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THERMAL STABILITY OF CLAY/ORGANIC INTERCALATION COMPLEXES

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Abstract

The comparison of thermal stabilities of different organoclay intercalation complexes is presented in this work. Montmorillonite/monomer and montmorillonite/polymer intercalation complexes with similar basal spacings show a pronounced difference in changes of d_{001} values after 30 min heating. The hydrophilic and/or organophilic surface modification of the starting montmorillonite is an important factor affecting the intercalated amount of organic material and thus the expansion of the sheet silicate structure.

Keywords: DTA, intercalation, montmorillonite, organoclay, XRD

Introduction

Since the work on montmorillonite swelling in poly-6-amide was published by Fukushima *et al*. [1], various organic compounds and methods were applied e.g. by Vaia *et al*. [2], Carrado and Xu [3] and recently Oya *et al*. [4] to achieve nanoscale dispersion of layered aluminosilicate particles in a polymer matrix.

One of the methods enabling more homogeneous dispersion of clay particles in the polymer could be based on the preparation of organoclay intercalates with expanded sheet silicate structure as an intermediate to clay-polymer nanocomposites. Such materials with reduced attraction forces between silicate layers could be used as fillers for plastics [5]. The thermal stability is one of the most important properties of these materials because elevated temperature is expected to be applied during extrusion and shaping processes. Therefore, it is highly desirable that the intercalation organoclay complex keeps its expanded basal spacing up to the temperatures above 300°C.

Experimental

Materials and sample preparation

Montmorillonite (JP), separated from bentonite Jelšový Potok by the conventional sedimentation method was used as a starting material. Montmorillonite was separated

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from 5% water suspension using automatic sedimentation apparatus designed by Jesenák [6]. Description of this montmorillonite in detail can be found elsewhere [7].

Tetramethylammonium chloride (TM): $(CH_3)_4NCl$,
cetyltrimethylammonium bromide (CTM): $CH_3(CH_3)_{15}N(CH_3)_3Br$,
diacetone acrylamide (DAA): $H_2C{=}CHCONH(CH_2)_2CH_2COCH_3$ and
polyvinylpyrrolidone (PVP): $(C_6H_9NO)_n$

with average molecular mass 10 000 and 40 000 were used in this work to prepare clay/organic intercalation complexes. The first step was preparation of monoionic organomontmorillonites by ion-exchange reaction of Ca–montmorillonite (Ca–JP) with TM and CTM in water solution. Interaction of DAA and/or PVP with Ca–JP, TM–JP and CTM–JP was carried out in methanol suspension. Resulting intercalation complexes were filtered, dried under ambient conditions and ground in an agate mortar.

Methods

XRD powder analysis was carried out on a Philips PW 1050 instrument using CuK_α Ni-filtered radiation, variable slits, $2°(2\theta)\ min^{-1}$ scan rate.

DTA/TG measurements were obtained on MOM Derivatograph OD-102 thermoanalyser adapted for registration of digitalized data, against α-Al_2O_3 standard, heated from 25 to 1000°C at 10°C min^{-1} under static atmosphere of air.

Results and discussion

The basal spacings of the intercalation complexes increase due to incorporation of guest molecules between the silicate layers. Each of the exchanged forms, however, has a different potential of structure expansion after interaction with the organic sorbate. This usually depends on the character of the exchangeable cations compensating the negative charge of the silicate layers. Hydrophilic Ca–JP shows only a slight increase of the d_{001} value after interaction with DAA solution. Behaviour of TM–JP is similar to Ca–JP in this respect. Basal spacings of both Ca–JP/DAA and TM–JP/PVP correspond to one layer arrangement of the interlayer sorbate. Organophilic form CTM–JP shows a significant swelling of the structure after DAA and PVP intercalation. The role of alkyl chain length of the exchanged alkylammonium cation, that was supposed to be a limiting factor for interlayer space expansion, was explained previously [8]. However, this applies for rather small molecules like DAA. Intercalation of large PVP molecules induces an extensive swelling and the interlamellar distance exceeds even the alkyl chain length of the exchanged CTM cations. Such a pronounced increase of the basal spacing was observed at the CTM–JP/DAA/PVP intercalation complex which was prepared by interaction of the CTM–JM/DAA sample with PVP solution (Table 1). Thermal stabilities of the most expanded intercalation structures CTM–JP/PVP and CTM–JP/DAA/PVP were examined.

Table 1 Basal spacings of exchanged montmorillonite forms and their intercalation complexes

Exchanged form of clay	d_{001}/nm after interalation of			
	original	DAA	PVP10	PVP40
Ca–JP	1.26	1.75	1.55	1.47
TM–JP	1.45	1.71	1.47	1.46
CTM–JP	2.16	3.61	3.68	3.56
CTM–JP/DAA	3.61	–	4.15	3.84

In this study, thermal stability of an intercalation complex means, first of all, the preservation of silicate structure in its expanded state. Needless to say, that some changes in the intercalates, obvious from the DTA/TG thermoanalytical curves (Figs 1, 2 and 3), take place in each sample. DTA/TG profiles of Ca–JP were described earlier [6]. Amount of CTM in CTM–JP exchanged form figures about 25% of the sample mass and the course of DTA/TG curves is also known [7]. Ca–JP/DAA shows initial 5% mass loss due to desorption of volatile fractions, residual methanol and water trapped in the sample and is completed at 140°C (Fig. 1). Endothermic peak on DTA curve around 50°C corresponds to melting of the free excess of DAA. Two-stage desorption process of DAA starts at about 150°C, accompanied by an exothermic effect on DTA curve at 220°C due to oxidation of free DAA, and is completed at about 310°C. Further temperature increase results in successive release and oxidation of organic decomposition products along with dehydroxylation of the montmorillonite structure and about 57% total mass loss.

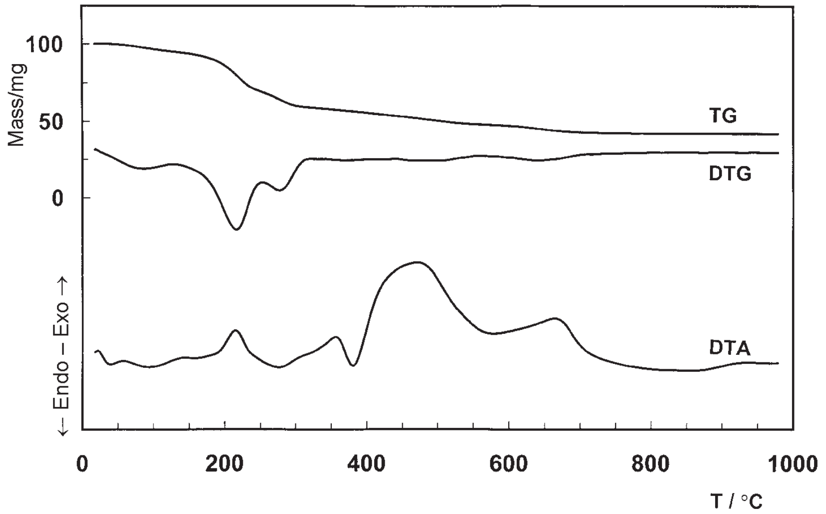

Fig. 1 TG, DTG and DTA data of intercalation complex Ca–JP/DAA

Both CTM–JP/PVP and CTM–JP/DAA/PVP samples show almost the same initial about 7% mass loss, due to desorption of the most volatile fractions (Fig. 2). The

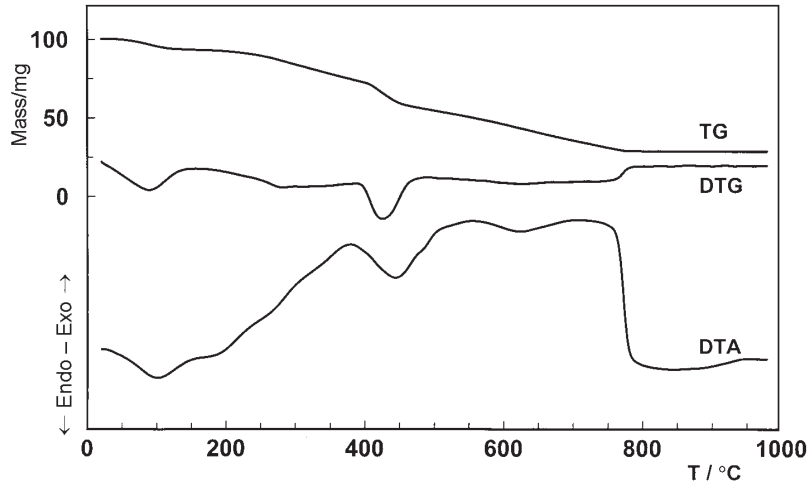

Fig. 2 TG, DTG and DTA data of intercalation complex CTM–JP/PVP

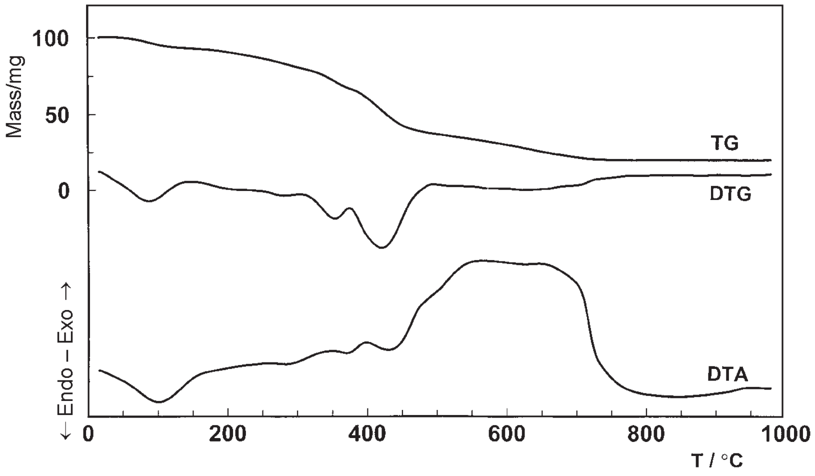

Fig. 3 TG, DTG and DTA data of intercalation complex CTM–JP/DAA/PVP

temperature interval from 150 to 370°C is characterized by a continuous mass loss for CTM–JP/PVP (25%). CTM–JP/DAA/PVP sample shows a more radical mass loss (35%) and the endothermic DTA maximum at 350°C (Fig. 3). The major degradation process starts at 370°C accompanied with endothermic effects with maxima at 440 and 430°C, respectively. This process is completed at about 450°C when CTM–JP/PVP shows 42% mass loss and CTM–JP/DAA/PVP more than 60% mass loss. Following gradual mass loss, due to oxidative decomposition of the residual organic material, totalling 70 and 80%, is completed at 780 and 740°C, respectively.

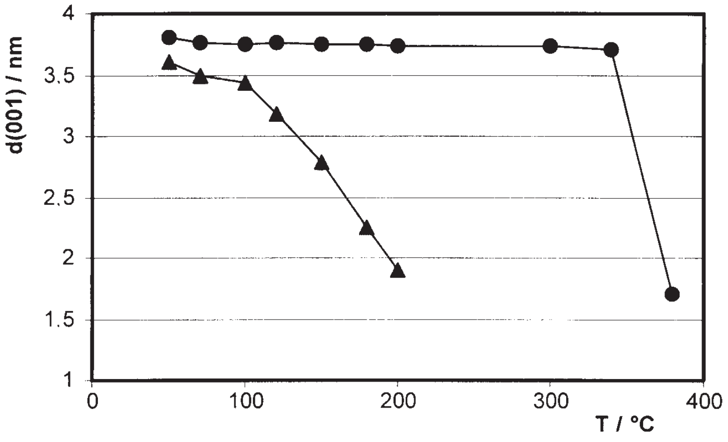

Fig. 4 The basal spacings of intercalates CTM–JP/DAA and CTM–JP/PVP after 30 min heat treatment

Thermal stabilities of two expanded structures CTM–JP/DAA and CTM–JP/PVP are shown in Fig. 4. A gradual decrease of basal spacing of CTM–JP/DAA sample and a relatively rapid collapse of interlayer space of CTM–JP//PVP sample at about 340°C are characteristic for their behaviour. The effect of intercalated guest molecule size (DAA, PVP) on the thermal stability of their intercalation complexes is quite obvious but no significant difference between intercalates with PVP 10 000 and 40 000 g mol^{-1} average molecular mass was observed. In spite of 20% mass loss at 340°C, CTM–JP/PVP sample still keeps the interlayer distance almost unchanged. Presence of DAA in CTM–JP/DAA/PVP makes the decomposition process slightly shifted towards lower temperatures.

Conclusions

The size of the guest molecule is one of the factors influencing thermal stability of organoclay intercalation complexes. Various organoclays show pronounced differences in thermal stabilities. The organophilic long chain alkylammonium montmorillonites as well as the intercalation complexes of organophilic CTM–JP with DAA show relatively low thermal stability. In contrast, CTM–JP/PVP sample shows a considerable capacity to keep the silicate structure expanded at higher temperatures during short time heat treatment. The presence of volatile compound DAA in the CTM–JP/DAA intercalation complex assists in increasing of its basal spacing during organoclay/polymer interaction but residual DAA decreases the thermal stability of resulting organoclay/polymer intercalation complex.

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References

1 Y. Fukushima, A. Okada, M. Kawasumi, T. Kurauchi and O. Kamigaito, Clay Miner., 23 (1988) 28.
2 R. A. Vaia, K. D. Jandt, E. J. Kramer and E. P. Giannelis, Chem. Mater., 8 (1996) 2628.
3 K. A. Carrado and L. Xu, Chem. Mater., 10 (1998) 1440.
4 A. Oya, Y. Kurokawa and H. Yasuda, J. Mater. Sci., 35 (2000) 1045.
5 A. Oya, in Polymer-Clay Nanocomposites, Ed. T. J. Pinnavaia and G. W. Beall, Wiley, Chichester 2000, p. 151.
6 K. Jesenák, Ceramics, 38 (1994) 35.
7 K. Jesenák, L'. Kuchta, L. Guller and J. Fúsková, Mineralia Slovaca, 29 (1997) 439.
8 V. Hlavatý and A. Oya, J. Thermal Anal., 46 (1996) 521.