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Thermal properties of fillers based on organoclays in the polymeric materials

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Abstract Nowadays, there is the widespread use of clay minerals as fillers in polymeric materials. One of the most widely used mineral is montmorillonite belonging to the smectite. We have prepared organically modified clays using two different types of accelerators TP and ZDT for sulfur vulcanization. Intercalation of these accelerators into the interlayer of clays was performed using a gas reaction at room temperature. They were examined (characterized) by thermal analysis (DTA, TG), X-ray analysis, and infrared spectroscopy (FTIR).

Keywords Montmorillonite · FTIR spectroscopy · TG · DTA · X-ray analysis

Introduction

Montmorillonite, with chemical composition (Na, Ca) 0.3 $(Al, Mg)_2Si_4O_{10}$ $(OH)_2 \cdot n\ H_2O$, is based on two mutually joined silica tetrahedral networks which are connected to octahedral networks of aluminum or silica hydroxide [1]. Tetrahedral and octahedral networks are bound by help of the oxygen atoms on the top, while these oxygen atoms belong to tetrahedrals and octahedrals [2]. Natural smectites can be the most frequently found as heteroionic forms with various interchangeable (inorganic) cations. For laboratory research, it is appropriate to use monoionic forms because they are defined more precisely [3].

The preparation of monoionic form is performed by appropriate cation saturation, and the given cation comes from appropriate aqueous solution of the chloride, nitrate, or acetate [4]. Montmorillonite is a mineral that has to be modified or treated to be used as filler. One of these possible modifications or treatments is closely connected with the intercalation processes which are used to implement the organic compound into the interlayer space of the clay minerals under certain conditions and it includes the cation exchange [5]. In relation to the intercalation of the organic compounds into the interlayer of the clay mineral, the given modification leads to the achievement of such properties which are necessary for application of the mentioned minerals in the function of the nanofiller in polymer nanocomposites [6].

Thermal (TG, DTA), XRD, and spectral (FTIR) analysis are very useful techniques for characterization of organoclays. Various characterization techniques have been used to evaluate structure, morphology, and properties of various materials [6–30].

For instance, XRD technique is based on X-rays and it is suitable for determination of distances of layers of organomodified clays via *d*(001) basal spacing [31, 32]. Infrared spectroscopy is a powerful method to study the bonding mechanisms on a molecular scale, and it provides structural information about the organoclays [33].

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Fig. 1 Diffraction patterns of monoionic form of CuMMT with accelerators TP, ZDT

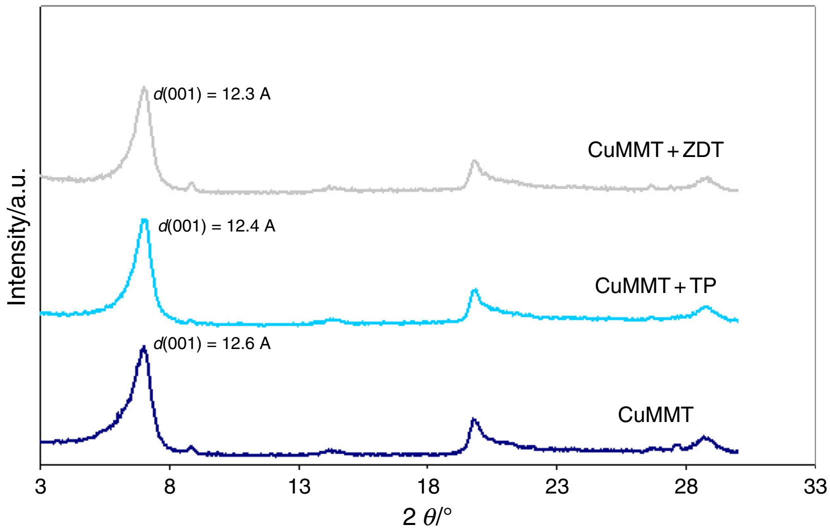
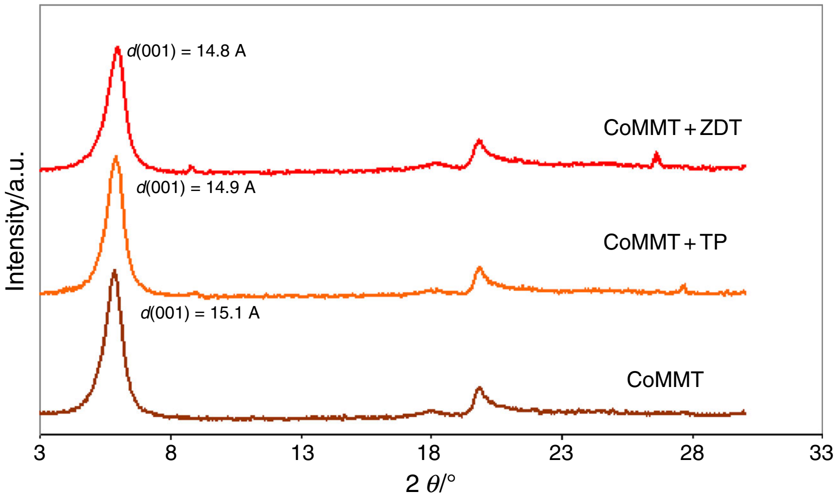


Fig. 2 Diffraction patterns of monoionic form of CoMMT with accelerators TP, ZDT



Thermogravimetric analysis (TG) provides the identification of different surfactant environments and structure arrangements and it can be also used for revealing of thermal and structural stabilities [31, 32]. The aims of this work are the systematic studies of fillers based on organoclays in the polymeric materials and also characterized them by thermal, XRD, and spectral analyses.

Experimental

The basic forms (CuMMT and CoMMT) were prepared using aqueous solutions of metal chlorides. After the ion exchange, the resulting solids were washed repeatedly with deionized water until a negative $AgNO_3$ test was obtained. The intercalation of TP and ZDT into CuMMT and CoMMT was carried out by solid–gas reactions.

The materials were characterized by measurements based on XRD, thermal (DTA, TG), and spectral (FTIR) analysis.

X-ray powder diffraction (XRD) patterns were recorded by Philips PW 1050 diffractometer using Cu Kα (0.154 nm) radiation in the region between 2° and 40° (2Θ) at speed 2° min^{-1}.

The thermogravimetry TG and DTA was carried out on a Derivatograph MOM Hungary from room temperature up to 800 °C in air atmosphere at a heating rate of 10 °C min^{-1}.

Infrared absorption spectra were recorded on a FTIR spectrometer tensor 27 in the wavelength range

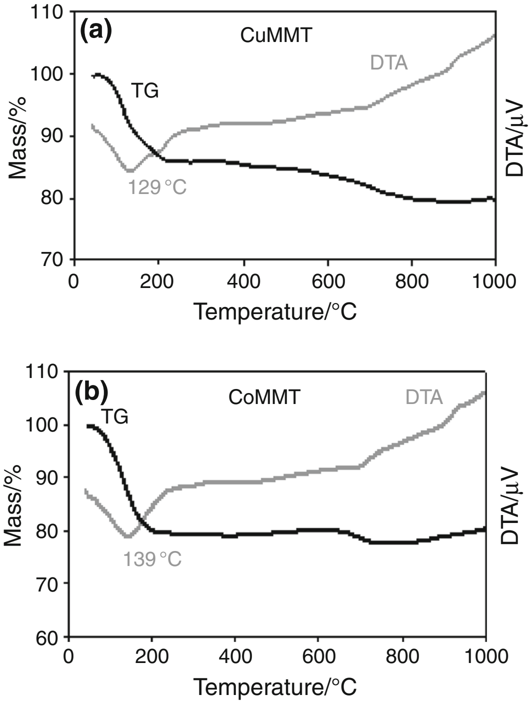


Fig. 3 TG and DTA curves of **a** CuMMT and **b** CoMMT

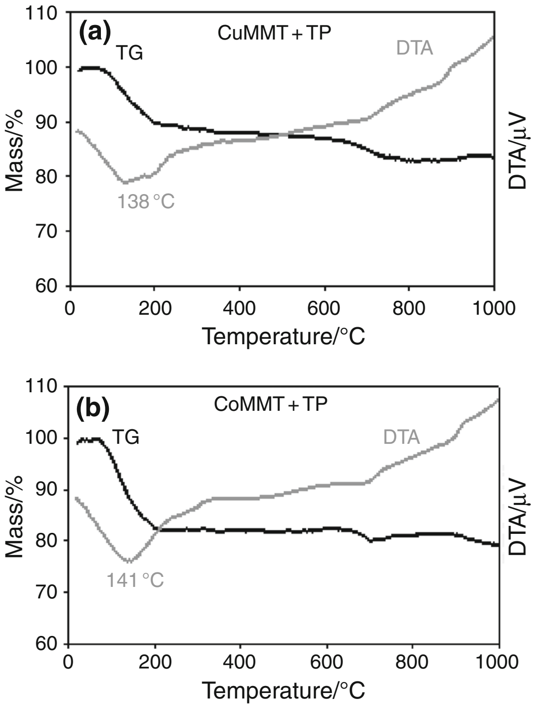


Fig. 4 TG and DTA curves of **a** CuMMT + TP and **b** CoMMT + TP

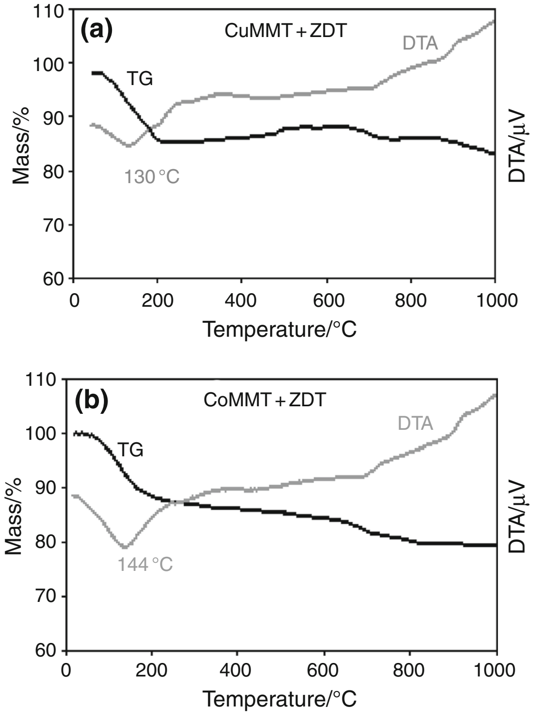


Fig. 5 TG and DTA curves of **a** CuMMT + ZDT and **b** CoMMT + ZDT

Table 1 The values of measured temperatures in relation to DTA

Monoionic form/ organoclays	Peak temperatures from DTA expressed in/°C	
	Dehydration/°C	Dehydroxylation/°C
CuMMT	129	683–737
CuMMT + TP	138	693–737
CuMMT + ZDT	130	695–736
CoMMT	139	669–729
CoMMT + TP	141	684–735
CoMMT + ZDT	144	681–719

4,000–400 cm^{-1} with the resolution of 4 cm^{-1}. The KBr pressed disk technique was used.

Results and discussion

X-ray analysis

Figures 1 and 2 show the X-ray diffraction patterns in the region 3–35° (2Θ) for the monoionic forms of montmorillonite (CuMMT, CoMMT) before and after modification using TP and ZDT. The *d*(001) value for CuMMT is 12,6 Å and for CoMMT is 15,1 Å.

Table 2 FTIR spectral data of the studied systems (4,000–400 cm^{-1})/cm^{-1}

Type of vibration	CuMMT	CoMMT	CuMMT + TP	CuMMT + ZDT	CoMMT + TP	CoMMT + ZDT
ν(Al–OH)	3,626	3,625	3,632	3,631	3,626	3,626
ν(Si–O)	1,025	1,023	1,036	1,038	1,039	1,041
δ(H–O–H)	1,641	1,638	1,640	1,639	1,642	1,642
ν(C–H)	–	–	2,961	2,966	2,963	2,965
ν(P–O–C)	–	–	960–1,040	960–1,040	960-1040	960–1,040
ν(P=S)	–	–	628	628	628	629

The interaction between the monoionic forms (CuMMT, CoMMT) and the surfactants (TP, ZDT) led to a shift of the *d*(001) diffraction peak toward higher 2θ values which imply the constriction of the interlayer spaces due to the surfactant intercalation. Due to a reduction in the interlayer space of clay, parallel arrangement of the intercalated organic molecules between the silicate sheets was observed [34]. It is necessary to point out that the given basal spacing *d*(001) exhibited lower values in comparison to the initial or staring material.

Thermal analysis

The thermoanalytical curves of the monoionic forms of montmorillonite (CuMMT, CoMMT) before and after modification using TP and ZDT are shown in Figs. 3–5. DTA curves of the basic forms CuMMT and CoMMT show a strong double peak (CuMMT: 129 °C and 196 °C; CoMMT: 139 °C) and this effect reflects the release of water molecules which are located in the interlayer of Cu^{2+} and Co^{2+} cations. The dehydroxylation process that is connected with the loss of water results from the decomposition of structural OH groups occurring in 400–800 °C [33]. The overall mass losses are following: CuMMT (20 %) and CoMMT (22 %).

The presence of organic molecules (TP and ZDT) in the monoionic forms of montmorillonite increases the number of decomposition steps. Thermal decomposition of organically modified clays starts with the release of physisorbed water and a small amount of physisorbed TP and ZDT. Endothermic peaks of DTA curves were observed at specific temperatures (CuMMT: 129–138 °C; CoMMT: 126–144 °C). The processes connected with dehydroxylation and thermal decomposition of TP and ZDT in organomodified products are shifted to higher temperatures and it is probably due to strong interaction between accelerators of vulcanization and Cu^{2+} and Co^{2+}. The overall mass losses of organically modified clays are following: CuMMT + TP (14 %), CuMMT + ZDT (14.1 %), CoMMT + ZDT (18.7 %) and CoMMT + TP (20 %). The values of measured temperatures of DTA for the CuMMT and CoMMT before and after modification are given in Table 1.

FTIR spectroscopy

There are several peaks in the studied region (4,000–400 cm^{-1}) of FTIR spectra of the monoionic forms of montmorillonite (CuMMT, CoMMT), and the given peaks were attributed to the stretching vibrations of OH groups (3626, 3625 cm^{-1}) and water (3441, 3432 cm^{-1}), stretching vibrations of Si–O groups (1025, 1023 cm^{-1}), bending vibrations of AlAlOH (914, 914 cm^{-1}) and Al-MgOH (842, 841 cm^{-1}), bending vibrations of Al–O–Si groups (524, 524 cm^{-1}) and Si–O–Si at (465, 465 cm^{-1}) [32–35]. The measured IR spectra of the organically modified MMTs are quite complicated. The significant difference between the monoionic forms of montmorillonite (CuMMT, CoMMT) and the intercalation products can be observed mostly in the region of 2,000–700 cm^{-1}. Spectra of the organically modified CuMMT and CoMMT involve bands in the region 2,958–2,966 cm^{-1} and it may be assigned to the vibrations of C–H groups. Stretching vibrations of P–O–C groups at 960–1,040 cm^{-1} and P = S groups at 628–629 cm^{-1} were observed. The amounts of the absorption bands of the non-modified and organo-modified clays are given in Table 2.

Conclusions

The main aim of this work was to prepare and characterize organically modified clays using two types of phosphate surfactants TP and ZDT. Based on the results, it can be concluded that d-spacing was reduced because the molecules of surfactants in the interlayer monoionic forms CuMMT and CoMMT were arranged in a parallel way. The presence of surfactants was also confirmed by IR spectroscopy where presence of the characteristic bands for these organic compounds was recognized and it was also proven by the measurements based on thermal (DTA, TG) and XRD analysis.

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