JOURNAL OF MATERIALS SCIENCE 31 (1996) 3123–3127

Synthesis and characterization of novel polyacrylate-clay sol–gel materials

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Organo-functional silanes which were able to form chemical bonds with kaolinite and could also have an affinity to the materials of concern here, were studied by the sol–gel process. Polymethacrylate with trialkoxy silyl functional groups were prepared, hydrolysed and co-condensed with kaolinite. The progress of the hydrolysis, which proceeded very slowly, was followed by Karl–Fischer titration. Thermal behavior was investigated by differential thermal analysis. The extent of the reaction leading to network formation was qualitatively followed by Fourier transform–infrared spectroscopy and X-ray diffraction. Free-radical polymerization was carried out ultrasonically in the presence of a catalyst. Trimethoxy silane end-capped silane was found to be covalently bonded to kaolinite. The copolymers, with various amounts of kaolinite, were then hydrolysed and co-condensed in the presence of a catalyst to yield sol–gel materials which have a controllable combination of properties of both the polymer and kaolinite.

1. Introduction

The development of new materials with improved performance profiles has become an increasingly urgent requirement. Several applications of inorganic–organic sol–gel materials have been described elsewhere [1–5]. Incorporation of organic polymers into an inorganic matrix via covalent bonding is particularly interesting, because the new hybrid materials could have a controllable combination of properties of both the organic polymers and the inorganic matrix.

The chemical synthesis of gels is performed in organic solutions at lower temperatures than in conventional methods. Organic molecules, therefore, can be incorporated easily into an oxide gel matrix. The mild conditions offered by the sol–gel process make it attractive for application in the formation of composite materials [6, 7]. The most common approach involves dissolving a preformed oligomer or polymer in sol–gel solution and then allowing hydrolysis and condensation of the inorganic network to proceed. Under the appropriate conditions, the polymer remains uniformly embedded within the inorganic gel throughout the synthesis and drying steps.

One of the more important ways of improving polymer quality is through cross-linking, leading to an improvement in thermal dimensional stability and in the resistance to solvents, permanent deformation, etc. In addition to the casual cross-linking which hinders processability, the utilization of cross-linking by organo-functional silanes [6–9] increased after the introduction of the system.

This paper presents the synthesis of polyacrylate clay composites in which trialkoxy silyl functional groups were hydrolysed and co-condensed to afford a molecular composite of clay with polymer. A novel material was developed which was proved to be able to overcome most of the described problems.

Free-radical polymerization of trialkoxy silyl end-capped acrylate with ultrasound in the presence of an inert gas was carried out to yield polymers which have clay contents of 10, 50, 100 mol % wt/wt, respectively. Hydrolysis and co-condensation in the presence of an acid catalyst gave composites in which polymers were covalently bonded.

The extent of the reaction leading to network formation was qualitatively followed by Fourier transform–infrared spectroscopy (FT–IR), and X-ray diffraction (XRD) revealed that the silicate layers of the composite were uniformly dispersed.

2. Experimental procedure

γ-Methacryloxypropyl trimethoxysilane used in these experiments was prepared in the laboratory using trichlorosilane and allyl methacrylate and purified following a similar procedure given in the literature [10].

Trichlorosilane and allyl methacrylate (both Fluka) were used after purification. The purity of the material was checked by ^{1}H NMR and FT–IR spectroscopy. Kaolinite, obtained from Çanakkale Clay Company, Turkey, was used as-received.

The development of kaolinite–polyacrylate sol–gel materials was carried out as a two-step process. First, γ-Methacryloxypropyl trimethoxysilane was prepared and purified, then silane was pre-hydrolysed with

0022–2461

different amounts of water, varying the water concentration between 1.5 and 3 mol/mol silane; water content was followed using a Karl–Fischer Coulometric titrator. The pH of the solution was adjusted to 5.5 by bubbling CO_2 through it [11]. After the addition of the water, the mixture were stirred for 24 h at 25 °C. The hydrolysis was followed by Karl–Fischer titration. In the second step, the pH was adjusted to 9 by addition of another catalyst. γ-Methacryloxypropyl trimethoxysilane and kaolinite were mixed. Polymerization in toluene at − 5 °C, started ultrasonically, was coupled directly to the reaction by a titanium horn from a Branson Sonifier Model 450 with ultrasonic energy at 20 kHz and an output intensity of 15.4 W, corresponding to an acoustic power of 48.4 W cm^{-2}. To confirm that the polymerization was actually initiated by ultrasound and not by some external agent, the experiments were repeated in an identical manner in all respects except that the ultrasound generator was not switched on. No detectable polymerization occurred over an 18 h period in the presence or absence of AIBN.

The content of polyacrylate units in the kaolinite varied from 10–100 mol %. The structures of the polymers were confirmed by FT–IR, differential thermal analysis (DTA) and XRD. The hydrolysed polymers were co-condensed with kaolinite to yield sol–gel materials. As a typical procedure for the preparation of sol–gel material, optimum conditions were tested by varying kaolinite to polyacrylate ratio; the best result was obtained with 15–85 mol % polyacrylate to kaolinite, respectively (KP4).

Thermal experiments described in this paper were performed on Schimadzu Net Work System 50 at a heating rate of 10 °C min^{-1} in an air atmosphere.

The structural investigation of a composite material thus prepared was carried out at room temperature using XRD. The Rigaku (System RadB) X-ray diffractometer equipped with a carbon monochromator employing molybdenum radiation with a scan rate of 1 °C min^{-1} was used for XRD analysis of the materials.

3. Results and discussion

In spite of its attractive features, the application of the sol–gel process in the synthesis of new composite materials is limited by the insolubility of many engineering polymers within the sol–gel solution. In addition, the extraordinary shrinkage which occurs upon drying the solvent-swollen gels [12] precludes most moulding processes and introduces considerable stress within these materials. The former problem could be circumvented by the *in situ* formation of both organic and inorganic components. In order to address the latter problem, we have synthesized a procurable polymerizable group in place of the standard alkoxide group.

In this procedure, the trimethoxysilane end-capped silane with kaolinite was studied. The copolymers were then hydrolysed and co-condensed with various amounts of clay in the presence of a catalyst to yield sol–gel composite materials which have a controllable combination of properties of both polymer and kaolinite. These reactions can be schematically represented as shown in Fig. 1.

In the additive procedure, trimethoxy end-capped silane with polymerizable acrylate groups was mixed with kaolinite. The silanols underwent self-condensation. The reaction rate of the condensation depends on the silane concentration, the content of kaolinite, H value, additives and the type and quantity of hydrolysis catalyst.

A drying process after the pre-treatment was found to be advantageous to remove excess water and to complete condensation of unbonded OH groups of silanols. By interaction of the organofunctional group of the silane with the functional group of the resin or with a polymer, bonds are formed which connect the inorganic substrate via the silane, acting as a bridge, with the polymer.

In order to complete the reaction with kaolinite, the material with an Si–O–Si backbone was chosen. Residual groups like Si–OR or Si–OH should remain in the polymer precursor in order to form reactive bonds with the kaolinite. As a result, by proper choice of composition, hydrolysis and condensation, polyacrylate kaolinite sol–gel composite materials were synthesized and characterized.

3.1. FT–IR characterization

Infrared-absorption curves for a variety of sol–gel materials prepared are given in Fig. 2. It has been established that the spectra are sensitive both to structural and compositional variations in these materials.

As a general rule, the layer silicate structural OH groups that are comparatively slightly associated, show absorption at high frequencies of 3600–3700 cm^{-1}, whereas the adsorbed water shows adsorption at lower frequencies of 3400 cm^{-1}, and another band around 1640 cm^{-1}.

A sample of kaolinite, with a broad band at around 3400 cm^{-1} showed a weak shoulder at 3240 cm^{-1} and a simpler band at 1640 cm^{-1}, all of which disappeared on heating to 200 °C and correlated with the adsorbed water. A strong absorption band between 3600 and 3700 cm^{-1}, which was not lost on heating to 200 °C, is correlated with structural OH groups. The band at 3677 cm^{-1} is attributed to the basal plane OH groups which probably involved at least two different kinds of associations: first, bands between groups within the hydroxyl plane, which could be the result of interlattice hydroxyls, and second, bonds involved in cementing unit layers together, which would be considerably weaker because of their large O–O distance. Therefore, some of the basal plane hydroxyls would contribute to one band and others contribute to the second band, the relative contribution depending upon the regularity of the stacking of the unit layer, i.e. upon the degree of order of crystallinity of the kaolinite.

Frequencies between 1150 and 400 cm^{-1} are attributed to lattice vibrations. Table I shows band assignment of kaolinite. Arising from Si–O stretching vibrations, absorption bands were observed in the 1150–960 cm^{-1} region. The two strongest in-plane

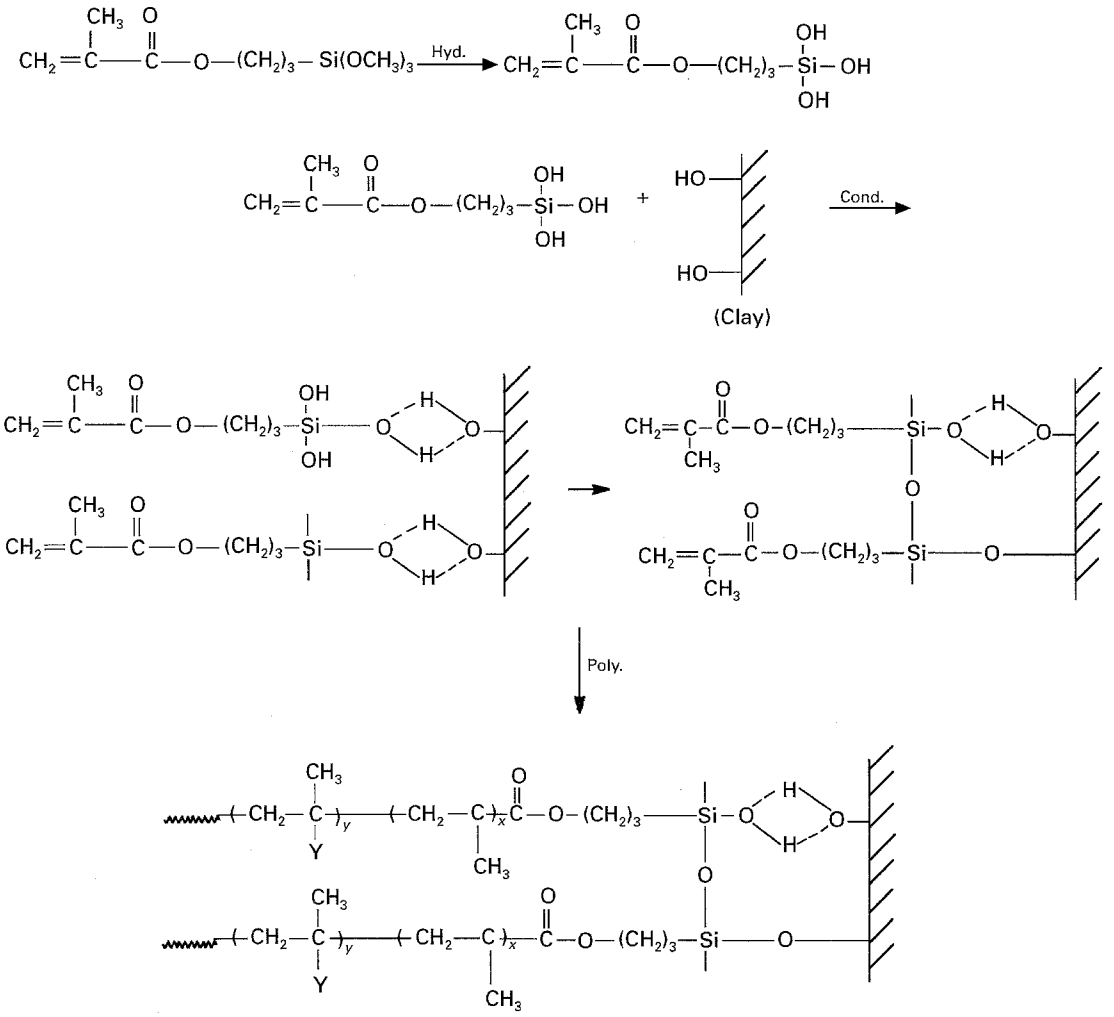

Figure 1 Schematic route for sol–gel material preparation.

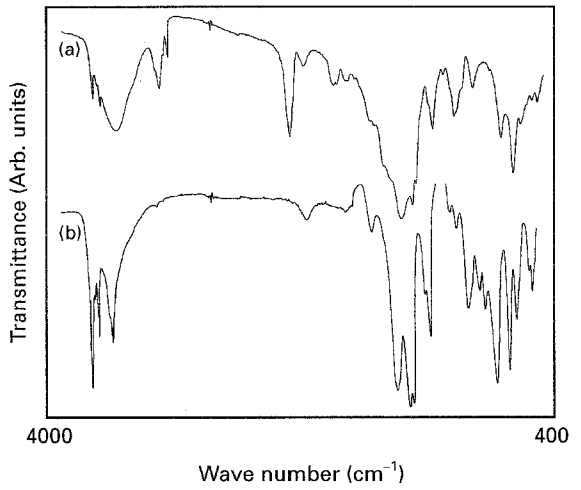

Figure 2 Infrared properties of the materials. (a) Kaolinite, (b) sol–gel composite material.

TABLE I Absorption frequencies used to follow the reaction

Structure	Wave number (cm^{-1})	Reference
–Si–OCH_3	800 (1090)	[13, 14]
–Si–OH		
Free	3691	[14]
H-bonded	3459 (3431)	[15]
– Si–O–Si–	1030	[13, 14]
– Si–O		
Stretching	1120, 1080(s), 1048, 1025	
R–O–H		
Bending	920, 890, 849	
–Si–O–R	523, 468	
C=O	1720	[10]

vibrations take place in the frequency range 1037–1018 cm^{-1}. Vibrations in the 960–550 cm^{-1} region are attributed to R–OH bending vibrations.

The spectra obtained for polyacrylate kaolinite sol–gel composite materials given in Fig. 2b, are comparable to kaolinite.

To follow the reactions, i.e. changes in structures, the absorption frequencies given in Table I were used.

For Si–OCH_3 the evaluation is straightforward, but for the two others the situation is more complex. The hydroxyl groups for silanols show several bands; free silanols at 3691 cm^{-1} and hydrogen bonded at 3549 and 341 cm^{-1}. The absorption of Si–O–Si appears as a shoulder on the larger band due to the Si–O bond in Si–OCH_3.

A comparison was made using the difference in spectra between kaolinite and composite material (KP4). According to the spectra, one can easily see the decrease in the absorption of the –OH peak and the increase of the Si–O–Si absorption. The initial rapid

decrease in the number of methoxy groups indicates that it should be possible to observe a corresponding increase in the content of Si–OH groups. This obviously observed before condensation takes place. Consistently, a strong increase in the absorption of Si–O–Si can be observed after condensation and drying in an autoclave.

The gradual disappearance of the OH absorption band of kaolinite is marked and can be correlated with the presence of polyacrylate instead of OH groups. The strong absorption for the –CO group at 1700 cm^{-1} is correlated with the structure as shown in Fig. 1. We cannot claim that all –OH groups could be replaced by polyacrylate; however, the gradual disappearance of the –OH band for kaolinite has led us to reach this conclusion, which was also supported by other methods.

3.2. DTA characterization

DTA curves for kaolinite and composite materials are given in Fig. 3a and b, respectively. Curves for kaolinite are flat up to about 400 °C showing little loss of water at lower temperatures, which correlates the absence of any thermal reactions in the lower temperature region. The precise temperature for the loss of lattice water is varied, which may be explained by variations in particle size, because the dehydration temperature is known to decrease with decreasing particle size. It may also be explained by variations in crystallinity, because the poorly crystalline material loses its hydroxyl water somewhat more readily than well-crystallized material [13].

DTA curves of kaolinite, Fig. 3b, show an intense, sharp endothermic reaction corresponding to the loss of water. The reaction begins at about 400 °C which is attributed to the partial melting. At 500–600 °C when metakaolin in the Si–O network for kaolinite remains largely intact and the Al–O network reorganizes itself in the form of edge-shared Al–O octahedral chains, there exists a sufficient amount of melting as indicated by the FT–IR data, to confirm the existence of a distinct metakaolin lattice. At around 600 °C, the peak shows that small amount of crystallization may have occurred; this could be a result of phase transformation or crystallization of the possible impurity phases. DTA curves for kaolinite lying between the peak for loss of hydroxyl water and intense exothermic reactions, are relatively flat, showing a slight endotherm which is attributed to the melting of the material.

In the case of KP4 (Fig. 3a), no reasonable reactions took place up to 280 °C; however, a sharp exothermic peak obtained at around 311 °C indicates the first phase transformation range at this temperature. At 360 °C, a wide endotherm occurred up to 470 °C, showing an even small amount of melting could have taken place. The second exothermic peak, at 470 °C, is attributed to the small amount of melting; examination of the rest of the peaks indicates the material has a tendency to melt.

Other composite sol–gel materials thus prepared demonstrate the same trend as KP4 as described. The data indicate that phase transformation is present which is in accordance with X-ray diffraction, which indicates that no crystallinity is present in such materials.

3.3. X-ray characterization

According to the overall degree of regularity in the atomic arrangement, the type of microstructure encountered in this work can be divided into two categories, amorphous and crystalline states.

The diffraction patterns of the examined materials are given in Fig. 4a–c. The results obtained from the polyacrylate material showed the formation of the amorphous state (Fig. 4a). A large halo (characteristic of the amorphous state) was obtained at around $2\theta = 10°$, indicating the absence of any long-range atomic arrangement and periodicity of the three-dimensional network in the polymeric material.

However, in the examination of kaolinite (KP1) as shown in Fig. 4b and also the diffraction pattern data given in Table II, much greater regularity and periodicity of the three-dimensional net-work is reached. Although this pattern is also a characteristic pattern for kaolinite and no further explanation is needed at this point, comparing Fig. 4a and b with Fig. 4c strongly indicates that a particular peak at $2\theta = 11.37°$

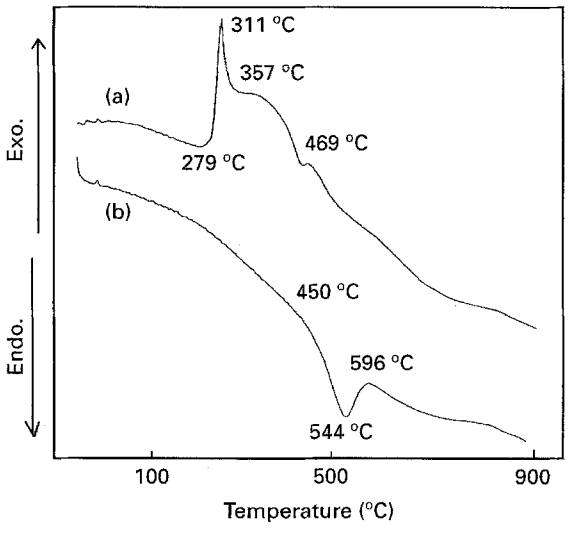

Figure 3 DTA curves of the materials. (a) Sol–gel composite material, (b) kaolinite.

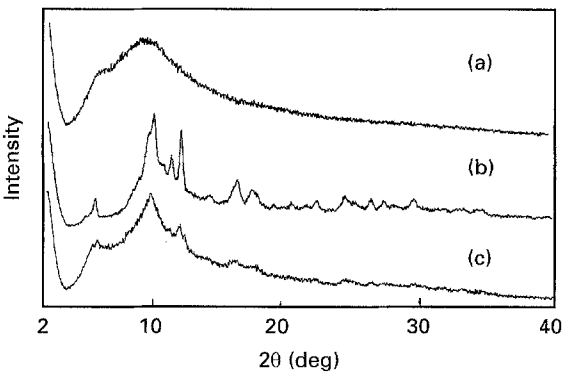

Figure 4 X-ray patterns of the materials. (a) Polymer, (b) kaolinite, (c) composite.

TABLE II Diffraction pattern data for kaolinite (molybdenum is used as the X-ray source)

No.	2θ (deg)	Intensity	d (nm)	I/I_o
–				
1	5.660	830	7.183	27
2	9.980	3039	4.077	100
3	11.370	2003	3.580	66
4	12.170	2633	3.346	87
5	14.220	1024	2.865	34
6	16.270	1397	2.506	46
7	17.390	1190	2.346	39
8	19.160	791	2.131	26
9	20.520	881	1.991	29
10	21.670	791	1.887	26
11	22.520	915	1.816	30
12	24.580	1028	1.666	34
13	25.260	878	1.622	29
14	26.540	957	1.545	31
15	27.520	896	1.491	29
16	28.240	784	1.454	26
17	39.780	896	1.380	29
18	31.960	670	1.288	22
19	33.390	686	1.235	23
20	34.850	660	1.184	22

and 5–6° for KP1, Fig. 4b, is largely deformed. This is attributed to the planar position distortion and results in a mixed state of amorphous and crystalline structure.

4. Conclusion

Polyacrylate is concluded to be bonded covalently to the kaolinite via OH groups already present in the kaolinite. This simply shows that the clay structure is surrounded by an amorphous material. If the reverse were true no peak shape change would be observed. Investigation of the structural properties of this material, including industrial application, is still in progress in our laboratory.

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Received 8 August
and accepted 21 December 1995