UDC 541.18.053+543.42

Mechanical Activation of the Mixtures of Kaolinite and Polymer*

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Abstract

The products of the joint mechanical activation of kaolinite with polymers (Sevilen, poly-N-vinylpyrrolidone and polyamide PA-6) in a high-energy ball mill were studied by means of IR spectroscopy and Xray phase analysis. It was established that for definite polymer content of the initial mixture the mechanochemical interaction of kaolinite with polymer occurs, and the chemical bond is formed between them.

Key words: mechanical activation, mechanochemical interaction, acidic and basic natural active centres

INTRODUCTION

The problem of the mechanochemical interaction between organic substances and the surface of inorganic substances, for example, during the joint mechanical activation of mixtures of a polymer with a modifying agent, is interesting not only from the viewpoint of surface chemistry. The practical aspect of this problem is important, too, especially when considering the formation of polymer composites for various functional purposes. Indeed, the joint mechanical activation of polymer-modifier mixtures involves polymer adhesion to the particles of the modifier, physical (adsorption) and chemical bonds are formed between the components of the mixture. Polymer adsorption depends on the physicochemical properties of the modifier surface, while the intensity of physicochemical interaction depends on the presence of functional groups in the polymer macromolecule and mobility of their unpaired electrons.

We have previously established that the joint mechanical activation of mixtures of kaolinite with organic and inorganic acids [1-4], as well as with higher alcohols and hydroxy acids [5] involves the solid-phase mechanochemical neutralization of the hydroxy groups of kaolinite (basic active centres) by the protons of acids or alcohols. As a result, strong chemical bonds between the components of initial mixture are formed. The IR spectrum of reaction product corresponds to the IR spectrum of a salt of organic or inorganic acid. In the case of an alcohol, mechanocomposite is formed, in which the surface metal silicate ions are chemically bound with alkyl through the oxygen bridge, that is, a bond of the same type as that in alcohoates.

The goal of the present work was to study mechanochemical interaction of some organic polymers with the surface of layered silicate kaolinite during their joint mechanical activation.

EXPERIMENTAL

Layered silicate kaolinite $Al_2(Si_2O_5)(OH)_4$ with the scaly particle shape was used in the work, along with polymers:

^{*} Materials of the IV Int. Meeting "Fundamentals of Mechanochemical Technologies", June 25-28, 2013, Novosibirsk, Russia.

Sevilen 113 (ethylene vinyl acetate) – copolymer of ethylene with vinyl acetate, structural formula: $[-CH_2-CH_2]_n-[-CH_2-CH-O-CO-CH_3]_m$ -.

Poly-N-vinylpyrrolidone (PVP) carbon chain linear polymer, hygroscopic, X-ray amorphous, structural formula:

 $[-CH_2CH-]_n$

Polyamide PA-6, structural formula (-NH-[CH_2-]₅-CO-)_n-, crystallinity degree 40–70 %, polymer macromolecules are bound with each other by hydrogen bonds, hydrogen of the amide group is able to get substituted by alkyl and other radicals.

IR absorption spectra (IRS) were recorded with Tensor-27 and Specord-75 IR spectrometers. The samples were prepared using the standard procedure. X-ray phase analysis (XPA) was carried out with a Bruker D8-Advance diffractometer (Cu K_{α} radiation). Mechanical activation (MA) was carried out in a ball planetary mill with water cooling, AGO-2.

RESULTS AND DISCUSSION

Mechanical activation of initial substances

Previously [6], we established that MA of kaolinite in an energy-strain mill within the first 20 s causes the rupture of hydrogen bonds holding the layers in packets. As a result, the bonds in tetra- and octahedral networks of the layer are distorted, and active centres of acidic and basic nature are formed on the silicate surface [7].

The analysis of IRS and XPA data for the polymers: Sevilen, PVP and PA-6 after MA for $\tau_a = 3-5$ min [8] showed that there are no substantial distortions in polymer structures.

Mechanical activation of the mixtures of kaolinite with polymers

Kaolinite + Sevilen. The mechanochemical interaction of Sevilen with nano-SiO₂ proceeds very actively, within the first 10 s [8]. However, in case of mixtures of Sevilen and kaolinite, as one can see in the IRS (Fig. 1, *a*, curves 1-3 and 5, 6), only after the joint activation for

4 min, independently of the polymer content in the mixture, the second maximum at 1700 cm^{-1} appears in the IRS near the band of stretching vibrations of carbonyl groups v C=O 1745 cm⁻¹. This maximum corresponds to the vibrations of bound C=O groups, v_{as} C=O. Therefore, only after activation of the mixture of kaolinite with Sevilen for 4 min definite distortions occur in kaolinite structure, and active centres are formed on its surface [7]. These active centres are necessary for the mechanochemical interaction of the silicate with the polymer. Indeed, the IRS of the mixtures activated for 4 min exhibit a decrease in the intensities of ν_{as} and ν_{s} bands of the tetrahedrons of the silicon-oxygen framework (in the regions 1150-1050 and 700-650 cm⁻¹, respectively) [9]. The intensities of the bands related to stretching and bending vibrations of hydroxy groups v, δ (OH) and, first of all, external hydroxyl groups (the bands with the maxima at 3670, 3655 and 940 cm^{-1} , respectively), that is, structural hydroxyl groups on the surface of microcrystals, including OH groups both on destroyed edges and on the surface of the octahedral layer, decrease noticeably [9]. The changes of the parameters of vibration bands v, δ of Si-O- bonds (in the region $1050-1000 \text{ cm}^{-1}$) and bands with maxima at 465 and 425 cm⁻¹, as well as v, δ Si-O-Al and Si-O-(Al) (in the region 800- 700 cm^{-1}) and the bands with the maximum at 535 cm^{-1} (see Fig. 1, *a*, curves 1, 2, 4) are not so essential.

The intensity of v_{as} C=O band gradually increases with an increase in the activation time. After MA for 10 min the intensities of v C=O and v_{as} C=O become equal. In this case, bands related to the vibrations of the silicon-oxygen framework (within the regions 1150–1050 and 700–650 cm⁻¹) become diffuse. However, the bands of vibrations of v, δ Si–O⁻, Si–O–Al and Si–O–(Al) bonds and bands v, δ (OH) inplane and internal hydroxy groups of kaolinite with the maxima at 3695, 3620 and 910 cm⁻¹ remain (see Fig. 1, *a*, curve 4).

It also follows from the analysis of XPA data (see Fig. 1, b, curves 1, 6) that the destruction of kaolinite structure slows down in the presence of Sevilen. All the major reflections of silicate are conserved in the diffrac-



60

50

 2θ , deg Fig. 1. IRS (a) and diffraction patterns (b) of the mixtures of kaolinite with Sevilen before (1, 5) and after MA for 1 (2), 4 (3, 6) and 10 min (4). Polymer content in the mixture

40

30

10

20

(%): 10 (1-4) and 30 (5, 6).

tion patterns of mixtures activated for 4-10 min, only the intensities of these reflections decrease, and the reflections broaden.

The data obtained allow to assume the following: kaolinite interacts with Sevilen during the joint mechanical activation due to unshared electron pair of oxygen atoms of the carboxylic groups-of Sevilen [11] and strong acidic centres of kaolinite [7] -[Si-OH]⁺ formed on its surface during MA as a consequence of the protonation of silanol groups [Si-OH] of the silicate. A similar interaction

was considered by the authors of [12] when studying the adsorption of polar organic sub-

$$\begin{array}{ccc} \mathbf{R}_{3}\mathrm{Si-O^{+}-H} + \mathrm{O=C-C}_{n}\mathrm{H}_{2n+1} \\ \mathrm{H} & \mathrm{OH} \\ & & \\ & & \\ & & \\ \mathbf{H} & \mathrm{OH} \\ \end{array}$$

Kaolinite + poly-N-vinylpyrrolidone. It was established in the studies of the joint MA of kaolinite with Sevilen on the basis of IRS data that for the polymer content in the mixture of 10 %, not the whole polymer is chemically bound with the silicate. This may be due to the insufficient amount of active centers of the acidic nature formed on the kaolinite surface during its joint MA with Sevilen. In this connection, the joint activation of kaolinite with PVP was carried out with 5 % polymer content in the mixture. In this case, IRS of activated mixtures of PVP with kaolinite do not contain the band related to the characteristic vibrations of carboxylic groups in the initial polymer v C=O 1675 cm⁻¹. Instead, slightly asymmetric band v_{as} C=O appears at 1660 cm⁻¹ ($\tau_a = 4$ min). In addition, characteristic bands v_{as} and v_{s} related to the vibrations of Si-O-Si bonds (1115, 1110, 685 cm⁻¹), Si-O-(Al) doublet (795, 790 cm⁻¹) and Si-O-Al (755 cm⁻¹) disappear. The intensity of bands of stretching and bending vibrations of OH groups de-



Fig. 2. IRS (a) and diffraction patterns (b) of the mixtures of kaolinite with poly-N-vinyl-pyrrolidone before (1, 3) and after MA for 4 min (2, 4). Polymer content in the mixture (%): 5 (1, 2) and 80 (3, 4).

creases sharply, first of all, this relates to the external hydroxyl groups with the maxima 3670, 3655 and 940 cm⁻¹ [9] (Fig. 2, *a*, curves 1, 2). Reflections belonging to kaolinite are almost absent from the diffraction patterns of the sample activated for 4 min; some new reflections appear in the region $2\theta = 15-47^{\circ}$, the most clear one appears at $2\theta = 31.6^{\circ}$ (see Fig. 2, *b*, curve 2).

The data obtained indicate a more substantial destruction of kaolinite structure during MA in mixture with PVP than in mixture with Sevilen. This may be due to the lower (by a factor of 2) polymer content in mixture, since a polymer, as a rule, hinders the destruction of the structure of layered silicates creating "soft" conditions for mechanical activation [13]. On the other hand, the difference in the physicochemical properties of the polymers (hardness, viscosity *etc.*) may manifest itself. Acidic centres and some amount of basic centres are formed on kaolinite surface as a result of activation [7]. The interaction of kaolinite with PVP is similar to the interaction of kaolinite with Sevilen. In addition, mutual neutralization of the active centres of acidic and basic nature in kaolinite is possible during activation of kaolinite mixtures both with PVP and with Sevilen. This is evidenced by the appearance of the stretching vibrations of water v OH (H₂O) with the maximum at ~3430 cm⁻¹ in the spectra of activated mixtures (see Fig. 1, curves 2, 4, and Fig. 2, curves 2 and 4).

Comparing the IRS of kaolinite + Sevilen and kaolinite + PVP mixtures after activation, one may assume that hydrogen bonds formed after activation in mixtures with Sevilen are stronger than those in mixtures of kaolinite with PVP: $\Delta v C=O$ for Sevilen is 55 cm⁻¹, for PVP 15 cm⁻¹ (see Fig. 1, *a*, curve 2, and Fig. 2, *a*, curve 2). This is due to the fact that carbonyl groups of PVP are located in heterocycles of the polymer; owing to what the ability to reactions involving an unshared electron pair of the oxygen atoms of the carbonyl groups is weakened, in comparison with sevilen.

With an increase of the concentration of PVP in the mixture with kaolinite, the mechanochemical interaction of the components weakens substantially. Thus, at the content of the polymer equal to 80 %, no noticeable changes are observed for kaolinite bands in the regions of 3800-3600, 1300-400 cm⁻¹ and PVP bands in the region of 1700-1300 cm⁻¹ (see Fig. 2, *a*, curve 4). The polymer slows down the destruction of the crystal structure of the silicate [13].

Kaolinite + polyamide PA-6. The mechanochemical interaction of kaolinite with polyamide PA-6 differs from the interaction of kaolinite with Sevilen and PVP, which is connected with the mesomeric effect in the amide group of the polymer:

Indeed, similarly to case of MA of pure kaolinite [6], in the IRS of kaolinite + polyamide (30 %) mixture after MA for 4 min (Fig. 3, a, curves 1, 2) the intensity of v, δ (OH) bands decreases, first of all those of the external hydroxyl groups with maxima at 3670, 3655 and 940 $\text{cm}^{-1},$ as well as v, δ Si–O–Al, Si-O-(Al) in the region of 850-780 cm⁻¹ and with the maximum at 545 cm⁻¹. The bands v_{as} and v_s of Si-O-Si stretching vibrations of the tetrahedrons of silicon-oxygen framework in the region of $1150-1050 \text{ cm}^{-1}$ and a peak with the maximum at 685 cm⁻¹ disappear almost completely. Similarly to the case of MA of pure kaolinite, we observe change of the parameters of vibration bands v, δ of Si-O bonds (in the region of $1050-1000 \text{ cm}^{-1}$) and with the maxima at 465 and 425 cm^{-1} . At the same time, the intensity of v, δ (NH) bands decreases, and their maxima shift: $3300 \rightarrow 3320 \text{ cm}^{-1}$ and $1540 \rightarrow 1550 \text{ cm}^{-1}$, respectively.

The diffraction patterns of the activated mixture (Fig. 3, b, curve 2) show that the major kaolinite reflections are conserved but their intensity decreases sharply. Polyamide reflections are superimposed on the series of kaolinite reflections $2\theta = 20-25^{\circ}$. These data provide evidence that kaolinite structure gets disordered as a consequence of (Al)-OH bond rupture and corresponding distortions of bonds in octa- and tetrahedral networks of the layers. As a consequence of distortions in silicate structure, active centres of acidic and basic nature are formed on silicate surface [7]. We suppose that the basic centres of kaolinite interact mechanochemically with the acidic centres of polyamide. It may be also assumed that this interaction proceeds according to the scheme proposed by the authors of [12], for the adsorption of polar organic molecules on kaolinite:

$$\begin{array}{c} \mathbf{R}_{3}\mathbf{Si}-\mathbf{O}-\mathbf{H} + \mathbf{H}-\mathbf{O}-\mathbf{C}-\mathbf{C}_{n}\mathbf{H}_{2n+1} \\ \mathbf{H} \\ \mathbf{O} \\ \end{array} \\ \xrightarrow{\mathbf{R}_{3}}\mathbf{Si}-\mathbf{O}\cdots\mathbf{H}-\mathbf{O}-\mathbf{C}-\mathbf{C}_{n}\mathbf{H}_{2n+1} \\ \mathbf{H} \\ \mathbf{H} \\ \mathbf{O} \end{array}$$

For a mixture of kaolinite with polyamide:

$$\begin{array}{c} \mathbf{R}_{3}\mathbf{Si}-\mathbf{O}-\mathbf{H} + \mathbf{H} & \xrightarrow{\mathbf{I}} & \mathbf{R}_{3}\mathbf{Si}-\mathbf{O} \cdots \mathbf{H} \\ \overset{\mathbf{I}}{\mathbf{(N-[CH_{2}]_{5}-C)_{\overline{n}}}} & \overset{\mathbf{I}}{\mathbf{H}} & \overset{\mathbf{I}}{\mathbf{(N-[CH_{2}]_{5}-C)_{\overline{n}}}} \end{array}$$

This schematic representation of mechanochemical interaction in the indicated system is in good agreement with the IRS data.

With an increase in the content of polyamide in the mixture above 50 %, the picture of changes in kaolinite IRS bands after MA activation for 4 min become completely different. The bands corresponding to v_{as} and v_{s} vibrations of Si-O-Si bonds in the tetrahedrons of the silicon-oxygen framework (1150- 1050 cm^{-1} and with the maximum at 685 cm^{-1}) do not disappear; only the intensity decreases and all kaolinite bands broaden. No shifts of polymer bands are observed, and new bands do not appear (see Fig. 3, a, curve 4). In the diffraction patterns of this sample (see Fig. 3, b, curve 4), there are very weak barely detectable reflections from the basal planes of kaolinite. Polyamide reflections broaden, which is the evidence of the distortion of polymer structure. These data allow us to assume that grad-



Fig. 3. IRS (a) and diffraction patterns (b) of the mixtures of kaolinite with polyamide PA 6 before (1, 3) and after MA for 4 min (2, 4). Polymer content in the mixture (%): 30 (1, 2) and 80 (3, 4).

ual amorphization of kaolinite occurs with an increase in polymer content in the mixture. Destruction of silicate structure proceeds slower in the presence of the polymer, which follows from the comparative analysis of the IRS of this mixture (see Fig. 3, curve 4) and pure kaolinite activated for 1 min [6].

CONCLUSION

It was established that the mechanical activation of kaolinite with Sevilen and poly-N-vinyl-pyrrolidone at their content in the mixture with less than 10 % involves the mechanochemical interaction of the silicate with the polymer due to the unshared electron pair of the polymer and active centers of the acidic nature on the kaolinite surface.

Basic active centres on kaolinite surface and acidic centres of polyamide participate in the mechanochemical interaction of kaolinite with polyamide PA 6 (with polymer content $\leq 30 \%$) participated by the basic active centres on kaolinite surface and acidic centres of polyamide.

REFERENCES

- 1 Grigorieva T.F., Vorsina I.A., Barinova A.P., Boldyrev V.V., *Dokl. AN*, 341, 1 (1995) 66.
- 2 Grigorieva T. F., Vorsina I. A., Barinova A. P., Boldyrev V. V., *Inorg. Mater.*, 32, 2 (1996) 66.
- 3 Grigorieva T. F., Vorsina I. A., Barinova A. P., Boldyrev V. V., J. Mater. Synth. Proc., 4, 5 (1996) 299.
- 4 Vorsina I. A., Barinova A. P., Lyakhov N. Z., Chem. Sustain. Dev., 12, 3 (2004) 303.
- URL: http://www.sibran.ru/en/journals/KhUR
- 5 Grigorieva T. F., Vorsina I. A., Barinova A. P., Lyakhov N. Z., Chem. Sustain. Dev., 12, 3 (2004) 139. URL: http://www.sibran.ru/en/journals/KhUR
- 6 Grigorieva T. F., Vorsina I. A., Barinova A. P., Lyakhov N. Z., *Zh. Neorg. Khim.*, 32, 1 (1996) 84.
- 7 Ikekawa A., Hayakawa S., Sib. Khim. Zh., 5 (1991) 19.
- 8 Vorsina I. A., Grigorieva T. F., Udalova T. A., Vosmerikov S. V., Struk V. A., Ovchinnikov E. V., Lyakhov N. Z., *Zh. Prikl. Spektr.*, 81, 2 (2014) 244.
- 9 Farmer V. C., The Infrared Spectra of Minerals, Mineralogical Society, Leipzig, 1974.
- 10 Plyusnina I. I., Infrakrasnye Spektry Mineralov, Izdvo MGU, Moscow, 1977, pp. 51–76.
- 11 Baramboym N. K., Mekhanokhimiya Vysokomolekulyarnykh Soyedineniy, Khimiya, Moscow, 1978, pp. 13–47.
- 12 Yariv S., Cross H., Organo-Clay Complexes and Interaction. Marcel Dekker, New York Inc., 1989, pp. 34–101.
- 13 Avakumov E. G., Mekhanicheskiye Metody Aktivatsii Khimicheskikh Protsessov, Nauka, Novosibirsk, 1986.