Synthesis, characterization and thermal properties of bentonite-polyacrylate sol–gel materials

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A new type of material incorporating bentonite with an alkoxide, $H_2C{=}C(CH_3)COO(CH_2)_3Si(OCH_3)_3$, has been prepared successfully using a sol–gel process. The structures and structural changes upon heating, of the bentonite and the sol–gel material were investigated by FTIR, XRD and DSC. Using the metal alkoxide and the corresponding clay mineral as precursors, the additive reaction followed by free radical polymerization resulted in a novel material in which polymer was attached covalently to silicate sheets of bentonite *via* hydroxy bonding.

The classical approach to the combination of the properties of clay minerals and polymers led to the development of new materials where two different physical properties were combined.[1–12] This approach not only offers access to materials with new or improved properties, but also allows the incorporation of organic polymers into clay minerals which have a number of applications in advanced material technology, such as improvement of the quality and durability of plastics, flame retardance with non-toxic substances, corrosion inhibition, water repellency and heat insulation. The development of the sol–gel processing method has also led to the design of new materials in which polymers are linked to inorganic matrices such as SiO_2 and TiO_2.[13,14] The general idea of attaching polymerizable organic groups to clays by sol–gel processing and then polymerizing the resultant derivatives led us to design novel composite materials in which an alkoxide, γ-methacryloxypropyl trimethoxysilane was used to link the polymer to bentonite clay *via* hydroxy bonding. Preparation of the material by sol–gel processing was followed by structural characterization by means of Fourier-transform IR spectrometry, X-ray diffraction and differential scanning calorimetry. The mechanism of covalent bond formation in layered silicates, either interaction with surface hydroxy groups or interlayer hydroxy groups of bentonite, and the thermal transformations of bentonite and bentonite–polyacrylate sol–gel materials up to 600 °C are discussed.

Experimental

General methods

The following instruments were used to obtain spectral data: an Ati Unicam Mattson 1000 FTIR spectrometer, a Mettler 2200 Model Karl Fischer coulometric titrator, a Schimadzu Network System 50 differential scanning calorimeter with a heating rate of 10 °C min^{-1} in air, a Rigaku (System RadB) X-ray diffractometer equipped with a graphite monochromator employing Mo or Cu radiation with a scan rate of 1° min^{-1} at room temperature, and a Philips PU9100X atomic absorption spectrometer interfaced with a computer for data collection in the absorption mode with an air–acetylene flame and a 50 mm single slot burner.

Characterization of the clay sample

The bentonite used in this study was from Çanakkale, Turkey. Purification was carried out by the sedimentation method and possible phases of the bentonite were examined by the XRD technique; diffraction peaks of the phases were determined by the fingerprint method. Smectite and kaolinite minerals have been determined in bentonite.[15] The chemical composition of the bentonite, determined by atomic absorption spectrometry, was found to be 34.7% Si, 12.5% Al, 1.61% Fe, 0.112% Mg, 5.08% K, 0.09% Na, 0.03% Mn.

Hydrolysis of γ-methacryloxypropyl trimethoxysilane (A-174)

γ-Methacryloxypropyl trimethoxysilane [97%, $\rho = 1.05\ g\ cm^{-3}$, bp 98 °C (5 mmHg); Aldrich] was used as received. A typical procedure for making up the sol solution was as follows. To a stirred solution of A-174 (2.48 g, 10 mmol) was added isopropyl alcohol (26.4 g, 440 mmol); after being stirred for 2 h, the mixture was hydrolysed with the required amount of water (1.35 mol H_2O per mol A-174) in isopropyl alcohol in the presence of an acid catalyst solution (HCl, 0.15 mol dm^{-3}) to maintain the pH at 4. The required amount of water, determined using a Karl Fisher coulometric titrator, was found to be 1.35 mol per mol silane. The mixture was stirred in ambient atmosphere at room temperature until a clear sol solution was obtained.

Preparation of bentonite–polyacrylate sol–gel materials (BP-1)

The quantity of A-174 required for a monomolecular coating was calculated from

$$g(\text{A-174}) = [g(\text{clay}) \times S]/S_W$$

where S is the specific surface area of the clay in $m^2\ g^{-1}$ and S_W is the specific wetting area of A-174 in $m^2\ g^{-1}$. The quantity of silane used throughout the reaction was calculated to be: $g(\text{A-174}) = [5\ g \times 7\ m^2\ g^{-1}]/314\ m^2\ g^{-1} = 0.11\ g$.

The development of bentonite + A-174 (BP-1) sol–gel materials was carried out as a two-step process. First, hydrolysed A-174 in tetrahydrofuran (15 cm^3), and distilled water (5 cm^3) were mixed with bentonite in a closed vessel and stirred overnight at room temperature; the pH of the solution was adjusted to 5.5 by bubbling CO_2. Then, free radical polymerization was carried out in toluene at 80 °C with benzoyl peroxide (recrystallized from methanol) for 8 h to yield polymer–clay composites. The solid product was ground and subjected to further hydrolysis with water, followed by condensation at 80 °C in the presence of acetic acid (25% solution); samples were then washed several times with dimethylformamide (DMF) in a Soxhlet apparatus to remove impurities and dried in a vacuum oven at 75 °C for 12 h, and at 100 °C for 24 h until the sample mass became essentially constant.

Results and Discussion

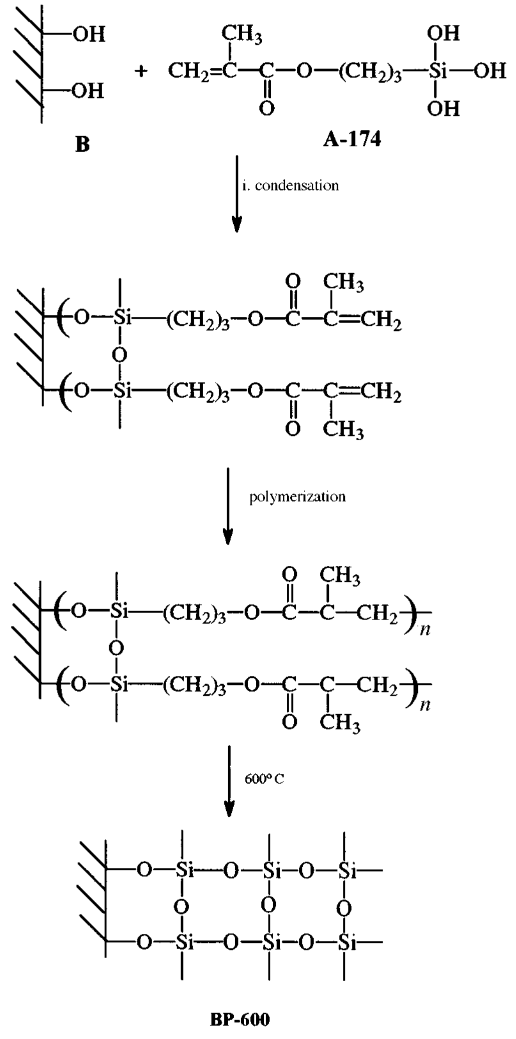
Free radical polymerization of hydrolysed A-174 bound covalently to bentonite B, and co-condensation in the presence of an aqueous acid were carried out. These reactions can be represented as shown in Scheme 1.

X-Ray characterization

Fig. 1(*a*) and (*b*) show the X-ray diffraction patterns of bentonite B and BP-1. By comparing the calculated 2θ values with the related unit-cell parameters (smectite phase: $a=5.1297$, $b=8.055$, $c=15.45$ Å, $\beta=99.13°$; kaolinite phase: $a=5.15$, $b=8.95$, $c=7.40$ Å, $\alpha=91.8$, $\beta=104.8$, $\gamma=89.9°$)[16] and the observed 2θ values, the phase peaks were matched and indexed as given in Table 1.

The X-ray diffraction pattern of pure bentonite B differed from that of sample BP-1. As can be seen in Fig. 1(b), which was obtained from a bentonite sample treated with A-174 and subsequently polymerized, the original bentonite structure was not completely destroyed; however, some peaks showed a decrease in intensity.

As shown by XRD the poly(γ-methacryloxypropyl trimethoxysilane) was in an amorphous state. The changes in peak intensity could be attributed to bond formation between O or OH groups of the smectite phase and polyacrylate attached to the Si—O matrix. Polyacrylate was formed in the layer and was identified by the (002) X-ray reflection of the kaolinite phase. The (132) plane atoms were also highly affected, whereas the interaction with (012) plane atoms was found to be weak. The observed (001) reflection remained unchanged and was attributed to the bonding that was not formed with interlayer hydroxy groups.



Scheme 1

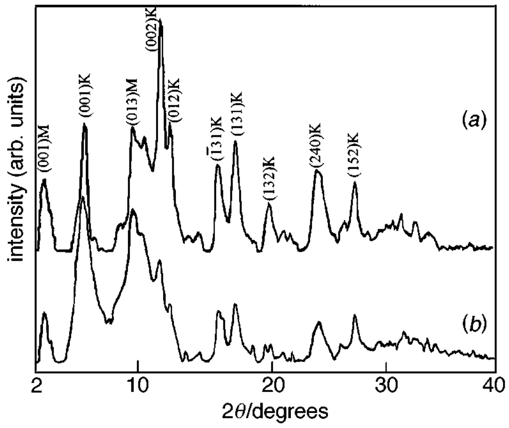


Fig. 1 X-Ray diffraction patterns of (*a*) bentonite B, (*b*) sol–gel material BP-1. K, kaolinite phase; M, montmorillonite phase.

Table 1 Diffraction data for the bentonite sample (Mo target) and related indices

	2θ	d	I/I_0	h	k	l	phase[a]
1	2.63	15.454	34	0	0	1	M
2	5.74	7.083	56	0	0	1	K
3	9.26	4.394	57	0	1	3	M
4	11.43	3.561	66	0	0	2	K
5	12.24	3.327	55	0	1	2	K
6	16.05	2.540	36	1	3	1	K
7	17.45	2.338	46	1	3	1	K
8	20.50	1.993	20	1	3	2	K
9	24.61	1.664	36	2	4	0	K
10	27.58	1.488	31	1	5	2	K

[a] K, kaolinite; M, smectite.

In order to further characterize B and BP-1, thermal effects on their XRD patterns were studied, and are illustrated in Fig. 2 and 3 respectively.

The thermally treated samples showed both the typical peaks of smectite and kaolinite phases and some new reflections due to Si—O linkages from the metal alkoxide.

The results showed that the bentonite used throughout these experiments contains kaolinite as interstratified layers of the separate minerals in which the thickness of the phase layers was of the order of one or a few single layers. A combination of discrete particles of kaolinite with bentonite was not likely to occur, because the dehydration characteristics were not in accord with those of the individual components (Fig. 7, later). The data indicated that water adsorbed in the channels was lost at *ca.* 100 °C, water in the channels attached to the silicate units was lost between 275 and 375 °C, and hydroxy water was lost at *ca.* 500–600 °C. Above this temperature, the loss of water was accompanied by a slight change in the dimensions of the structure.

On the basis of X-ray diffraction and heating data, the complete loss of interlayer water resulted in the reduction of the c dimension to 9.4–10 Å. On further heating to the dehydroxylation temperature, the diffraction data showed little change, indicating that the silicate structure was virtually unchanged. Above this temperature, structural transformation was likely to take place giving rise to a new peak that was attributed to quartz.

In the case of BP-1, the same trend was observed. The data was in accord with the data obtained from DSC and FTIR

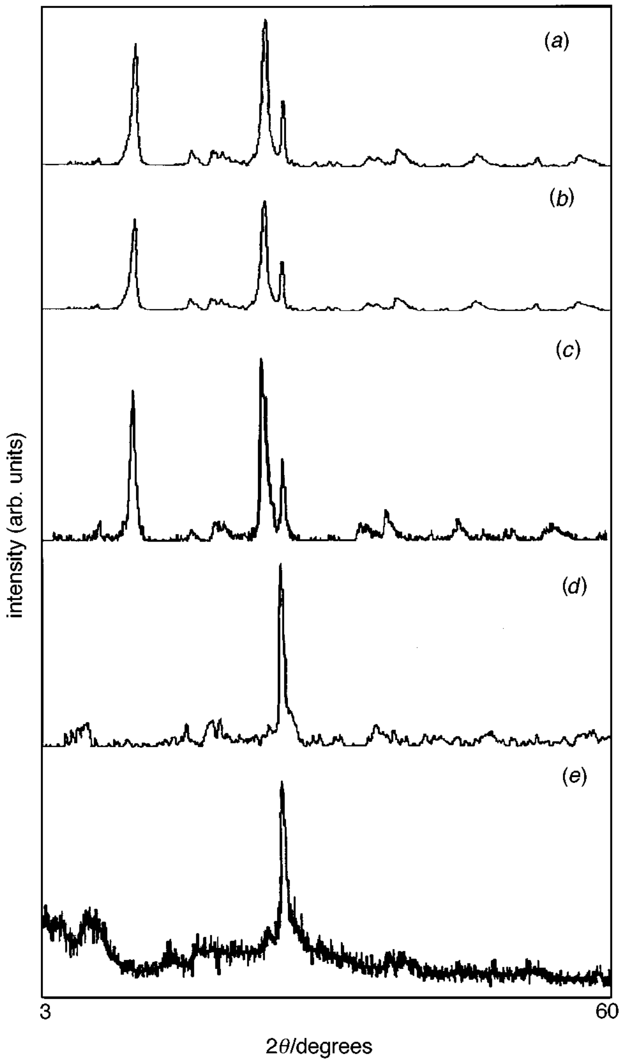


Fig. 2 XRD pattern of the heat-treated bentonite (B) at (*a*) 100, (*b*) 200, (*c*) 400, (*d*) 500 and (*e*) 600 °C (Cu-Kα radiation with a scan rate of 1° min^{-1} at room temp.)

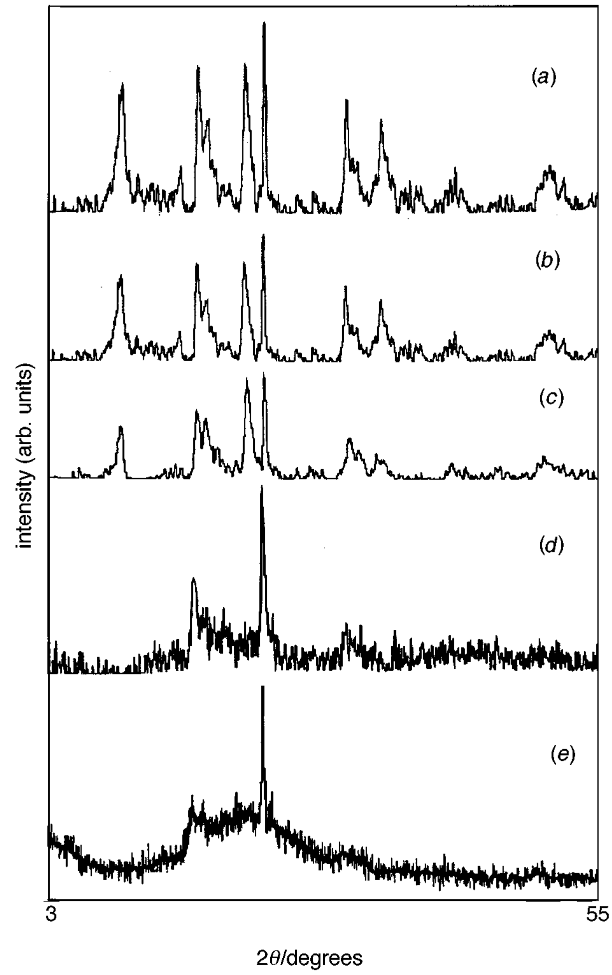


Fig. 3 XRD pattern of the heat-treated material BP-1 at (*a*) 100, (*b*) 200, (*c*) 400, (*d*) 500 and (*e*) 600 °C (Cu-Kα radiation with a scan rate of 1° min^{-1} at room temp.)

studies. After heating for 5 h at 600 °C, the interlayer distance was found to be 14.8 Å, indicating the elimination of polyacrylate, probably forming dispersed Si—O—Si bonds on bentonite.

FTIR characterization

The absorption frequencies of B and BP-1 were elucidated from the data obtained (Fig. 4). The absorption bands of B at 3693, 3667 and 3623 cm^{-1} were attributed to O—H stretching modes, indicating the dominance of the smectite and kaolinite phases.[16]

Bands at 3693, 3667 and 3623 cm^{-1} which did not disappear on heating to 200 °C were correlated with structural OH groups. The bands at 3623 and 3667 cm^{-1} were assigned to a bond between the basal hydroxy groups of one sheet and the puckered oxygens of the next sheet, and the band at 3693 cm^{-1} was attributed to interlayer hydrogen bonding.

The sharp decrease in the O—H frequency in sample BP-1 was assigned to covalent bonding between the OH groups of bentonite and A-174. It is unlikely that all the OH groups would be displaced; however, note the sharp decrease in the peak associated with the bonding as given in Scheme 1.

An FTIR study of BP-1, after subtracting bentonite as the reference, indicated the presence of an Si—OH stretching frequency at 3700 cm^{-1}, Si—O—Si at 1041 cm^{-1} (br), and a peak at 1735 cm^{-1} that was attributed to C=O.

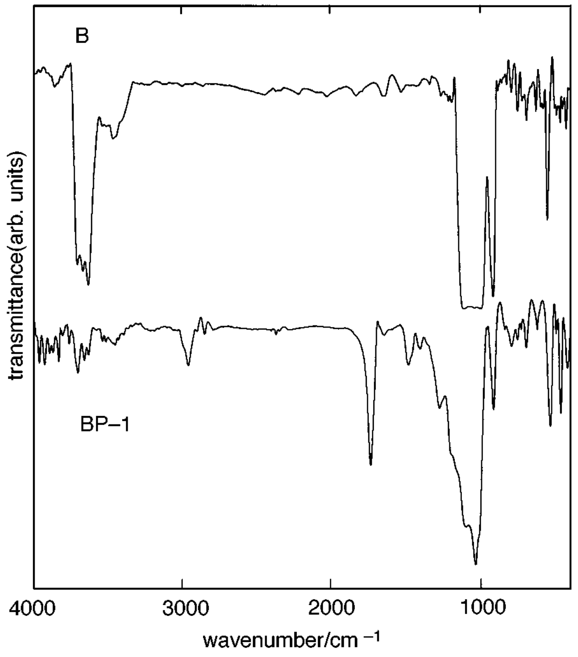


Fig. 4 FTIR spectra of the sol–gel materials B and BP-1

Peaks at 462, 539 cm^{-1} were assigned to Si—O—R, and at 919, 1041 and 1112 cm^{-1} to Si—O stretching vibrations.

The FTIR spectra of B and BP-1 heated between 100 and 600 °C are shown in Fig. 5 and 6, respectively. In Fig. 5, the bands at 3600–3700 cm^{-1} from OH groups in the lattice were seen to decrease rapidly in intensity between 500 and 600 °C, corresponding to the observed endotherm in the DSC curves. Coincident with the dehydration, a change in the spectrum was evident in the 700–900 cm^{-1} region. In particular the Al—OH band at 910 cm^{-1} disappeared, and the band at 1100 cm^{-1} broadened and merged into the main band at 1000 cm^{-1}. This change in the spectrum was attributed to the formation of meta-kaolin in bentonite.[17,18] A decrease in the coordination of the aluminium from six to four was evidenced by the rapid broadening of the FTIR spectral bands of the Si—O network.[19] Upon further heating, a band at 550 cm^{-1} was seen to form, and the shapes of the peaks between 650 and 1200 cm^{-1} were changed, corresponding to the formation of mullite and γ-alumina spinel type structures containing some silica.[20]

DSC characterization

DSC curves for B and BP-1 are given in Fig. 7(a) and (b) respectively. Curves for bentonite up to 511 °C showed a slight loss of water at 267 °C, which was attributed to the loss of interlayer water that was lost on heating the sample to 300 °C. Bentonite [Fig. 7(a)] showed an intense endothermic peak starting at 461 °C and ending at 511 °C, which was assigned to the dehydration and to loss of the crystal structure.

As seen in Fig. 7(b), BP-1 showed two exotherms, the first at 383 °C attributed to the crystalline transition temperature of the polymer in the matrix, and the second at 460 °C assigned to the degradation of the organic matrix verified by thermogravimetry; a mass loss of *ca.* 40% occurred in this temperature region.

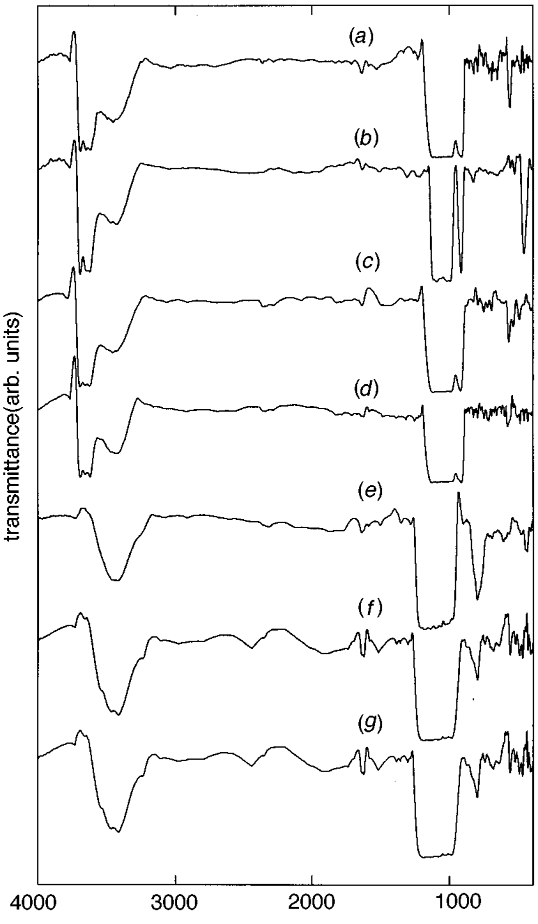


Fig. 5 FTIR spectra of (*a*) bentonite (B) and of B heated to (*b*) 100, (*c*) 200, (*d*) 300, (*e*) 400, (*f*) 500 and (*g*) 600 °C (sample was kept for 5 h in each temperature region)

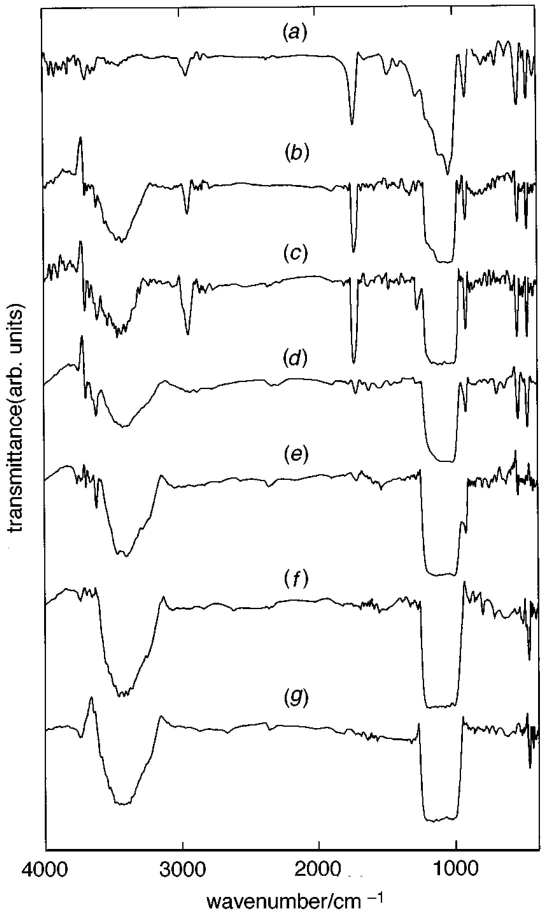


Fig. 6 FTIR spectra of (*a*) BP-1, and of BP-1 heated to (*b*) 100, (*c*) 200, (*d*) 300, (*e*) 400, (*f*) 500 and (*g*) 600 °C (sample was kept for 5 h in each temperature region)

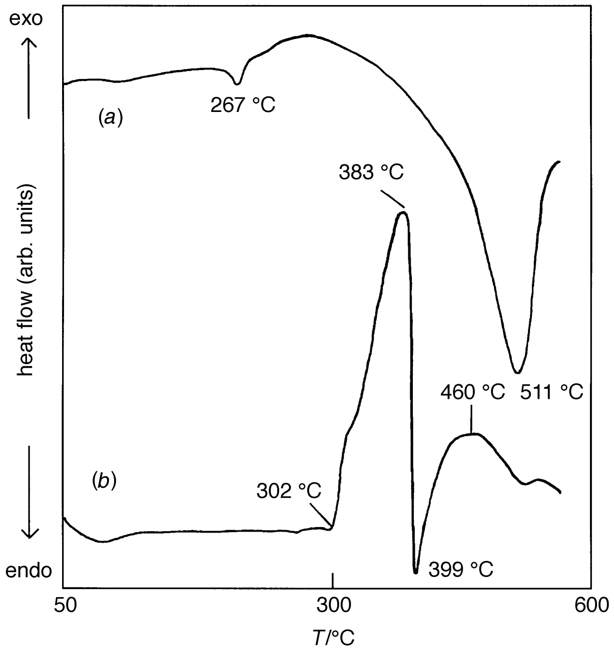


Fig. 7 DSC curves for (*a*) B and (*b*) BP-1 (heating rate 10 °C min^{-1})

Conclusion

It has been demonstrated that novel composite materials prepared from bentonite and alkoxy vinylsilanes formed covalent bonding between the OH groups of the kaolinite phase in bentonite and the OH groups of the silanols. FTIR, XRD and DSC experiments enabled the study of the thermal transformations and structures of the clay–polymer composite materials. Structural changes in bentonite upon heating were demonstrated and correlated with the DSC and X-ray diffraction results.

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