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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 X-ray 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 alcohols.

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.

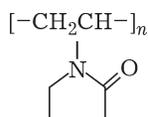
EXPERIMENTAL

Layered silicate kaolinite $\text{Al}_2(\text{Si}_2\text{O}_5)(\text{OH})_4$ with the scaly particle shape was used in the work, along with polymers:

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Sevilen 113 (ethylene vinyl acetate) – copolymer of ethylene with vinyl acetate, structural formula: $[-\text{CH}_2-\text{CH}_2]_n-[-\text{CH}_2-\text{CH}(\text{O}-\text{CO}-\text{CH}_3)]_m-$.

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



Polyamide PA-6, structural formula $(-\text{NH}-[\text{CH}_2]_5-\text{CO}-)_n-$, 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 (CuK_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- SiO_2 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 $\nu\text{ C=O } 1745\text{ cm}^{-1}$. This maximum corresponds to the vibrations of bound C=O groups, $\nu_{\text{as}}\text{ C=O}$. 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 $700-650\text{ cm}^{-1}$, respectively) [9]. The intensities of the bands related to stretching and bending vibrations of hydroxy groups ν , 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 ν , 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 ν , δ Si–O–Al and Si–O–(Al) (in the region $800-700\text{ cm}^{-1}$) 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 $\nu_{\text{as}}\text{ C=O}$ band gradually increases with an increase in the activation time. After MA for 10 min the intensities of $\nu\text{ C=O}$ and $\nu_{\text{as}}\text{ C=O}$ become equal. In this case, bands related to the vibrations of the silicon-oxygen framework (within the regions $1150-1050$ and $700-650\text{ cm}^{-1}$) become diffuse. However, the bands of vibrations of ν , δ Si–O[–], Si–O–Al and Si–O–(Al) bonds and bands ν , δ (OH) in-plane 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-

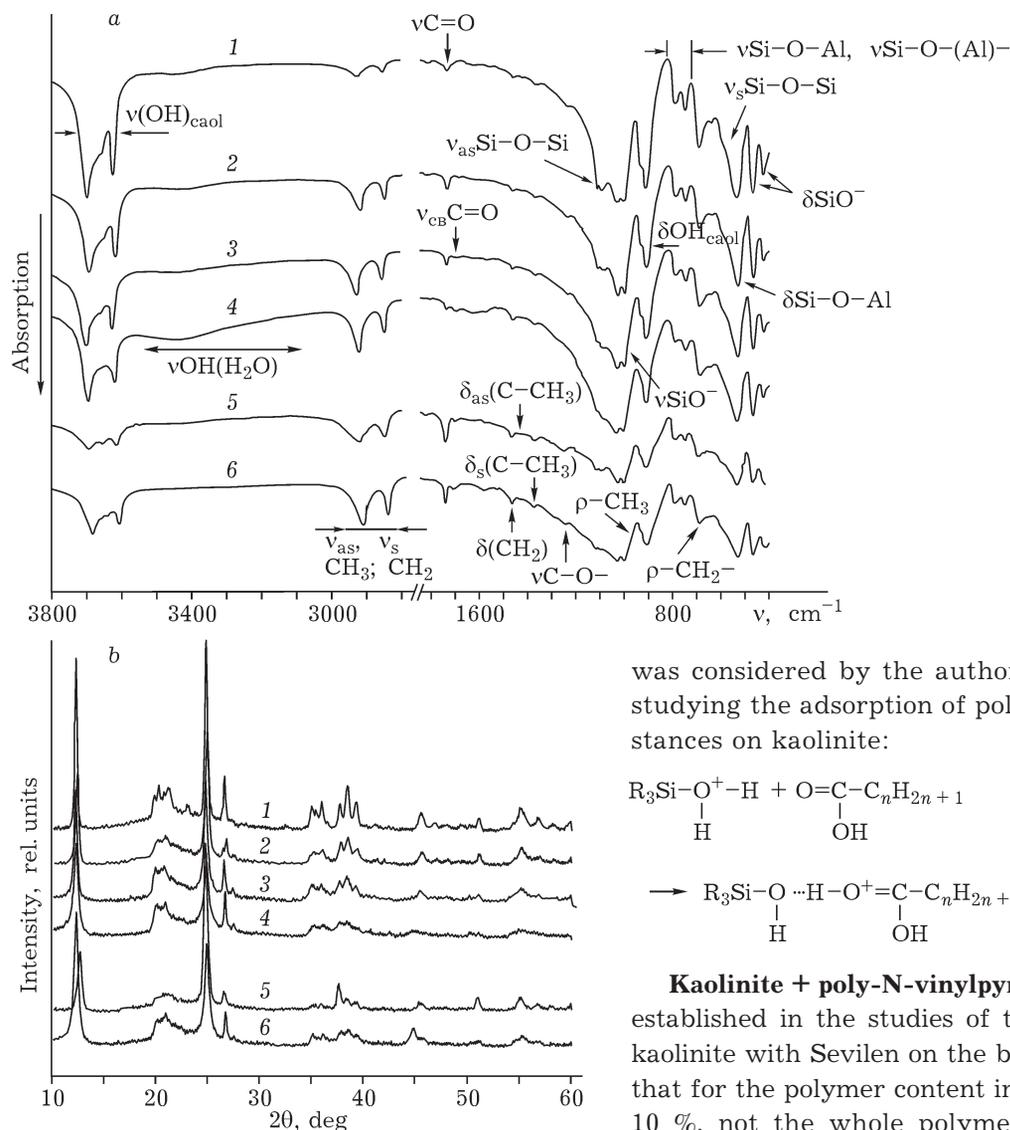
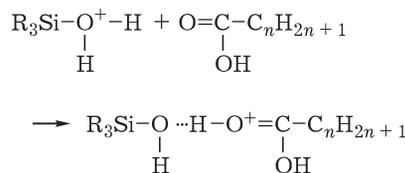


Fig. 1. IRS (a) and diffraction patterns (b) of the mixtures of kaolinite with Sevilen before (1, 5) and after MA for 1 (2), 4 (3, 6) and 10 min (4). Polymer content in the mixture (%): 10 (1-4) and 30 (5, 6).

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] $-\text{[Si-OH]}^+$ formed on its surface during MA as a consequence of the protonation of silanol groups $[\text{Si-OH}]$ of the silicate. A similar interaction

was considered by the authors of [12] when studying the adsorption of polar organic substances on kaolinite:



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 $\nu\text{C}=\text{O}$ 1675 cm^{-1} . Instead, slightly asymmetric band $\nu_{\text{as}}\text{C}=\text{O}$ appears at 1660 cm^{-1} ($\tau_a = 4$ min). In addition, characteristic bands ν_{as} and ν_{s} related to the vibrations of $\text{Si}-\text{O}-\text{Si}$ bonds (1115 , 1110 , 685 cm^{-1}), $\text{Si}-\text{O}-\text{(Al)}$ doublet (795 , 790 cm^{-1}) and $\text{Si}-\text{O}-\text{Al}$ (755 cm^{-1}) disappear. The intensity of bands of stretching and bending vibrations of OH groups de-

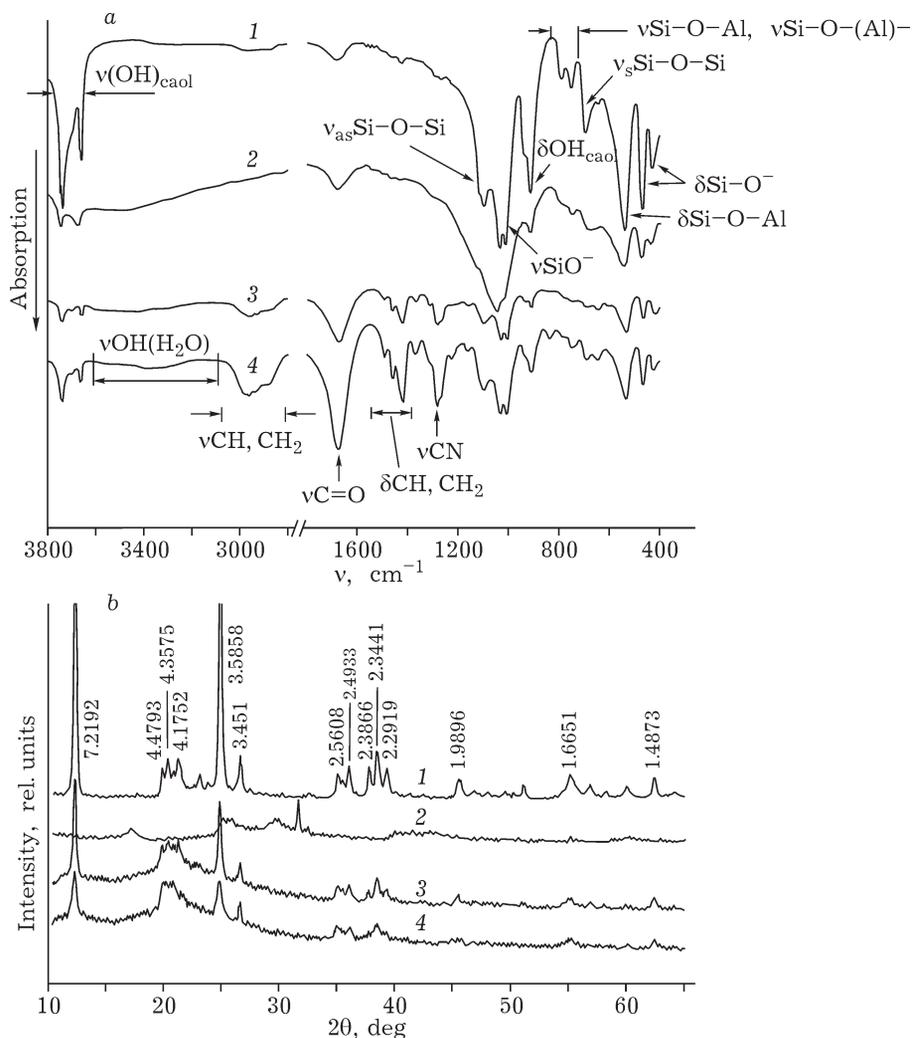


Fig. 2. IRS (a) and diffraction patterns (b) of the mixtures of kaolinite with poly-N-vinyl-pyrrolidone before (1, 3) and after MA for 4 min (2, 4). Polymer content in the mixture (%): 5 (1, 2) and 80 (3, 4).

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 $2\theta = 15\text{--}47^\circ$, 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 phys-

icochemical 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 $\nu\text{OH}(\text{H}_2\text{O})$ with the maximum at $\sim 3430\text{ cm}^{-1}$ 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,

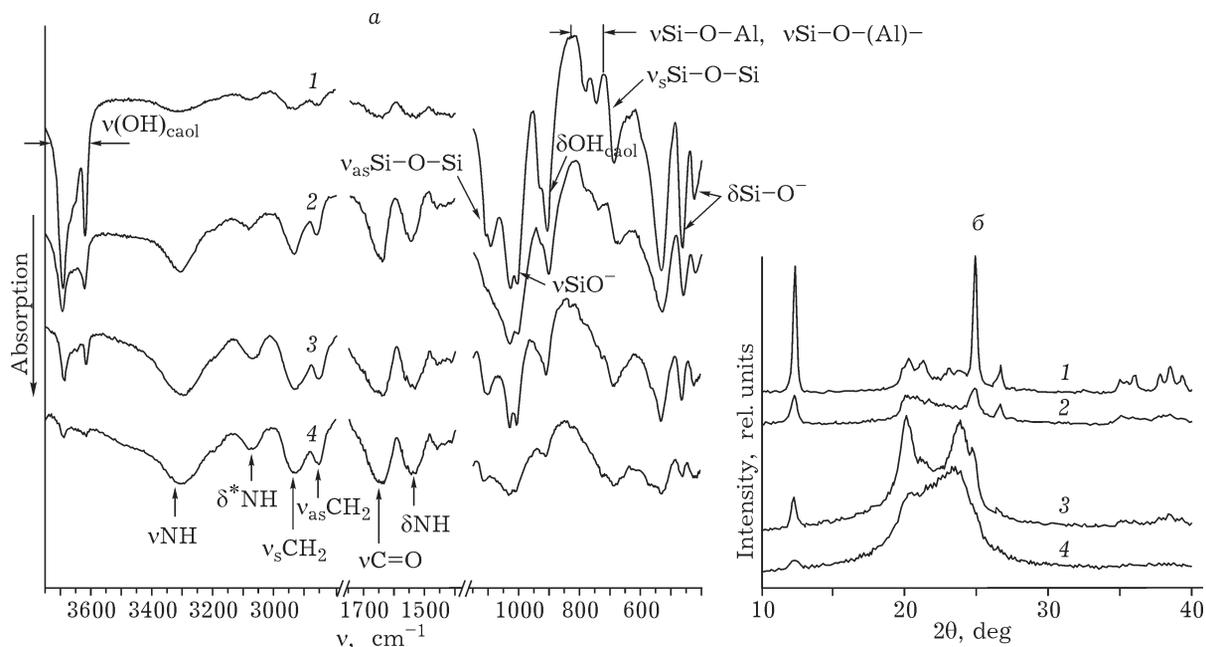


Fig. 3. IRS (a) and diffraction patterns (b) of the mixtures of kaolinite with polyamide PA 6 before (1, 3) and after MA for 4 min (2, 4). Polymer content in the mixture (%): 30 (1, 2) and 80 (3, 4).

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.

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