

## ARTICLE INFO

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## **X-RAY DIFFRACTION STUDY OF MONTMORILLONITE MODIFIED WITH TETRAFLUOROPHTHALIC ACID AND ITS ANHYDRIDE**

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**Abstract.** Structure of montmorillonite modified with tetrafluorophthalic acid and its anhydride was studied by X-ray diffraction analysis at small- and wide diffraction angles. X-ray phase analysis established the composition of initial clay, including 98 % by weight of montmorillonite. It was shown that immobilization of tetrafluorophthalic acid and tetrafluorophthalic anhydride is accompanied by formation of organomineral structures, both at the surface and in the interlayer spaces of aluminosilicate.

**Keywords:** tetrafluorophthalic anhydride, tetrafluorophthalic acid, organofluorine compounds, fluoropolymers, montmorillonite, immobilization, structure.

### **Introduction**

One of the ways to develop polymeric materials with improved set of properties is the creation of fluorine-containing composites containing organomineral components [1–4]. Using of layered montmorillonite clays (MMT), which are characterized by particle shape anisotropy (as carriers of organofluorine compounds of various chemical structures [5]), opens up the fundamentally new possibilities for obtaining fluorinated materials. As a rule, the appending of poly-, perfluorinated compounds and MMT into macromolecular systems is accompanied by

increase in thermal stability, wear resistance and level of physicochemical characteristics of resulting composites [1–5], and also by decrease in its flammability and gas permeability.

Formation of organophilic layers, i.e. organophilization of clay, will facilitate the penetration of polymer macromolecules into its interlayer galleries by increasing the distance between layers [6]. Herewith, the features of immobilization at MMT tetrafluorophthalic acid and its anhydride, as well as the structural studies of these organoclays, are not described in the literature. The presence of reactive groups in the composition of these compounds determines the possibility of their further chemical transformations with appending of immobilized forms of these substances at the stage of synthesis or processing of polyamides, polyesters and polyurethanes.

The purpose of this paper is to study MMT, modified with tetrafluorophthalic acid and tetrafluorophthalic anhydride using small- and wide angle X-ray diffractometry.

### Experimental part

We used sodium MMT with specific surface area of  $595\text{m}^2\text{ g}^{-1}$  (by water) and cation exchange capacity of 100 mg-eq/100 g (LLP «B-Clay», Kazakhstan). Tetrafluorophthalic acid (m.p. 150–155°C) and tetrafluorophthalic anhydride (m.p. 94–96 °C) were provided by P&M-Invest Company (Dolgoprudny, Moscow reg.). The mass content of main substance in the samples was 97%.

Clay modification by fluorinated compounds was carried out by means of ultrasonic dispersion (at frequency 40 kHz) in analytical grade cyclohexanone medium at 50 °C for 2 h. Structural studies of vacuum-dried samples were carried out at room temperature via Bruker D8 Advance automated diffractometer (by Bragg-Brentano reflection method,  $\text{CuK}\alpha$ , radiation,  $\lambda = 1.5418\text{ \AA}$ , Ni-filter). The experimental diffraction patterns were processed using «Diffrac.Eva» and «Topas» software packages. Diffraction patterns were recorded for air-dried samples of initial MMT and two organoclays containing respectively, 5% wt. acid and its anhydride.

Registration of diffraction patterns of initial MMT at wide angle range (in Debye-Scherrer geometry, transmission method) was carried out at a wavelength of X-ray radiation 1 Å (RDE «Kurchatov Institute», station «Structural Materials Science» of Kurchatov Synchrotron Radiation Source). The crystalline standard  $\text{Na}_2\text{Al}_2\text{Ca}_3\text{F}_{14}$  ( $a = 10.24\text{ \AA}$ ) was used as a calibrant of angular scale.

### Discussion of results

Using X-ray phase analysis (in transmission mode), it was revealed that X-ray pattern of initial clay is represented by a significant amount of crystalline phases (in wt. %): 98 - MMT, 1.2 -

gypsum, 0.3 - quartz and silica modifications, 0.2 - calcite, 0.2 - phosphates, 0.1 - feldspars. Characteristic line with a pronounced asymmetry  $23.3^\circ$  ( $d = 4.46 \text{ \AA}$ ), observed earlier by the authors in [7], refers to MMT phase and corresponds to intralayer ordering of layered aluminosilicate structure. Its shape indicates a two-dimensional nature (there is no orientational ordering between adjacent layers of aluminosilicate structure).

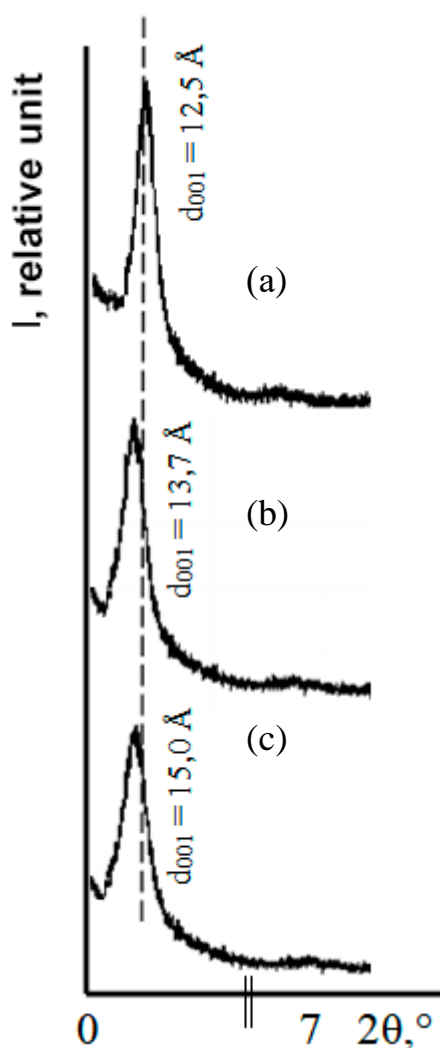
In passing from initial MMT to clay samples containing immobilized tetrafluorophthalic acid and its anhydride, two types of changes appear at the diffraction patterns (in reflection mode), see Table 1 below.

**Table 1.** Indices ( $hkl$ ), interplanar distances ( $d$ ) and diffraction intensity ( $I$ , %) of reflections for clay samples (at wide diffraction angle range)

| Indices<br>$hkl$ | Clay modifier    |         |                          |         |                               |         |
|------------------|------------------|---------|--------------------------|---------|-------------------------------|---------|
|                  | None             |         | Tetrafluorophthalic acid |         | Tetrafluorophthalic anhydride |         |
|                  | $d, \text{ \AA}$ | $I, \%$ | $d, \text{ \AA}$         | $I, \%$ | $d, \text{ \AA}$              | $I, \%$ |
| (003)            | 5,00             | 61      | 4,48                     | 55      | 4,45                          | 50      |
| (110)            | 4,47             | 32      | 4,42                     | 30      | 4,37                          | 27      |
| (004)            | 3,75             | 31      | 3,61                     | 30      | 3,60                          | 24      |
| (005)            | 3,01             | 60      | 3,00                     | 54      | 2,57                          | 50      |
| (200)            | 2,59             | 40      | 2,56                     | 38      | 2,50                          | 34      |
| (006)            | 2,49             | 75      | 2,45                     | 71      | 2,40                          | 70      |
| (007)            | 2,15             | 15      | 2,10                     | 10      | 2,00                          | 9       |
| (008)            | 1,85             | 20      | 1,80                     | 13      | 1,76                          | 10      |
| (009)            | 1,67             | 30      | 1,61                     | 27      | 1,60                          | 20      |
| (060)            | 1,50             | 28      | 1,47                     | 21      | 1,42                          | 20      |

First of all, the lines of MMT structure, initially observed at diffraction angle range  $2\theta = 15\text{--}75^\circ$ , are shifted for organoclays towards smaller angles ( $\Delta 2\theta = 1\text{--}3^\circ$ ). This shift is associated with processes of intercalation of tetraphthalic acid molecules and its anhydride into interlayer spaces of this clay. Another strong change in diffraction patterns is associated with appearance of a peak near  $2\theta = 21^\circ$  ( $d = 4.94 \text{ \AA}$ ), due to formation of separate phase by tetrafluorophthalic acid and its anhydride (including multicenter proton-donor and proton-acceptor interactions with functional groups of aluminosilicate plates [6, 8]), both at MMT surface and its interlayer spaces. The intensity of this component is maximum ( $I = 45\%$ ) in the case of organoclay containing immobilized tetrafluorophthalic anhydride ( $I = 18\%$  for MMT modified with tetrafluorophthalic acid).

According to small-angle diffractometry data (see Fig. 1 below), at a fixed content of organofluorine compound (5% wt.) in clay, increasing in interplanar distance between aluminosilicate layers (according to position of small-angle basal reflection  $d_{001}$ ) is maximum for MMT containing tetrafluorophthalic anhydride. These changes (including some increasing in asymmetry of small-angle reflection line) are associated with partial chemical interaction of carboxyl groups of tetrafluorophthalic acid with mineral base of clay (metal oxides, displacement of polysilicic acids from salts) [6], which hinders the further penetration of molecules of this acid into interlayer spaces of MMT.



**Figure 1.** Small angle diffraction patterns for clay samples:

*a - initial MMC;*

*b - contains the tetrafluorophthalic acid;*

*c - contains the tetrafluorophthalic anhydride.*

### Conclusion

Aggregative data analysis of small- and wide angle diffractometry ( $d_{001}$  values, diffraction intensity, position of reflections and line shapes) indicates that chemical structure of organofluorine modifier determines its ability to intercalate into MMT interlayer space. The immobilization of

tetrafluorophthalic acid at the clay is accompanied by its predominant chemical interaction with MMT mineral basic to formation of corresponding salts, which leads to a lower  $d_{001}$  value (in comparison with  $d_{001}$  value for organoclay containing immobilized tetrafluorophthalic anhydride).

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