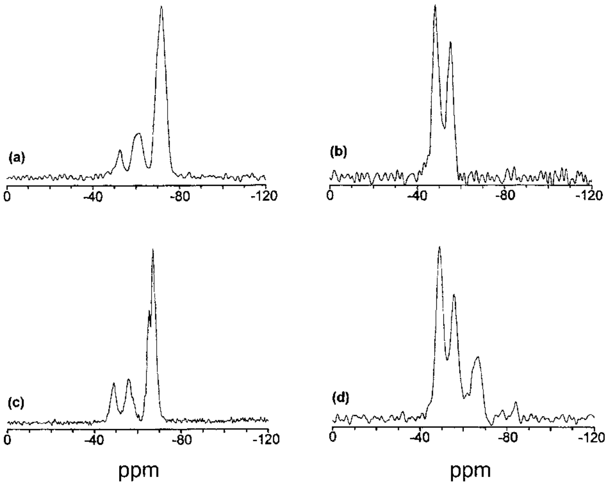
	$d_{(001)}$-spacing /Å
Mg-EPTMS	15.9
Mg-EDTMS	15.3
Mg-ITES	13.2
Mg-ALTMS	11.1

Fig. 2 XRD pattern for Mg-ALTMS. The pattern, which is typical for the synthesized magnesium organosilicates, is indexed according to the 2:1 trioctahedral phyllosilicate structure of talc. Inset shows values of the interlayer spacings (d_{001}) for the synthesized materials.

The integrity of the organic functionalities and retention of the Si—C bond under the synthesis conditions was confirmed by FTIR and solid state ^{13}C CP MAS NMR spectroscopy. In each case, characteristic absorptions from the organic functionalities[13] and the inorganic framework[14] were observed in FTIR spectra. Assignments in the ^{13}C CP MAS NMR spectra were consistent with intact, unreacted organic functionalities.[15] Significantly, the epoxide ring in Mg-EPTMS was retained as shown by the sharp ether (δ 73 and 72) and epoxide (δ 51 and 44) carbon resonances of the epoxypropoxypropyl side chains of the functionalized siloxane. Relatively narrow line widths indicated mobility of the organic groups within the interlayer regions.

Solid state ^{29}Si DP MAS NMR spectroscopy indicated that for each of the magnesium phyllo(organo)silicates prepared, condensation of silicon centres onto the brucite framework was incomplete (Fig. 3).[16] Silanol-containing T^1 and T^2 as well as fully condensed T^3 species were observed for all samples except the ethylenediamino-containing sample, which showed only T^1 and T^2 resonances[17] [$T^n = RSi(OMg)(OSi)_{n-1}(OH)_{3-n}$]. This was probably due to the geometric strain generated at the inorganic–organic interface or slow condensation kinetics of the functionalized organotrialkoxysilanes, or both. In addition, the T^2 centres might originate from significant numbers of edge sites present in samples with small particle size. Quantitative evaluation of the silanol content [$Si_8R_8Mg_6O_{16-x/2}(OH)_{4+x}$, where x indicates the number of silanol groups] was not determined, although such data can be obtained from variable contact time studies which correct for differences in the magnetization rates of different silanol species.[6]

The results indicate that both the inter- and intra-layer regions of magnesium organosilicates prepared with epoxy, ethylenediamino, imidazole or allyl functionalities contain significant structural disorder. This is not surprising because



	T^1	T^2	T^3
a Mg-ALTMS	-52 (8 %)	-61 (21.5 %)	-72 (70.5 %)
b Mg-EDTMS	-49 (58.2 %)	-56 (41.8 %)	-
c Mg-EPTMS	-49 (13.6 %)	-56 to -60 (18.5 %)	-65 to -68 (67.9 %)
d Mg-ITES	-49 (43.6 %)	-56 (34.5 %)	-66 (21.9 %)

Fig. 3 ^{29}Si CP MAS NMR spectra for (a) Mg-ALTMS, (b) Mg-EDTMS, (c) Mg-EPTMS and (d) Mg-ITES organoclays. Chemical shifts (ppm) for T^n resonances [$T^n = RSi(OMg)(OSi)_{n-1}(OH)_{3-n}$] and approximate percentage contents are also listed. Shifts are measured relative to tetramethylsilane at 0 ppm.

condensation of the trialkoxysilanes onto the regular lattice of the trioctahedral sheet will result in significant strain. In particular, accommodation of the organic functionalities within the gallery space will be governed in part by packing constraints which in turn influence the epitaxial mismatch that can be tolerated at the interface of the brucite and organosilicate layers. Furthermore, replacing the four-oxygen bridged Si centres of the smectite parent structure, with T^n ($n = 1$–3) centres reduces the connectivity of the brucite framework to produce substantial puckering of the inorganic sheets within the hybrid structure.[4,5]

Ethylenediamino-functionalized magnesium phyllo(organo)silicates

The effect of pH on the synthesis of the ethylenediamine-containing magnesium organosilicate was studied by preparing samples from an ethanolic solution at neutral pH without the addition of aqueous base. The resultant XRD pattern of the isolated product was indexed as a 2:1 trioctahedral phyllosilicate structure with an interlayer spacing of 18.5 Å, which was 3.3 Å greater than the corresponding Mg-EDTMS prepared under predominantly aqueous conditions at high pH (Fig. 4). EDX analysis detected the presence of chloride in the sample prepared at neutral pH, suggesting that the increased interlayer spacing was due to the intercalation of counter ions within the lamellar nanocomposite. Indeed, FTIR spectroscopy showed characteristic absorptions from both protonated primary and secondary amines.[18] This was also consistent with the solid state ^{13}C CP MAS NMR spectrum which showed resonances that were slightly different in chemical shift compared to those from the base-synthesized Mg-EDTMS organoclay.[18]

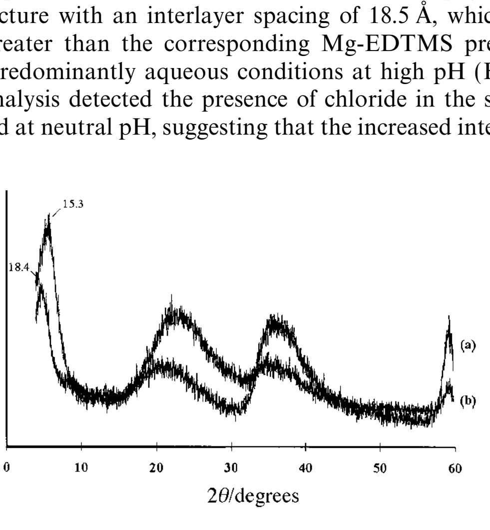


Fig. 4 XRD patterns for Mg-EDTMS organoclays prepared from (a) aqueous solution, pH 12, and (b) ethanol at pH 7.6

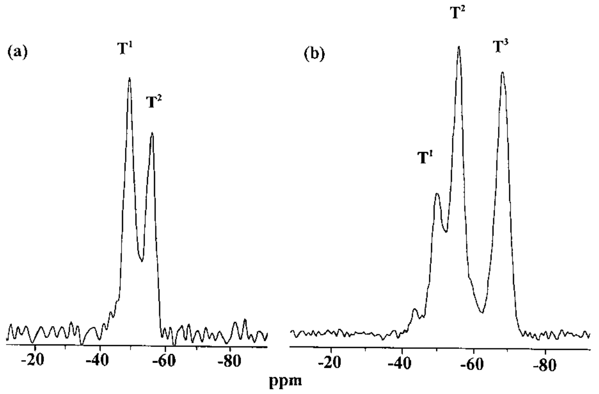


Fig. 5 ^{29}Si CP MAS NMR spectra for (a) Mg-EDTMS synthesized from water–ethanol mixtures at pH 12, and (b) Mg-EDTMS synthesized ethanolic solutions at pH 7.6. Chemical shifts are given relative to tetramethylsilane at 0 ppm. $T^n = RSi(OMg)(OSi)_{n-1}(OH)_{3-n}$.

In contrast to the Mg-EDTMS organoclay prepared at pH 12, the ^{29}Si NMR spectrum of the sample synthesized at pH 7.6 showed the presence of fully condensed T^3 silicon centres (Fig. 5). Under alkaline conditions, the rate of hydrolysis of organotrialkoxysilanes is slow relative to condensation,[19] and formation of Si—O—Mg and Mg—OH—Mg bonds is promoted.[20] The lower degree of condensation in the ethylenediamine-functionalized organoclay prepared at high pH suggests that the organotrialkoxysilane molecules are rapidly self-assembled on preorganized brucite lamellae with the consequence that the covalently linked moieties are sterically constrained. The extent of in-plane condensation is increased in the corresponding hybrid synthesized at neutral pH, presumably because formation of the brucite sheet is retarded such that a significant degree of intermolecular condensation occurs prior to coupling onto the inorganic framework. Depending on the relative rates of these two processes, formation of the layered hybrid could be dominated by self-organization of partially condensed organoalkoxysilane molecules that act as organic templates for brucite assembly.[6] Alternatively the process could involve the cooperative assembly of inorganic and organic components similar to that described for the synthesis of silica–surfactant mesophases.[2] In each case, hydrophobic interactions between the organic functionalities are likely to be a key aspect of the assembly process, as well as playing an important role in the stabilization of the highly disordered structure of the lamellar nanocomposite.

In principle, the ethylenediamino-functionalized organosilicate consists of organized arrays of potential metal-ion binding sites that might be useful in processes requiring high-capacity ion-selective sequestration. The ion-binding properties of Mg-EDTMS were investigated by incubation of the organoclay in an aqueous solution of $CoCl_2$ for 24 h. The initially white clay rapidly changed colour to yield a mauve solid after isolation. The presence of cobalt was confirmed by EDX analysis (Fig. 6) and FTIR spectroscopy showed a shift in the 1597 cm^{-1} primary amine bending mode to a value of 1630 cm^{-1}, consistent with metal-ion complexation.[21] The XRD pattern showed a lowering in the intensity of the diffraction peaks but no change in basal spacing. Further work is in progress to determine the ion-exchange capacities and metal-ion selectivities of the ethylenediamino moieties present in the gallery spaces of the Mg-EDTMS organoclay.

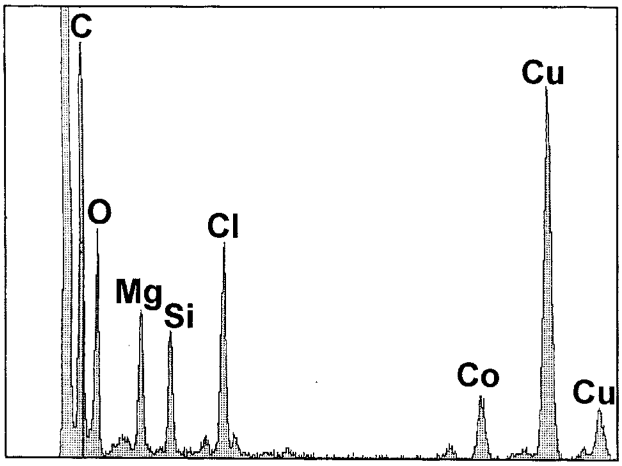


Fig. 6 EDX spectra showing the presence of Co binding in a Mg-EDTMS organoclay

Reactivity of epoxy-functionalized magnesium phyllo(organo)silicate

The epoxide-containing organosilicate, Mg-EPTMS, was used as a precursor for the synthesis of a polymer–inorganic lamellar nanocomposite. This was achieved through *in situ* crosslinking of the epoxide groups by dry thermal heating of ground samples in the presence of a curing agent, *m*-phenylenediamine (*m*-PDA), for 4 h at 125 °C. The product gave rise to broad XRD reflections that were indexed to the 2:1 trioctahedral phyllosilicate structure with an interlayer spacing of 17.9 Å. The broadness of the peaks and intensity of the (001) reflection were comparable with those of the unheated material, but the $d_{(001)}$ value was increased by 2 Å. The interlayer spacing was also 1.6 Å larger than that determined for a Mg-EPTMS sample heated under identical conditions but in the absence of *m*-PDA. ^{29}Si DP MAS NMR showed no significant changes in the T^n resonances except for a small decrease (0.5%) in the T^1 component indicating further condensation of the silicon centres. However, corresponding ^{13}C CP MAS NMR spectra showed extensive line broadening, particularly for the ether-carbon resonances, when the organoclay was heated in the presence of the curing agent (Fig. 7). This suggests a decreased mobility of the organic moieties in the 8.3 Å (17.9 [interlayer spacing] −9.6 [2:1 clay layer]) wide gallery space and is consistent with the formation of a relatively rigid network upon crosslinking of the epoxide residues. Although non-broadened epoxide resonances at δ 44 and 51 were observed in the spectrum, they were of significantly lowered relative intensities. The use of non-quaternary suppression, which for a completely rigid lattice would detect only quaternary carbons in the NMR spectrum, revealed the presence of mobile epoxide groups, whilst the corresponding difference spectrum showed intense broad peaks for the ether group but no evidence for rigid epoxide carbons (Fig. 7, inset). Overall, the data indicate that the heat-treated/cured organoclay contained both unreacted and crosslinked epoxide groups within the interlayer regions of the organosilicate nanocomposite. Although there was only a marginal increase in the interlayer spacing and no significant structural modification of the polymer–inorganic hybrid, thermogravimetric analysis showed an increased thermal stability with the main exotherm occurring at 450 °C, compared with 390 °C for the as-synthesized Mg-EPTMS organoclay (Fig. 8).

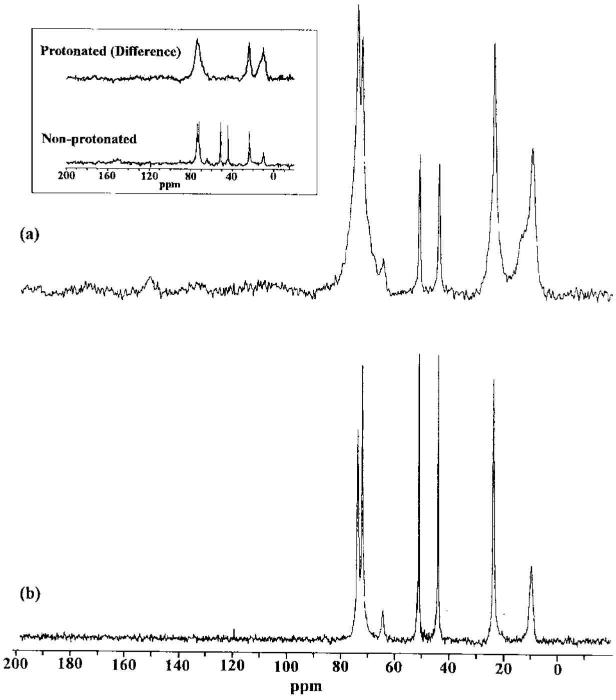


Fig. 7 ^{13}C CP MAS NMR spectra of (a) heat-treated Mg-EPTMS in the presence of *m*-PDA, and (b) heat-treated Mg-EPTMS. Inset shows the results of a non-quaternary suppression experiment for (a). Sharp resonances in the non-protonated spectrum indicate organic group mobility. Broad resonances in the difference spectrum show the presence of immobilized organic groups.

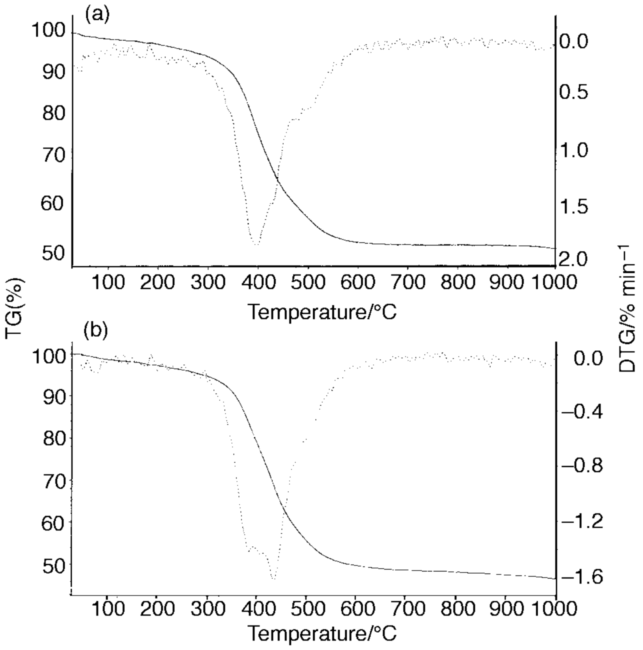
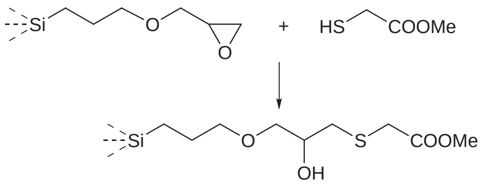


Fig. 8 Thermogravimetric analyses for Mg-EPTMS organoclay (top) and Mg-EPTMS clay treated with *m*-PDA cross-linking agent (bottom)

The reactivity of the covalently-linked epoxy functionality present within the gallery spaces was also investigated by undertaking a ring-opening reaction in the presence of a suitable organic nucleophile.[22] This was achieved by refluxing Mg-EPTMS at 70 °C for 24 h in THF with methyl thioglycolate, $[CH_3OC(O)CH_2SH]^{23}$ (Scheme 1) The XRD pattern of the product showed an extensively broadened basal reflection with significantly lower intensity than the unreacted Mg-EPTMS organoclay. However, other reflections of the 2:1 trioctahedral structure were unchanged. This indicates that intercalation of the nucleophilic species and reaction with the epoxy functionality result in increased disordering and disrup-



Scheme 1 Reaction between covalently linked epoxide and methyl thioglycolate

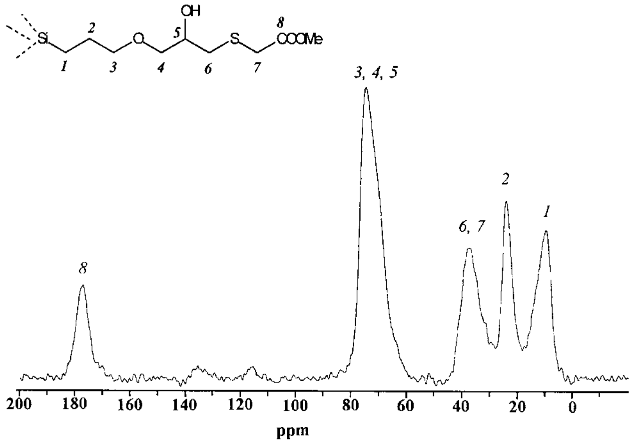


Fig. 9 ^{13}C CP MAS NMR spectrum for the product after reaction between Mg-EPTMS and methyl thioglycolate. The resonances are consistent with a ring-opened adduct within the interlayer space. The spectrum before reaction was similar to that shown in Fig. 7(b).

tion of the layered structure. ^{13}C CP MAS NMR confirmed the presence of a ring-opened hydroxysulfide derivative. All the carbon resonances, except for the methoxy group, could be assigned (Fig. 9).[23] No signals were observed for unreacted epoxide residues. The absence of the methoxy resonance suggests that saponification of the ester group to a carboxylic acid may have occurred. This was consistent with FTIR data which showed the presence of a carbonyl group at 1720 cm^{-1}.

The results illustrate the potential accessibility of the interlayer region to small organic molecules and the availability of covalently linked organic functionalities for *in situ* intermolecular reactions with guest species. In the case of the epoxy functionality, nucleophilic addition to give the hydroxysulfide derivative results in significant disordering of the interlayer periodicity, presumably because the gallery space is structurally disrupted by chain elongation. The NMR peaks were broad indicating a lower degree of mobility of the ring opened derivative compared with the unreacted epoxy-functionalized organosilicate.

Conclusions

A range of layered magnesium organosilicates with covalently linked organic functionalities can be synthesized *via* a simple low temperature route using water or ethanolic solutions at a high or neutral pH, respectively. The functionalized organoclays show long range disorder and chemical heterogeneity which is not surprising considering the potential for structural mismatch and discontinuity at the interface between the brucite and organosiloxane layers. However, the general applicability of the synthesis method used indicates that it should be possible to prepare a wide range of functionalized lamellar nanocomposites, including materials with covalently linked organometallic moieties. The scope for tailored chemical reactivity and physical properties remains to be determined, although the preliminary results described here and elsewhere[5] indicate that ion-binding, cross-linking, adduct formation and nanoparticle formation[5] are potential routes to derivatized lamellar nanostructures based on the magnesium phyllo(organo)silicate structure.

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8 An alternative proposal for this system involves a mechanism driven by the formation of a lamellar template of self-assembled silane triols. Binding of aqueous metal species to these negatively charged surfactant layers results in condensation with the silanol hydroxyl groups and formation of the magnesium (organo)phyllosilicate structure (see ref. 6 for details).

9 C,H,N microanalysis. Calculations based on $Si_8R_8Mg_6O_{16}(OH)_4$; Mg-EPTMS Calc.: C, 35.7; H, 5.7. Found: C, 33.3; H, 6.0%. Mg-ALTMS Calc.: C, 28.2; H, 4.3. Found: C, 27.5, H, 4.4%. Mg-ITES Calc.: C, 36.4, H, 7.0, N, 14.2. Found: C, 22.1, H, 5.9; N, 5.5%, Mg-EDTMS Calc.: C, 32.4; H, 7.0; N, 14.2. Found: C, 16.8; H, 5.8; N, 6.5%.

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13 FTIR. Organic assignments (cm^{-1}). Mg-EPTMS: 1346 (CH epoxy), 1400–1450, 2850, 2937 (CH_2), 3000, 3100 (CH_2/CH epoxy). Mg-EDTMS: 1460 (CH_2), 1597 (NH_2), 2850, 2930 (CH_2), 3000–3600 (OH/H_2O, NH/NH_2). Mg-ITES: 1470 (CH_2), 1655 (N=C), 2850, 2920 (CH_2). Mg-ALTMS: 900 (CH_2 alkene), 950 (CH alkene), 1390 (CH_2 alkene), 1420 (CH_2), 1640 (C=C), 2850–2970 (CH_2), 3050 (CH alkene)

14 FTIR. Inorganic assignments (cm^{-1}). Mg—O (480), Si—O (550), Si—O—Si (1000–1120), Si—C (*ca.* 1200), O—H (adsorbed H_2O, Si—OH, 3200–3600), MgO—H (3700).

15 ^{13}C CP MAS NMR (75 MHz, TMS, 20 °C). Mg-EPTMS: δ 73.71, 72.08, 51.08, 44.04. 23.81, 13.20, 9.75. Mg-EDTMS: δ 49.00, 38.66, 23.19, 14.45. Mg-ALTMS: δ 132.41, 115.66, 20.81. Mg-ITES: δ 164.50, 50.18, 46.17, 39.74, 23.71, 14.61.

16 ^{29}Si DP MAS NMR (60 MHz, TMS, 20 °C). Mg-EPTMS: δ −49 (T^1, 13.6%), −56 to −60 (T^2, 18.5%), −65 to −68 (T^3, 67.9%). Mg-EDTMS: δ −49 (T^1, 58.2%), −56 (T^2, 41.8%). Mg-ITES: δ −49 (T^1, 43.6%), −56 (T^2, 34.5%), −66 (T^3, 21.9%). Mg-ALTMS: δ −52 (T^1, 8.0%), −61 (T^2, 21.5%), −72 (T^3, 70.5%). Peak intensities are not quantitative with mol% Si.

17 The lack of T^3 silicon centres in Mg-EDTMS is probably due to the slow condensation kinetics of amino-functionalized alkoxysilanes. The product of hydrolysis, the silanol species, may be stabilized through hydrogen-bonding between amine and hydroxyl groups and the rate of condensation is decreased (H. Ishida, C. H. Chiang and J. L. Koenig, *Polymer*, 1982, **23**, 251).

18 Data for Mg-EDTMS prepared under neutral pH conditions in ethanol. FTIR: organic assignments (cm^{-1}). 1466 (CH_2), 1570–1650 (NH_2^+, NH_3^+), 2100 (NH_3^+), 2600 (NH_2^+), 2850–2950 (CH_2), 3200–3500 (NH_3^+). ^{13}C CP MAS NMR (75 MHz, TMS, 20 °C): δ 49, 38, 23, 14. ^{29}Si DP MAS NMR

(60 MHz, TMS, 20 °C): δ −44 to −49 (T^1, 15%), −56 (T^2, 48%), 68 (T^3, 37%); C,H,N microanalysis calculated for $Si_8R_8Mg_6O_{16}(OH)_4$: Calc. C, 32.4; H, 7.0; N, 14.2%. Found: C, 26.1, H, 7.0; N, 10.9%.

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23 Physical properties of the hydroxysulfide moiety formed from reaction between Mg-EPTMS and guest thiolate molecules. FTIR (cm^{-1}): 480, 555, 1032, 1115, 1200, 1400, 1590, 1720, 2850, 2940, 3200–3600, 3740. ^{13}C NMR (75 MHz, TMS, 20 °C): δ 9.88, 24.06, 37.12(br), 74.08, 176.80. ^{29}Si DP MAS NMR (60 MHz, TMS, 20 °C): δ −48.7 (T^1, 12.7%), −55.6 (T^2, 24.1%), −66.8 (T^3, 63.2%).

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