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THERMAL STABILITY OF METHACRYLAMIDE/MONTMORILLONITE INTERCALATION COMPLEX

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Abstract

Thermal stability of methacrylamide intercalated octadecylammonium montmorillonite (OD–M/MA) is limited by rapid desorption of methacrylamide (MA) at 140°C. It was improved by γ-irradiation. The irradiation intercalation complex OD–M/MA γ shows significant shift of the whole desorption process towards higher temperatures. However, part of the adsorbed organic material is released at 50°C signalizing presence of some volatile fractions. Decomposition products of the intercalated material and long-chain alkylamides in the acetone extract indicate complex reactions between MA and octadecylammonium chains. An additional swelling of the silicate structure occurs after γ-ray initiation and is probably related to the reaction products with a certain degree of cross-linking in the interlayers.

Keywords: methacrylamide-montmorillonite intercalation, thermal stability

Introduction

The basal spacing is one of the most important characteristics of the clay-organic complexes and other clay based materials. Therefore the control of interlayer distance is a useful tool to influence the properties of the clay such as particle size, interlamellar attractive forces, sorption selectivity, etc. The resulting effect depends on the nature and arrangement of the interlayer sorbate. Increasing the distance between the silicate layers by intercalation of suitable organic compounds is just one possibility to reduce their mutual interaction forces [1, 2]. The organoclay complexes can find the practical use as potential fillers for organic resins [3], provided that we reduce the attractive forces between silicate layers, or selective sorbents [4, 5] if we achieve suitable interlayer micropores. The thermal stability of e.g. alkylammonium montmorillonites determines the acceptability of the organoclay for given purpose [6].

Alkylammonium montmorillonites are thermally relatively stable up to about 150°C [7] though some authors showed that measurable changes of or-

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ganic cation (decomposition to corresponding free amines and halogenated alkanes) occur from 100°C [8, 9] and their thermal stability decreases with number of carbon atoms in the alkyl chain of the alkylammonium cation.

Experimental

Materials

Methacrylamide (MA) was used for intercalation into the interlayer space of montmorillonite (Kunipia F, Japan; *C.E.C.* = 119 meq/100 g clay). Exchanged forms were prepared by repeated saturation of the montmorillonite with solutions of chlorides and subsequent washing with water and a water-methanol mixture (1:1) until the supernatant was free of chloride anions ($AgNO_3$-test). Following derivatives were used:

Derivative	Abbreviation
sodium montmorillonite	Na–M
calcium montmorillonite	Ca–M
hexylammonium montmorillonite	HA–M
dodecylammonium montmorillonite	DD–M
octadecylammonium montmorillonite	OD–M
cetyltrimethylammonium montmorillonite	CT–M
cetylpyridinium montmorillonite	CP–M

Sample preparation

Thin films of montmorillonites on the glass slides, prepared by drying of 4% clay suspension (Na–M and Ca–M in water, organophilic montmorillonites in methanol) under ambient conditions (T = 25°C) for 24 h, were immersed in saturated solutions of MA. The reactants were kept in contact for 24 h at room temperature. Samples were then dried under ambient conditions, irradiated by γ-rays (10^4 Gy and $2\cdot10^5$ Gy) and subjected to XRD-measurements. These tests allowed us to select the optimal combination of conditions for preparation of a powder sample.

The powder sample OD–M/MA was prepared by interaction of MA with OD–M (3:1 weight ratio) in methanol at T = 60°C for 24 h under stirring. The suspension was then cooled to room temperature, filtered, freeze-dried and exposed to γ-rays ($2\cdot10^5$ Gy). The irradiation sample OD–M/MA γ was extracted with acetone (ultrasonic dispersion) and the reaction products were analysed by GC/MS.

Methods

Diffraction patterns were recorded on a Rigaku RAD-B diffractometer (CuK_α, 2°–20° 2θ).

Thermoanalytical data were obtained from a Rigaku TG 8110 thermoanalyser with αAl_2O_3 as reference material.

The IR spectra of selected samples (KBr-discs) were measured by a Hitachi 270–50 infrared spectrophotometer.

The acetone extract of the irradiated sample was analysed with a Shimadzu GCMS-QP1000 gas chromatograph coupled with a mass spectrometer.

Results and discussion

XRD investigation

The d_{001} values of starting materials were unchanged after pure solvent treatment and air drying for 24 h. Hence, the effect of pure solvents on the montmorillonite structure expansion under conditions described in paragraph sample preparation can be neglected.

The basal spacings of MA-intercalated oriented samples are in Table 1.

Table 1 Interlayer distances of exchanged montmorillonites before (original) and after the MA intercalation. (All samples are air dired at T = 25°C for 24 h)

Sorbent	d_{001} / nm					
	Original	After intercalation of MA				
		Methanol	Acetone	Water	Chloroform	Toluene
Na–M	1.41	1.89	1.91	1.84	1.5	1.5
Ca–M	1.54	1.89	1.95	1.72	1.58	1.54
HA–M	1.35	1.87	–	1.88	1.86	1.86
DD–M	1.79	2.83	–	2.18	2.39	2.19
OD–M	1.97	3.22	3.23	3.03	2.69	2.67
CT–M	1.97	3.35	3.36	2.82	2.74	2.48
CP–M	2.07	3.34	2.99	2.68	2.84	2.41

Considering the diameter of methacrylamide molecule about 0.55 nm, the interlayer separation $\Delta(\Delta = d_{001} - 0.96\,\text{nm})$ of MA-intercalated Na–M and Ca–M roughly corresponds to one or at maximum two layers of MA. The large basal spacing of MA-intercalated organophilic species results from a multilayer arrangement of MA. The changes of shape and position of d_{001} reflections of the MA-intercalated OD–M after γ-irradiation (OD–M/MA γ) indicate a rearrangement of the interlayer structure.

The basal spacing of the powder sample OD–M/MA, prepared in methanol is somewhat smaller (d_{001}=2.49 nm) than for the oriented samples as non-saturated methacrylamide solution was used during the intercalation. Nevertheless, after irradiation (by the dose of 10^4 Gy), the basal spacing increased to 2.92 nm and after another dose ($2\cdot10^5$ Gy) to 3.31 nm [10]. The d_{001} value of OD–M/MA after extraction with acetone decreased to 2.3 nm while the basal spacing of the OD–M/MA γ remained unchanged. This suggests the presence of some unsoluble substances in the interlayer space, including polymerization products, which were not removed with acetone.

Infrared spectroscopy

The IR spectra of Na–M and OD–M were described in detail elsewhere [2].

The MA monomer can be detected by the νN–H vibrations (3390 and 3190 cm^{-1}), absorption bands at 1668 and 1606 cm^{-1} corresponding to νC=O, νC=C and δNH_2 vibrations, series of peaks between 1470 and 1370 cm^{-1}, ascribed to ($-CH_3$, $-CH_2-$ and $CH_2=$) deformations and a distinct out of plane deformations ($CH_2=$ group) at 934 cm^{-1} [11].

Irradiation of the OD–M/MA sample brings about the following principal changes in the IR spectra:

The intensity of peaks at 3390 and 3190 cm^{-1} decreases significantly as well as the intensity of peaks at 1606, 1234, 934 cm^{-1} and the series of peaks around 1390 cm^{-1}. A new, weak peak appears at 1206 cm^{-1}, which can be assigned to the skeletal vibrations of a branched chain.

Thermal analysis

Study of the thermal properties of OD–M revealed that there is no significant difference between the DTA/TG curves of the OD–M with octadecylamine excess and a mixture of montmorillonite and octadecylamine with first weight loss occurring from 140°C [12].

The first significant weight loss of OD–M free of octadecylamine excess, accompanied by series of exothermic peaks, occurs from about 200°C due to successive decomposition of the organic cation and oxidation of products.

The gradual weight loss from 400 to 600°C may be ascribed to the oxidation of residual carbon, part of which is oxidized at higher temperature, along with the dehydroxylation of the clay [13].

The sample OD–M/MA shows a large weight loss (52% of the total weight loss) between 80 and 200°C accompanied by endothermic effects at 110 and 140°C due to the melting and evaporation of MA.

Desorption of MA from the interlayers occurs already after heating at 60°C for 1 h (Fig. 1).

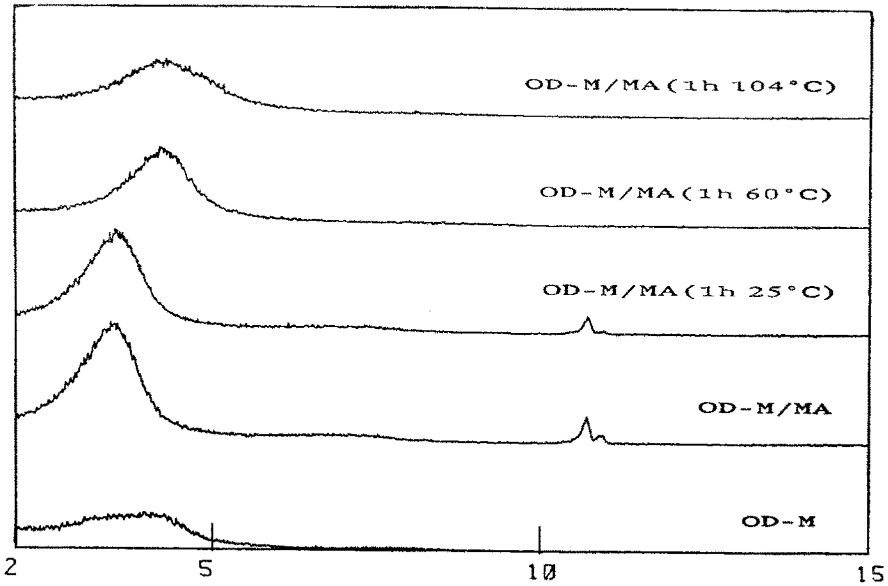

Fig. 1 XRD patterns of the oriented samples: OD–M and the OD–M/MA (heat treated at various temperatures – 1 h)

For the OD–M/MA γ sample, the desorption of intercalated material occurs by several stages (Fig. 2c). The first part of products is released at about 50°C followed by a gradual weight loss with an endothermic peak at 170°C. The weight loss at 140°C corresponding to the desorption of MA is significantly reduced. At 250°C OD–M/MA (Fig. 2b) loses 27% of its mass while OD–M/MA γ loses only 7% of its mass.

Changes of thermal properties of the OD–M/MA γ sample suggest the presence of some volatile fractions and on the other hand some of thermally more stable products. The part of organic material corresponding to the free monomer is substantially reduced. The DTA and TG curves of the intercalation complexes: OD–M/MA and OD–M/MA γ are shown in Fig. 2, in comparison with the starting host samples: Na–M (Fig. 2d) and OD–M (Fig. 2a).

GC/MS analysis

In an acetone extract of the irradiated sample OD–M/MA γ the following compounds were identified:

methacrylamide monomer
aliphatic compound of the composition $C_{19}H_{39}CONH_2$.

The occurrence of residual methacrylamide monomer is checking the low conversion rate of the methacrylamide polymerization (in solid state) initiated

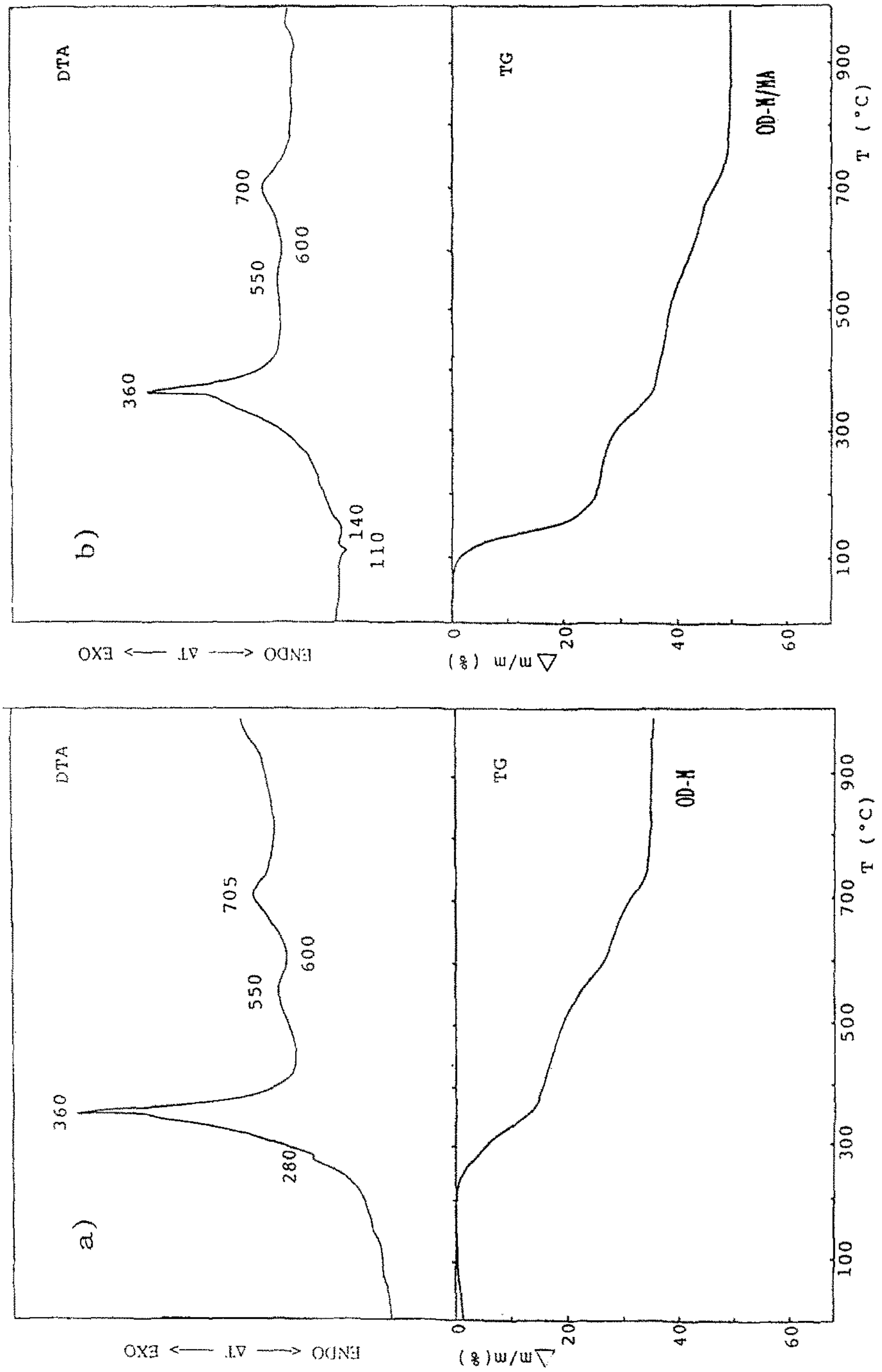

Fig. 2 The thermoanalytical data of powder samples: a) OD–M, b) OD–M/MA

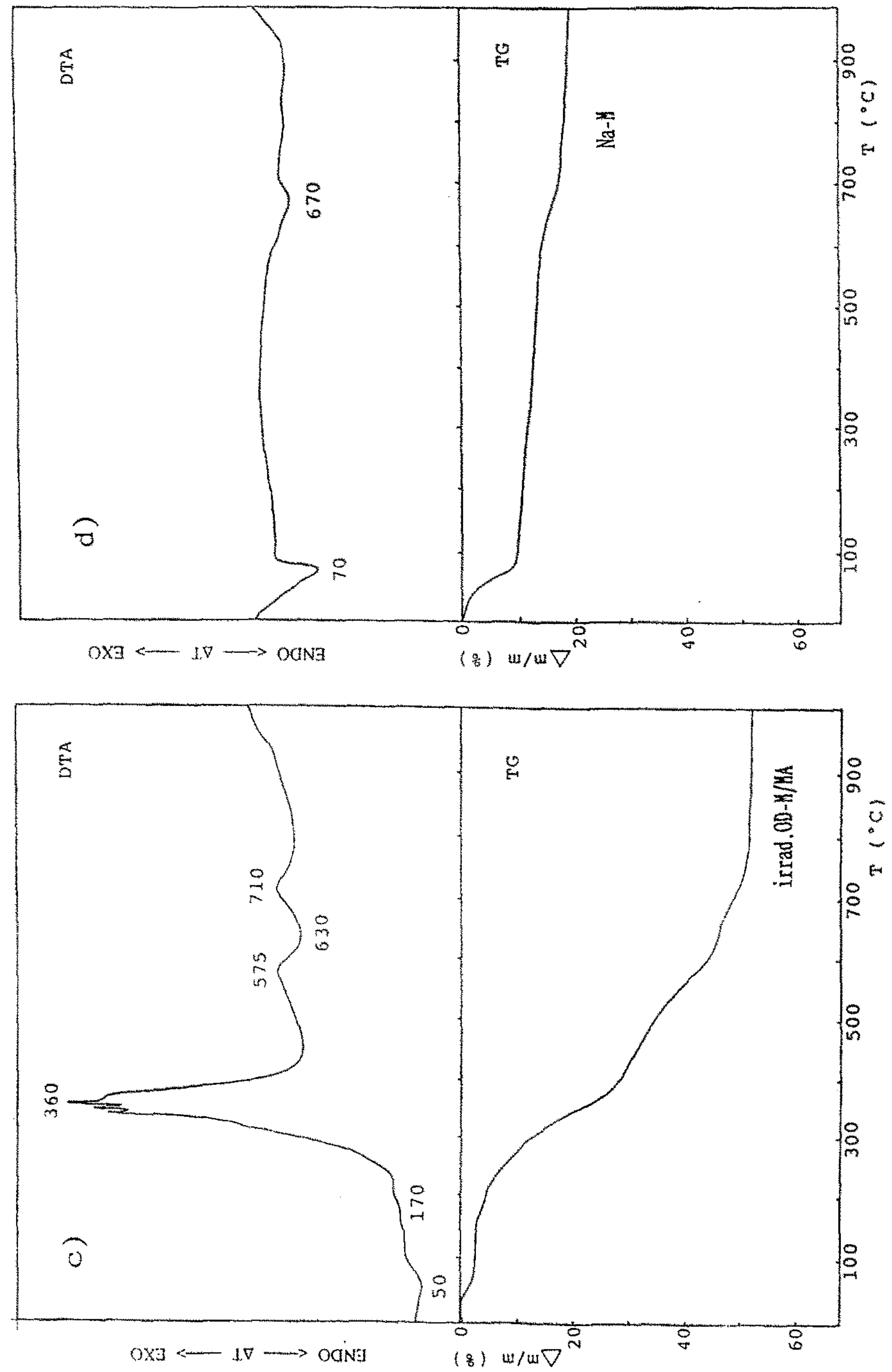

Fig. 2 The thermoanalytical data of powder samples: c) OD–M/MA γ (OD–M/MA irradiation by 2.10^5 Gy), d) Na–M

by γ-ray [14, 15]. The polymer fractions were not detected in the acetone extract, however, this does not exclude the presence of polymer in the interlayers.

Conclusions

The OD–M/MA sample shows a relatively low thermal stability. The increase of its thermal stability after γ-irradiation, additional swelling of the silicate structure and presence of the long-chain amide indicates that a reaction of MA with the alkyl chains of the host structure is taking place suggesting a model of cross-linked interlayer sorbate.

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