XRD Characterization of Organically Modified Gyrolite

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Organic modification of layered silicate gyrolite was achieved by ion exchange reaction between the interlayer metal cations and octadecylammonium ions. X-ray diffraction (XRD) and thermal analysis were used to estimate and evaluate the influence of modification temperature, octadecylamine purity and gyrolite chemical composition on the efficiency of organic modification of synthetic gyrolite. It was established that long-chain ammonium ions do not change the basic interplanar distance (001) of sodium substituted gyrolite after modification, however, a new crystal structure – organically modified compound of gyrolite and octadecylammonium ions have been formed. It was found that organic chains are located inside silicate layers as intercalated species and outside layers – as complexed species. Otherwise organic modification of pure gyrolite was unsuccessful.

Keywords: layered silicates, gyrolite, nanoparticles, octadecylammonium chloride, modification, intercalation, XRD.

1. INTRODUCTION

Polymer nanocomposites are of great importance for a multitude of industrial uses in automotive, health care, electronics, aerospace, mechanical engineering, construction, health care, building and etc. [1–4]. The use of inorganic nanoparticles in polymers presently is a widely investigated area of research. Depending on which properties are to be altered, nanoparticles are chosen for their chemical composition, their size and their morphology. The addition of less than 5 wt.% of nanoscale filler to a polymer, the resulting composition exhibit enhanced mechanical, thermal, dimensional and barrier performance properties, when compared to the ordinary material due to the much stronger interfacial forces between well-dispersed nanometer-sized filler and the matrices [5]. For example, layered silicates are widely used in the improvement of mechanical properties, in the decrease of gas permeability and as additives for flame retardancy of composites [6–8]. Nanoclays were the start of polymer nanocomposite materials (PNCM) in the 1990's when Toyota for the first time used Nylon 6 nanoclay nanocomposites to produce timing belt covers [9].

Incorporation of nanoparticles in a polymer matrix is concerned with the problems of components compatibility, uniform distribution, nucleation, agglomeration and etc. [8]. Layered silicates are one of several ideal reinforcements for polymers due to its high aspect ratio and low cost, but unmodified silicate is not easily dispersed in most polymers because of its natural hydrophilicity and incompatibility with organic liquid and polymers to achieve good dispersion and adhesion [10]. Thus surface modifications are required in order to achieve better interaction of silicates surface with a polymeric matrix. The exchangeable hydrated cations (K^+, Li^+, Na^+, Ca^{2+}) present in the layered silicates interlayer space [11, 12] can be replaced by organic modifiers. The most commonly used organic cations contain one or more octadecyl groups,

derived from hydrogenated animal fat tallow are di ($C_{18}H_{37}$) dimethyl ammonium, di ($C_{18}H_{37}$) benzyl methyl ammonium and ($C_{18}H_{37}$) benzyl dimethyl ammonium [13].

Each combination of amine (e.g. primary, quaternary, long-chain, short-chain, polyamines) and layered silicate (e.g. montmorillonite, mica, vermiculite) yields a complex with its own unique characteristics [13]. Some of the investigators for organophilic modification used quaternary long-chain ammonium salts: trimethyl cocoammonium bromide, trimethyl tallow ammonium chloride, trimethyl dodecylammonium chloride and others [14]. Modification leads to reduce the physical or electrostatic bonding force of clay interlayer's, an extension of the interlayer galleries due to the changes of inorganic cations contained in these galleries allowing the alkylammonium ions to intercalate between the plates. It is well known that the interlayer distance increases with increasing alkyl chain length. For example, after modification of layered silicate montmorillonite with alkylammonium ions, interlayer spacing increases from 6.9 Å for $n = 4$ to 17.4 Å – 27.1 Å for ions with n in the range 8–18 so this process facilitates the formation of an exfoliated nanocomposite. The modified silicate was characterized by XRD analysis [15, 16]. Organically treated layered silicates (clays) can be mixed with normal polymer matrix materials to form a nanocomposite in which clay layers are intercalated or exfoliated throughout the material. The exfoliated layers are sufficiently separated and randomly orientated to allow full interfacial bonding and to contribute all of their strength to improve the properties of the nanocomposite [17].

Gyrolite is one type of calcium silicate hydrates (C–S–H) with a layered most likely structure $NaCa_{16}Si_{23}Al_{60}(OH)_8 \cdot 14H_2O$ and rarely occurs as a natural mineral in association with zeolites [18]. Structure and element composition repeatability, crystallite size, purity are characteristic for synthetic gyrolite. Layered silicates, organically modified by octadecylammonium salt, have been adopted to successfully fabricate the exfoliated organic silicate/polymers nanocomposites [10, 12].

In this investigation synthetic pure and sodium substituted layered nanosized gyrolite was organically

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modified with octadecylammonium chloride (ODA-Cl) $CH_3(CH_2)_{17}NH_3^+Cl^-$ in order to prepare the new filler for epoxy polymer-layered silicate nanocomposite.

2. EXPERIMENTAL

The material used in the present work was hydrated calcium silicate gyrolite pure with most likely the crystal chemical formula $Ca_{16}Si_{24}O_{60}(OH)_8(14+x)\cdot H_2O$, $x \leq 3$ and sodium substituted gyrolite – $NaCa_{16}Si_{24}O_{60}(OH)_8\cdot 14H_2O$ [18], synthesized in Kaunas University of Technology Department of Silicate Technology. Synthetic gyrolite is mesoporous material with specific surface area $SBET$ ~ 71 m²/g – 95 m²/g, the total pore volume ΣV_p ~ 150 mm³/g and micropore volume ~ 11 mm³/g [19, 20].

The XRD analysis of materials was performed using a diffractometer DRON-6. Diffraction patterns were re-corded at 35 kV and 20 mA. Scanning was carried out at a step size of 0.02° (2θ). Counting time was 5 s per step for as prepared synthetic gyrolite and 0.5 s per step for organically modified gyrolite. Flat diffracted beam pyrolitic graphite monochromator was used to separate CuK_α radiation. Equipment was calibrated by corundum α-Al_2O_3 (99.9 %) Alfa Aesar standard. Silicon powder standard has been added to analyzing synthetic gyrolite samples for precision lattice parameter measurements. The powder X-ray diffraction patterns of synthetic and modified gyrolite were identified with those available in PDF-2 data base [21].

Simultaneous thermal analysis (differential scanning calorimetry – DSC and thermogravimetry – TG) was also performed for evaluation of the thermal stability and phase transformation of synthetic unmodified and organically modified gyrolite at a heating rate of 15 °C/min, the temperature ranged from 30 °C up to 1000 °C under air atmosphere. The test was carried out on a Netzsch instrument STA 409 PC Luxx. The ceramic sample handlers and crucibles of Pt-Rh were used.

Octadecylamine $(CH_3(CH_2)_{17}NH_2$ 90.0 %, 99.9 % purity) and 10 N hydrochloric acid (HCl) were used for synthesis of octadecylammonium chloride (ODA-Cl) according by Le Pluart technique [24]. ODA-Cl was prepared by mixing 5.66 g of octadecylamine with 2.1 ml HCl (10 N) in 300 ml distilled water and solution stirred vigorously for 3 h at 80 °C temperature. Than a small excess related to the silicate's CEC (cation exchange capacity) of the pure or sodium substituted gyrolite was dispersed in prepared ODA-Cl solution and stirred for 3 h at 80 °C temperature. A white precipitate formed was filtrated and washed several times with hot distilled water until no chloride was detected in the filtrate by one drop of 0.1 N AgNO₃ solution. Washing of precipitate ensures the elimination of an excess of ODA-Cl and the secondary products of the cationic exchange. The resulting organogyrolite was dried at 85 °C during 36 h and kept dry in desiccator.

3. RESULTS AND DISCUSSION

The XRD patterns of pure and sodium substituted gyrolite were refined with a GSAS program and instrumental as well as lattice parameters determined during Le Bail's fitting (Fig. 1) [22, 23]. In order to obtain instrumental profile

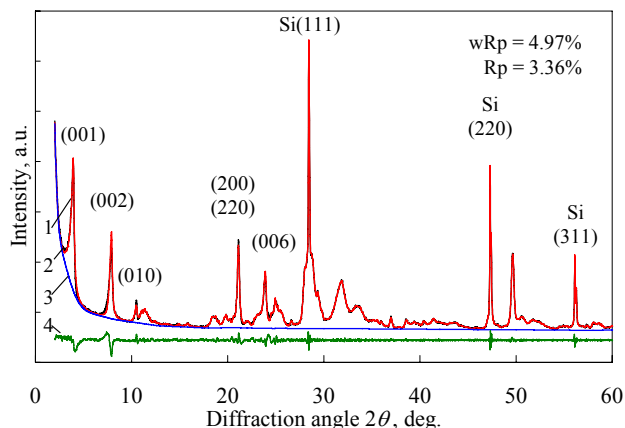parameters of DRON-6 (Bragg-Brentano flat plate X-ray powder diffractometer) the CeO₂ standard also was refined.

Fig. 1. The powder X-ray diffraction patterns of pure synthetic gyrolite after the final Le Bail's fitting: 1 – the observed scattered intensity (Y_i^{obs}), 2 – the calculated intensity (Y_i^{calc}), 3 – background and 4 – the difference between the observed and calculated intensities ($Y_i^{obs} - Y_i^{calc}$)

Phase identification and calculated lattice parameters have shown that the synthetic gyrolite has crystal structure vary close to Merlino's investigated natural gyrolite [18] (Table 1) and the calculated crystallite size of gyrolite varied in the range of 10 nm – 50 nm depending on synthesis conditions. This result has proved that repeatability of crystal structure and elemental composition of layered calcium silicate hydroxide hydrate – gyrolite can be obtained by isothermal synthesis.

Table 1. The calculated lattice parameters of pure and sodium substituted gyrolite

Lattice parameters	Pure gyrolite*	Sodium substituted gyrolite*	Sodium substituted gyrolite (by S. Merlino [18])
a, nm	0.9735	0.9741	0.974
b, nm	0.9727	0.9737	0.974
c, nm	2.2463	2.24	2.24
α, °	95.48	95.69	95.70
β, °	91.50	91.51	91.50
γ, °	120	120	120

* gyrolite synthesized in Kaunas University of Technology.

XRD studies of organically modified pure and sodium substituted gyrolite is shown in Figure 2 (curves 2 and 3). The crystal structure of pure gyrolite remains unchanged after organophilic modification with ODA-Cl (Fig. 2, curve 2). The basic interlplanar distance (001) around 2.24 nm was not affected during the organical treatment. However, the dramatic structural changes took place when sodium substituted gyrolite was organically modified with ODA-Cl (Fig. 2, curve 3). Although, the expected expansion of interlayer distance (001) did not occur (such expansion is the usual thing when the layered silicates, e. g. montmorillonite, are modified), the new Bragg peak around the 3.27 nm has originated and a noticeable broadening as well as the significant intensity increase of diffraction peak around 0.42 nm from planes (200) and ($\bar{2}$20) took place. The latter is probably related to the

transformation of the silicate layers. Meanwhile, the origin of new Bragg peak could be for two reasons.
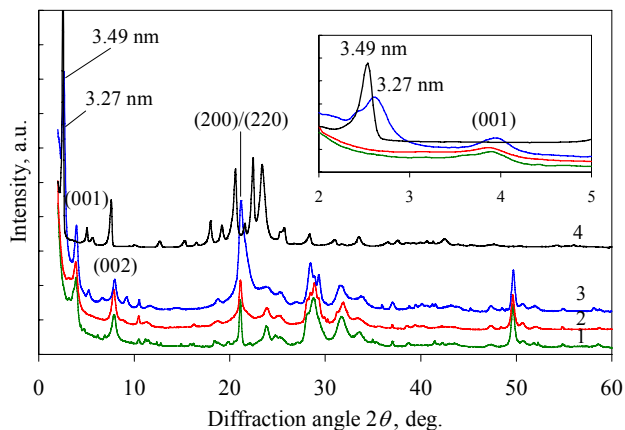

Fig. 2. X-ray diffraction patterns: 1 – synthetic gyrolite, 2 – organically modified pure gyrolite, 3 – organically modified sodium substituted gyrolite, 4 – ODA-Cl

Either a simple mixture of gyrolite and ODA-Cl is formed and a new peak matches ODA-Cl, or intercalation occurred by cationic exchange between these two compounds and new peak shows a novel crystallographic structure formation. The latter preposition has been confirmed by several arguments. At first, a new Bragg peak has position around 3.27 nm (Fig. 2, curve 3) which considerably differ from Bragg peak around 3.49 nm of pure ODA-Cl (Fig. 2, curve 4).

Furthermore, differential scanning calorimetry (DSC) analysis showed dissimilar thermal properties of as synthesized gyrolite, organically modified sodium substituted gyrolite and ODA-Cl (Fig. 3, curves 1 – 3).
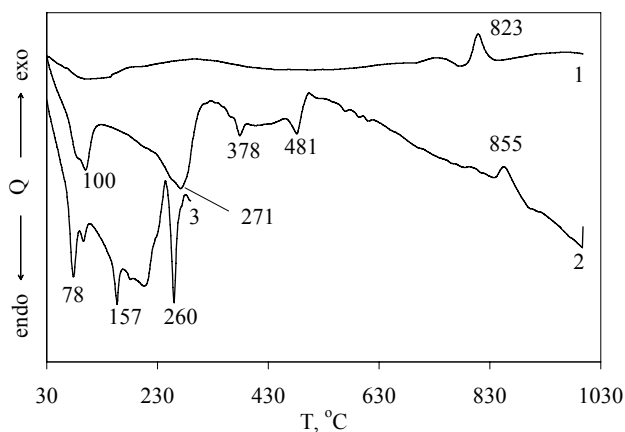

Fig. 3. DSC curves of gyrolite. Indexes: 1 – sodium substituted gyrolite, 2 – organically modified sodium substituted gyrolite, 3 – octadecylammonium chloride

After the cationic exchange, some octadecylammonium ions remain only adsorbed on silicate plates and are not intercalated between the layers. The thermal decomposition of this compound takes place in the range 200 °C – 350 °C (Fig. 3, curve 2) while as synthesized ODA-Cl completely decomposes at 270 °C (Fig. 3, curve 3). The well intercalated modifying ions show higher thermal stability so the decomposition temperature is between 350 °C and 500 °C and depends on interaction between octadecylammonium groups and the gyrolite plates (Fig. 3, curve 2). At temperatures higher than

700 °C, the dehydroxylation of the gyrolite takes place (Fig. 3, curves 1, 2).

Thus in the organically modified gyrolite octadecylammonium chains locate inside silicate layers as intercalated species (indicates by the intensity increasing and broadening of Bragg peak (200/$\bar{2}$20)) and outside layers – as complexed species (indicates by new peak originating around 3.27 nm).

Multifold washing with water of organically modified gyrolite does not change character of X-ray diffraction pattern that also indicates the successful cationic exchange reaction result.

In order to determine the optimal organic modification conditions the reaction was performed at various temperatures. Powder X-ray diffraction analysis showed that the most intensive Bragg peak has originated around 3.27 nm in XRD pattern of gyrolite, modified at 80 °C (Fig. 4, curve 1) while at 120 °C this peak disappeared (curve 3), moreover Bragg peak (200)/($\bar{2}$20) around 4.2 nm increases mostly at 80 °C temperature too (curve 1).
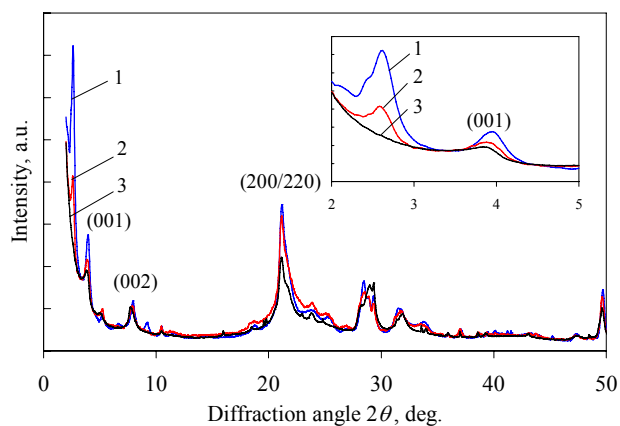

Fig. 4. X-ray diffraction patterns of organically modified sodium substituted gyrolite. Modification temperature: 1 – 80 °C, 2 – 100 °C and 3 – 120 °C
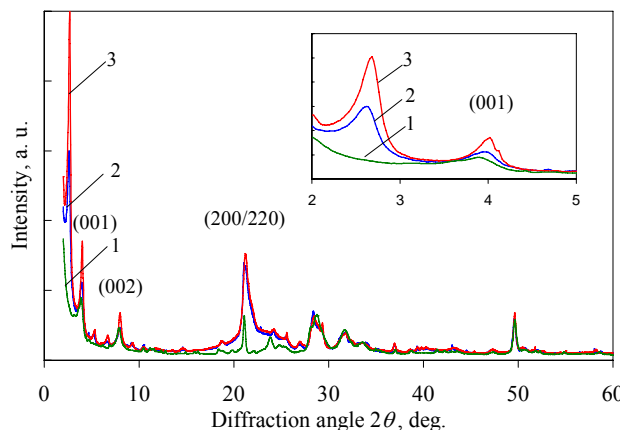

Fig. 5. X-ray diffraction patterns of sodium substituted gyrolite. Indexes: 1 – unmodified, 2 – organically modified with ODA-Cl synthesized from 90 % ODA and 3 – organically modified with ODA-Cl synthesized from 99.9 % ODA

An ions substitution reaction did not proceed at lower temperatures and crystal structure of gyrolite remains unchanged, thus indicating that optimal temperature of modification is 80 °C.

The purity of octadecylamine also plays a significant role in ions exchange reaction of gyrolite (Fig. 5, curves 1–3). So the most intensive Bragg peak around 3.27 nm has originated in the XRD pattern of gyrolite organically modified with ODA-Cl synthesized from 99.9 % purity octadecylamine (curve 3).

This study showed that XRD analysis is very informative method for evaluation of modified low base calcium silicate hydrates structural changes. A series of interesting results were established but not all fully yet explainable. Further investigations will be performed to clarify the mechanism of organic modification of synthetic pure and sodium substituted gyrolite with octadecylammonium chloride and to achieve complete intercalation of silicate.

CONCLUSIONS

The XRD and thermal analysis showed that pure nanosized gyrolite is difficult to modify with octadecylammonium chloride (ODA-Cl) likely due to structural features.

Bragg peak $(200)/(\bar{2}\,20)$ broadening and intensity increasing proved that nanosized sodium substituted gyrolite was successfully modified using ODA-Cl. The origin of new Bragg peak around 3.27 nm also confirms this result. The necessary conditions for modification are 80 °C temperature of solution and 99.9 % purity of octadecilamine. The modification was through an exchange reaction between the inorganic cations on the gyrolite and the octadecylammonium ions in the solution.

It was established that organic chains locate inside silicate layers as intercalated species and outside layers – as complexed species.

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