

The Method of Quantifying the Intercalation Degree of Clay Minerals by Organic Compounds

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Abstract

Clay-polymer nanocomposites are one of the most intensively developing classes of construction materials which find wide application in many fields of industrial production. Physical mechanical properties of these materials are essentially determined by the quality of organoclays derivation which are their main functional component. Development of control methods of organoclays derivation is an important element of technological process. It ensures high quality of synthesized nanomaterials and guarantees completeness of functionalization process of mineral raw materials. A new approach to quantitative assessment of intercalation degree of clay particles is represented in the paper. This approach is based on the analysis of diffractometric curves of layered crystal structure with defined correlation between intercalated packages and their order of sequence determined via DFT calculations. An example of the suggested approach implementation for the case of successive intercalation of montmorillonite by a long-chain organic compound is also represented in the paper. The assessment of dynamics and character of behavior of main basal reflections of the intercalated system diffraction patterns is given in the paper.

Keywords: Intercalation; clay minerals; organoclays; X-ray diffraction; DFT.

INTRODUCTION

Polymer nanocomposite materials filled with organic modified clay minerals (organoclays) find their wide application in different fields of engineering, biomedicine, ecology [1,2]. These composites arouse growing research interest successfully combining many useful properties: immunity to aggressive outward influences, mechanical durability, fire resistance, thermal stability and other specific properties [3-5]. The degree and quality of organoclay dispersion in polymer matrices is a determining factor for reaching the advanced properties in all these applications. The efficiency of organoclays used as fillers for polymers is connected with possibility of clay particles exfoliation into monolayers and their even dispergation in polymer matrix [6]. High degree of such exfoliation is a necessary condition when organoclay is introduced into a polymer matrix. In this case a necessary complex of conditions will be reached. Herewith the quality of exfoliation of clay particles in polymer matrix is determined by a number of factors. These include a type of

organic modifier used, size and degree of particles order, and also the quality of the process of clay particles organomodification [7]. Inasmuch as it's impossible to reach the wanted exfoliation in a polymer matrix without high quality and completely performed process of clay particles organomodification, the control of this parameter is both of great theoretical and practical interest.

A good number of scientific papers is devoted to the issues of studying the structure of intercalated clay minerals complexes [8-13] There has also been a number of attempts to state correlation interconnection between structural characteristics of organoclays and the observed parameters obtained due to the use of X-ray diffraction, IR-spectroscopy and thermal analysis [7,14]. Nevertheless, the applied in many well-known approaches empirical integral criteria of analysis of the process of clay minerals intercalation don't allow to obtain the information on the content of intercalated particles within total volume of the sample under analysis and the completeness degree of organomodification process.

New approach to quantitative analysis of intercalation process of clay minerals particles and to control of formation completeness of organoclay complexes is represented in the paper. This approach is based on the analysis of diffractometric curves of layered crystal structures with defined correlation between intercalated packages and their order of sequence determined via DFT calculations. An example of the suggested approach implementation for the case of successive intercalation of montmorillonite by a long-chain organic compound is also represented in the paper. The assessment of dynamics and character of behavior of main basal reflexes $00l$ of the intercalated system diffraction patterns is given in the paper. The criteria of intercalation degree assessment of clay particles is determined on the basis of relative intensity of basal reflexes $00l$.

MATHEMATICAL BASIS OF XRD ANALYSIS OF INTERCALIATED CLAY MINERALS

The task of simulation of X-ray diffraction on crystal structures makes the basis of X-ray diffraction analysis [15]. Crystal structures are 3D diffraction gratings formed by parallel atomic planes. Herewith, X-ray radiation is scattered in the preferred directions determined by Bragg's law [16]. The observed diffraction pattern depends on mutual arrangement and scattering ability of atoms of crystal lattice.

The diffraction pattern is determined by electron density distribution and is proportional to atomic number of elements. Thus diffraction pattern is unambiguously determined by the parameters of unit cell and by the coordinates of atoms in it [17]. Positions of diffraction pattern reflexes are changed in the result of unit cell transformations. The observed intensity of X-ray scattering by unit cell atoms is described by the expression [18]:

$$J(\theta) = \sum_{hkl} \Lambda_{hkl} (\theta - \theta_{hkl}) |F_{hkl}|^2, \quad (1)$$

where h, k, l – totality of integers, which determine possible reflections of X-ray radiation for the given crystal lattice; θ – reflection angle; θ_{hkl} – reflection angle for the reflex hkl ; Λ_{hkl} – instrumental profile determining the dependence of reflex intensity hkl on spatial orientation of unit cell and X-ray polarization; F_{hkl} – structural function determining X-ray scattering in the direction of hkl – plane.

Structural function F_{hkl} contains information on crystal structure which is determined by the reaction of unit cell atoms on X-ray impact considering their thermal movement. It can be represented in the form of:

$$F_{hkl} = \sum_{\mu} T_{\mu} \exp(i\mathbf{q}_{hkl}\mathbf{R}_{\mu}) \int_0^{\infty} \rho_{\mu}(r, R_{\mu}) \frac{\sin(q_{hkl}r)}{q_{hkl}r} r^2 dr, \quad (2)$$

where \mathbf{q}_{hkl} – reciprocal lattice vector of hkl reflex, $\rho_{\mu}(r)$ – electron density of the μ –th atom, \mathbf{R}_{μ} – equilibrium position of μ –th atom, T_{μ} – Debye-Waller factor for the μ –th atom.

Thus, data on crystal nuclear configuration and electron subsystem density $\rho(\mathbf{r}, \mathbf{R})$ in equilibrium state are necessary for calculation of diffraction pattern of crystal system in the general case.

DETERMINATION OF EQUILIBRIUM INTERCALATED STRUCTURE OF CLAY MINERALS

Density functional theory is applied in the paper in order to obtain the necessary equilibrium structure of clay mineral which is intercalated by long-chain organic compound. DFT is the most efficient instrument for simulation of electron structure of connected with it physical properties of solid bodies [19-21].

The basis of DFT was embedded in the works of L. Thomas and E. Fermi [22], later on it was developed by P. Hohenberg [23] and W. Kohn [24]. Introduction of electron density state, which depends only on three independent variables, enables to reduce many-electron task in the Born-Oppenheimer approximation to the solution of Kohn-Sham equation in the form of:

$$\left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial r^2} + V_{SCF}(\rho, r, R) \right) \psi_n(r, R) = \varepsilon_n \psi_n(r, R), \quad (3)$$

where n – number of state, \mathbf{r} – radius vector corresponding

the electron subsystem, \mathbf{R} – radius vector determining the position of crystal structure nucleus, $V_{SCF}(\rho, r, R)$ – potential of Kohn-Sham self-consistent field, which is determined by electron density of many-atom system

$$\rho(\mathbf{r}, \mathbf{R}) = \sum_n |\psi_n(\mathbf{r}, \mathbf{R})|^2. \quad (4)$$

Iteration procedure is used for numeric solving of Kohn-Sham equations. Within this procedure calculation of electron states participating in the formation of chemical bond is performed. Pseudopotentials are used in order to account the electrons of deep atomic shells while calculating energetic characteristics of the system. Pseudopotentials are calculated for every atom of crystal structure [25]. Solution of Kohn-Sham equations for electron subsystem is performed on every step of minimization procedure with fixed positions of atomic ions. Numeric stability of iterating procedure is ensured by blending electron density of two latest iterations via the method of conditionally conjugated gradients [26]. Minimization of system total energy is performed in correspondence with BFGS algorithm [27]. The Monkhorst-Pack method is used in order to generate the grid of k – points in the Brillouin zone [28].

Super cell approximation is used for applying the DFT theory to crystal systems with inclusion into the structure of non-periodic many-atom compounds [29]. Super cell approximation ensures elimination of model edge defects and increases the calculation accuracy of equilibrium state of similar subsystems. Application of this approximation for the search of new equilibrium states of partially intercalated clay minerals ensures the demanded scale sizes of the simulated system.

METHODOLOGY FOR ASSESSING THE DEGREE OF CLAY INTERCALATION

The possibility of assessing the degree of clay particles intercalation and their portion (for which the process has been completed) is determined by the peculiarities of X-ray diffraction method. As known, the diffraction pattern for different crystal structures is unique which ensures the possibility of their identification. With reference to this study there is a principle possibility of identification of intercalation of clay particle separately taken from the blend which is determined by the position of diffraction reflexes and by the possibility of obtaining the value of interlayer distance. The resizing control of interlayer distance within the process of intercalation enables to establish the moment of its completion.

Application of DFT method for calculating possible equilibrium states of the intercalated clay particle provides wide opportunities for assessing the dynamics of reflexes of diffraction pattern and for obtaining mutually-unique correspondence between the degree of intercalation of clay particle and the position of main basal reflexes.

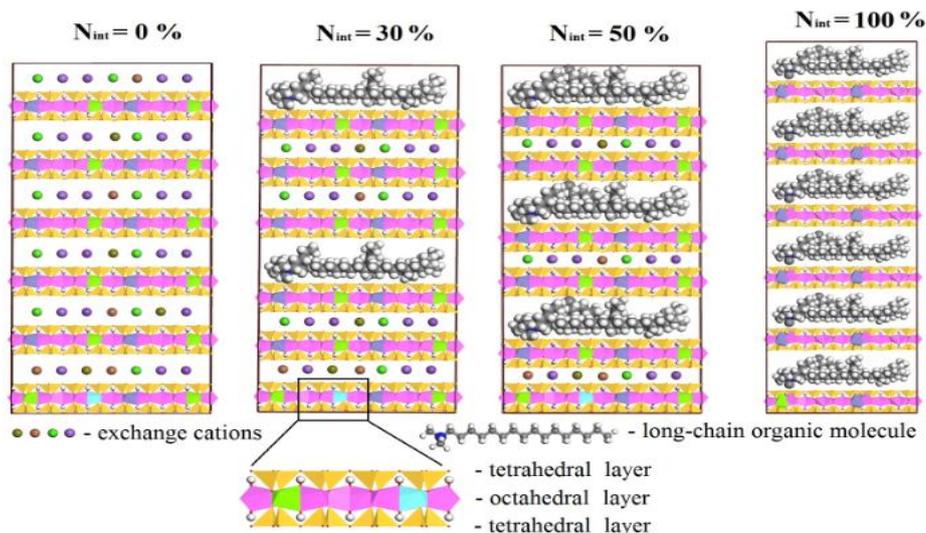


Figure 1: Model of intercalated clay nanoparticle. N_{int} – quantity of the substituted layers expressed as a percentage of their total number.

Establishing of clay mineral crystal structure is performed at the first stage of assessment procedure. The Rietveld method has been implemented in the paper [30]. This method was first implemented to clarify the structure using the data obtained via neutron radiation [31, 32]. FullProf software package [33] can be implemented in order to solve the task. This software package applies Rietveld method and has wide opportunities for establishing structural characteristics of crystal phases in heterogeneous samples. Crystal structure of clay mineral must be obtained in the result of the performed calculations and initial X-ray reflexes must be selected. Further analysis of the reflexes will enable to assess the development of clay mineral intercalation process.

The search of equilibrium states of the system with different quantity of intercalated layers is performed at the second stage of the developed approach with the use of defined crystal structure of clay mineral. Figure 1 represents the possible scheme of consistent clay particle intercalation. Variation of substitution methods of layers in a clay particle with moderate values N_{int} doesn't influence the final result of intercalation process. A number of stages to reach total substitution by organic molecules of interlayer space can be increased. The most typical among possible variants of cation substitution of interlayer ions by organic molecules are represented. Intercalation of organic molecules into the interlayer space of definite quantity N_{int} of clay particle layers is performed for every case of this scheme. The quantity of clay particle layers is expressed as a percentage of their total number. Calculation of equilibrium states of intercalated models of a clay particle, represented in fig. 1, can be performed with the use of program code accessible in CASTEP package [34, 35]. Thus, the obtained equilibrium states enable to assess the dynamics of X-ray reflexes correctly.

Calculation of diffraction curve $J(\theta)$ in correspondence with (1) and (2) is performed for every case of the defined scheme with obtaining the demanded dependence of clay particle

intercalation degree on the position of X-ray reflex. This calculation is performed at the third stage. So the obtained dependence enables to control the development of clay particles intercalation process and determine the expansion of particles in accord with degree of its completion.

RESULTS OF NUMERICAL EXPERIMENT

One of the most widely spread minerals belonging to smectite group—montmorillonite has been selected to perform calculation experiment. Dioctahedral montmorillonite (SWy-2) with total crystal chemical formula $\text{Li}_{0.62}[\text{Al}_{3.01}\text{Fe(III)}_{0.41}\text{Fe(II)}_{0.04}\text{Mg}_{0.54}](\text{Si}_{7.8}\text{Al}_{0.2})\text{O}_{20}(\text{OH})_4$ is formed by two tetrahedral grids which have the peaks directed towards one another. There is an octahedral layer between these peaks (figure 1). Unit cell with monoclinic crystal system C_{2h} and the following lattice parameters is used: $a = 5.175 \text{ \AA}$, $b = 8.896 \text{ \AA}$, $c = 12.45 \text{ \AA}$, $\alpha = \gamma = 90^\circ$, $\beta = 99.69^\circ$ и $V = 564.981 \text{ \AA}^3$ [36]. Three aluminum cations (Al^{3+}) are substituted by two magnesium cations (Mg^{2+}) and by one iron cation (Fe^{3+}) in order to account isomorphic substitutions within crystal structure SWy-2. Negative charges of clay sheets is brought into equilibrium by adding nine lithium (Li^+) cations (naturally present in clays nonorganic sort) into the interlayer space. A super cell with the size $103.5 \times 177.9 \times 87.15 \text{ \AA}$ is constructed with the purpose of carrying out simulation.

Calculation of diffraction spectrum in accord with (1) and (2) for the super cell optimized structure is performed in order to assess the clay mineral intercalation degree by molecules. This is done at the first stage. Calculation is performed for the characteristic radiation of K_α – copper atom transition (table 1). Values of the main basal and nonbasal reflexes, intensities and interplanar distances have been obtained when calculating diffraction spectra.

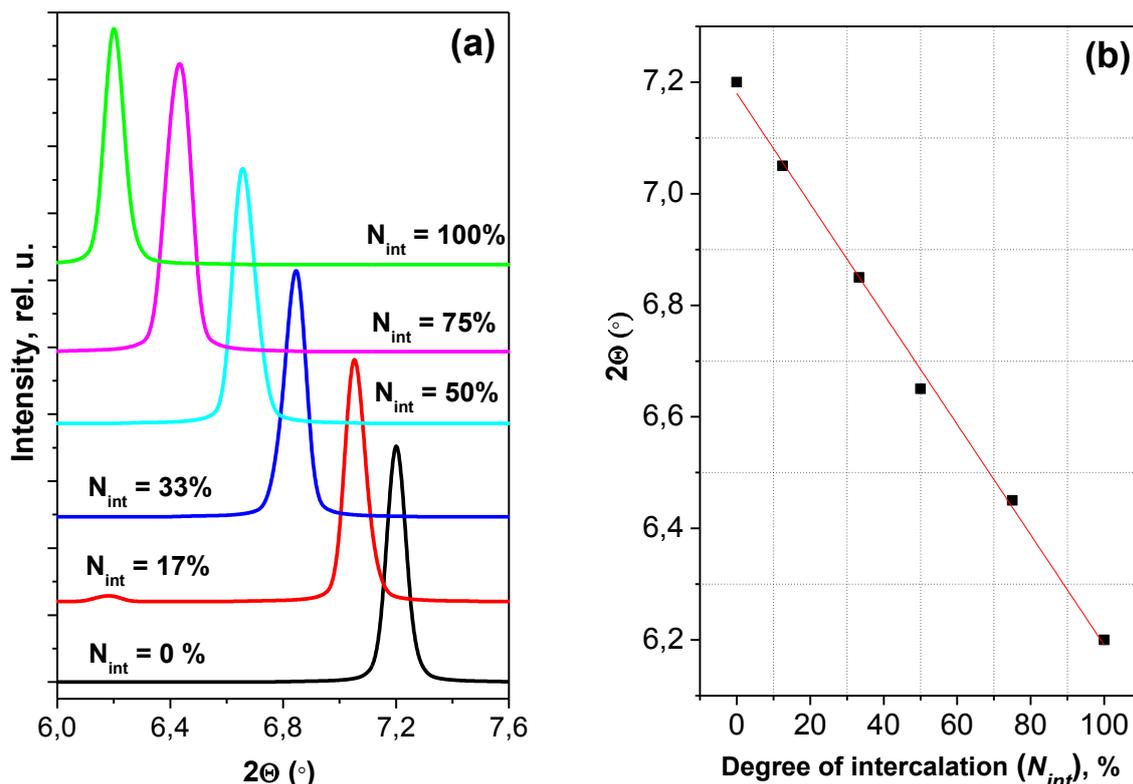


Figure 2: Montmorillonite (SWy-2) basal reflex position **001** in case of different intercalation degree of mineral nanoparticle (N_{int}): (a) dependence of intensity on intercalation degree; (b) dependence N_{int} on scattering angle 2θ (°).

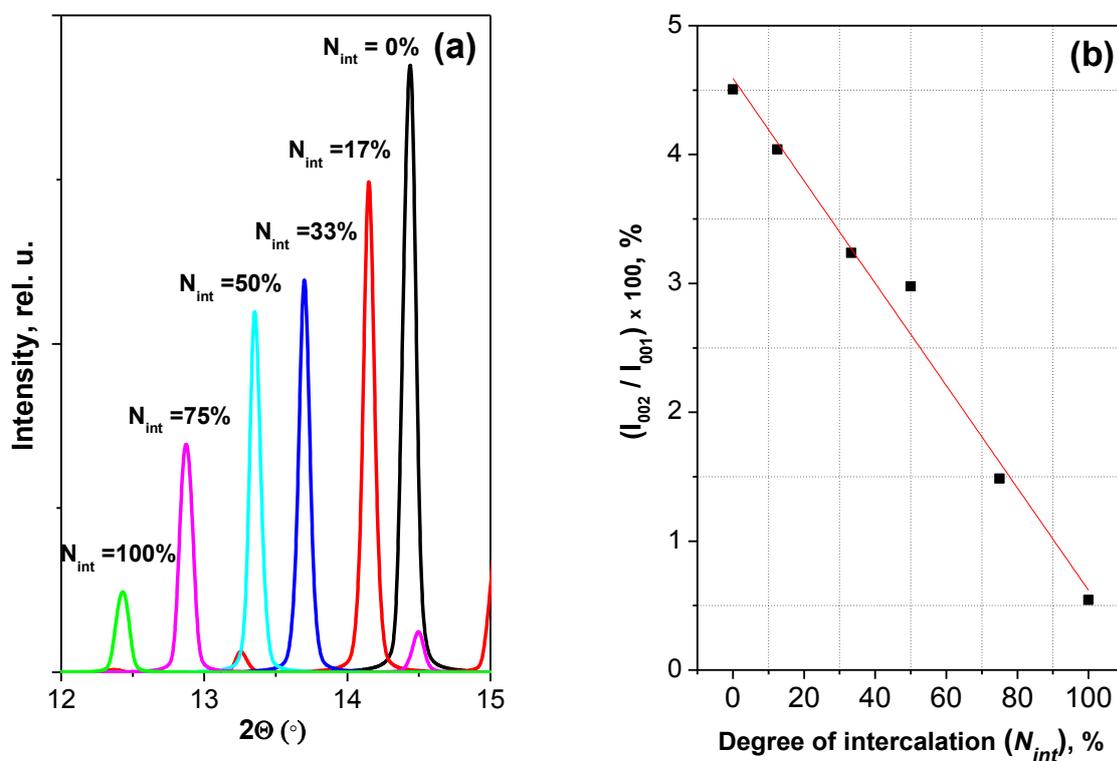


Figure 3: Montmorillonite (SWy-2) basal reflex position **002** different intercalation degree of mineral nanoparticle (N_{int}): (a) dependence of intensity on intercalation degree; (b) dependence N_{int} of basal reflex on relative intensity I_{002}/I_{001} .

Table 1; Results of theoretical simulation of montmorillonite diffraction spectra (SWy-2) with the data of experiment from the work [36].

$2\theta, ^\circ$		Intensity		Interplanar spacing $d, \text{\AA}$		Miller's indices		
Experiment	Theory	Experiment	Theory	Experiment	Theory	h	k	l
7.20	7.20	100.00	100.00	12.2724	12.2724	0	0	1
14.43	14.45	7.36	4.50	6.1362	6.1362	0	0	2
19.96	19.95	8.40	6.29	4.4480	4.4480	0	2	0
20.31	20.30	4.87	3.73	4.3715	4.3715	-1	1	1
21.25	21.25	2.90	1.46	4.1818	4.1818	0	2	1
21.72	21.70	1.93	1.31	4.0908	4.0908	0	0	3
22.33	22.33	1.58	0.98	3.9815	3.9815	1	1	1
23.00	23.00	3.26	1.55	3.8671	3.8671	-1	1	2
24.72	24.70	1.13	0.81	3.6014	3.6013	0	2	2
29.11	29.10	1.59	0.75	3.0681	3.0681	0	0	4
31.89	31.85	1.61	1.01	2.8066	2.8066	1	1	3
35.15	35.10	1.15	0.54	2.5531	2.5530	-1	3	1
36.40	36.35	2.65	1.09	2.4680	2.4680	1	3	1
36.61	36.60	1.22	0.58	2.4545	2.4545	0	0	5
36.84	36.80	2.51	1.65	2.4401	2.4400	-1	3	2

Intercalation scheme, within the framework of which consistent substitution of exchange cations in interlayer space with growth N_{int} by organic molecules happens, has been chosen for the second stage of calculation procedure. DFT calculation of equilibrium state of intercalated crystal structure SWy-2 is performed for every case. Diffraction spectra calculation has been performed in accord with (1) and (2) for obtaining optimized systems in accord with (3) and (4). The most intensive basal X-ray reflexes of diffraction spectra with indices 001 and 002 (table 1) have been chosen for the analysis.

Intercalation degree value N_{int} corresponds the mass fraction of intercalated nanoparticles which is defined when calculating via different successions of substitutions of packages. This succession is formed in the result of substitution of different type packages (intercalated and nonintercalated) that are added in turn to placements by one, by two, by three etc. The example is shown in figure 1.

Basing on calculation results we can conclude that increase of clay mineral interlayer space is observed in case of intercalation. Concentration increase of intercalated nanoparticles results in the changes of intensities of peaks of basal reflexes and also results in the shift of these peaks into small-angle spectral region. The shift of basal reflexes 001 and 002 of montmorillonite (SWy-2) is in direct ratio to concentration of intercalated nanoparticles (figure 2, 3).

The analysis of the obtained regularities shows that the implementation of dependences of intensities and position of basal reflexes 001 and 002 on the diffractograms measured on different stages of the process of clay particles organomodification is possible with the purpose of quantitative assessment of intercalation degree of organic molecules into interpackage space of clay particles. Correlation of intensities of basal reflexes 001 and 002 of clay particles of the type 2:1 can be implemented as a criterion of intercalation degree assessment.

CONCLUSIONS

New approach to assessment of intercalation degree of clay particles by long-chain organic molecules is represented in the paper. It is based on the analysis of diffractometric curves of layered crystal structures with the defined correlation of intercalated packages and order of their consequence and determined via DFT calculations. The regularities of position changes and intensity of basal X-ray reflexes 001 can be the basis of technique of X-ray diffraction establishing the mass proportion of intercalated clay nanoparticles and control of organoclay complexes formation process. The technique is aimed at the boost of technology quality of their production. Correlation of intensities of basal reflexes 001 and 001 of clay particles of the type 2:1 can be implemented as a criterion of intercalation degree assessment.

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