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# Mechanochemical synthesis of organic compounds and composites with their participation

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**Abstract. The results of experimental studies in the mechanochemical synthesis of organic compounds and composites with their participation published over the last 15 years are described systematically. The key reactions of organic compounds are considered: synthesis of the salts of organic acids, acylation, substitution, dehalogenation, esterification, hydrometallation and other reactions. Primary attention is devoted to systems and compounds that cannot be obtained by traditional chemistry methods. The bibliography includes 264 references.**

## I. Introduction

The mechanochemical approach to the preparation of composites from various compounds most of which are inorganic provides for the development of environmentally safe industrial processes because this type of processes is based on chemical reactions in the solid phase, *i.e.*, without solvents or processing operations not involving the use of solvents.[1–6] In recent years, considerable attention has been paid to mechanochemical synthesis of organic compounds. The traditional synthesis of organic compounds is a multistage process usually carried out in a liquid medium using various types of organic solvents at different stages of product synthesis and purification. The traditional production of organic compounds is accompanied by the formation of large amounts of organic sewage, which must be neutralized and disposed.[7] The development of environmentally clean production processes of organic compounds and composites involving them requires the use of 'dry' technology, *i.e.*, chemical reactions carried out in the solid phase. In addition, many organic compounds are volatile, which requires performing the reactions in closed space. Therefore, the use of mechanochemical processes for the production of both organic compounds and composites involving them appears a topical and practicable task.

This review presents a systematic account of the experimental data on the problems and prospects of using mechanochemical synthesis of various systems with participation of organic compounds published in the last 10 – 15 years. The attention is focused on the systems and compounds that cannot be prepared by traditional chemistry methods.

As a rule, mechanochemical synthesis is carried out in mixtures comprising at least two components, each of them responding in its own way to mechanical impact. Moreover, during the synthesis the reaction products are formed, which affect the synthesis process. Therefore, it appears reasonable to consider first the effect of mechanical action on individual compounds.

## II. Mechanochemistry of individual organic compounds

### 1. Mechanical action on polymers

Systematic research of the mechanical action on organic compounds started with the study of mechanical destruction of polymers. In a study of rubbers,[8,9] poly(methyl methacrylate), polystyrene, polyacrylonitrile, poly(vinyl alcohol), *etc.*,[10,11] it was shown that mechanical action gives rise to free radicals.

According to a publication,[12] homolytic cleavage of macromolecular chains located at the trajectory of the main crack produces numerous radical type active sites. It was shown[11] that the growth of a new surface and radical formation in a solid polymer are different processes: the number of radicals exceeds the number of breaks in the backbone. However, it is obvious that cleavage of interatomic bonds with generation of free radicals results in the formation of new functional groups capable of chemical reactions.[12–14]

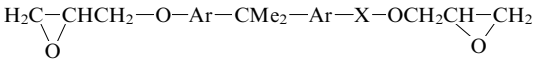
A more recent review by Radtsig[15] presents the results of original studies of free radical processes that accompany the mechanical treatment of carbochain polymers. The

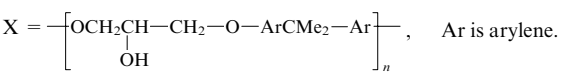
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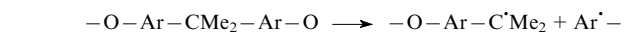
kinetic regularities of the mechanical destruction of polymers, the bond scission mechanisms, the spatial distribution pattern of the chemically active sites thus formed, and the structure of macroradicals stabilized in the products of the mechanical destruction of polymers were considered in detail.

The uniaxial compression of polymer plates has been studied.[16,17] It was shown that at a particular pressure, a short-term acoustic emission is initiated and an elastic wave pulse spreads over the polymer. This phenomenon was called rheological explosion. The study covered a number of polymers, in particular, high- and low-density polyethylenes, polypropylene, poly(ethylene terephthalate), polyamides, poly(vinyl chloride), polystyrene. Later studies dealt with the chemical processes that accompany the rheological explosion in glass-like polyepoxides such as





Aleksandrov *et al.*[18] assumed that the elastic wave pulse acting on solid polyepoxides induces rupture of the polymer chains as shown below



giving rise to stable ($-O-Ar-C^{\bullet}Me_2$) and unstable (phenyl) terminal radicals. These radicals abstract hydrogen atoms from the polymer chain thus generating unstable alkyl radicals, which are destroyed upon relay transfer of the electron density along the polymer chains, resulting in the formation of double bonds and hydrogen molecules.

Free radical reactions were also detected upon the mechanical impact on protein molecules.[19] Butyagin *et al.*[20] studied the free radical stages of mechanochemical transformations in various proteins: casein, gelatine, serum and egg albumin, haemoglobin and keratins. Different type radicals were detected upon mechanochemical destruction of polypeptides: $-C^{\bullet}HR(R_t)$, $-CO-C^{\bullet}R-NH-(R_i)$, $-R_S$ [where t stands for the primary (terminal) radicals arising upon chain rupture, and i and S denote secondary (internal) or the radicals with the free valence on sulfur, respectively].[21]

Mechanical grinding of polymers induces cleavage of weak intermolecular bonds and cleavage of the valence bonds in the backbone. The destruction of the intermolecular bonds leads to structural disordering and loosening. Cleavage of the valence bonds furnishes free radicals, which facilitate the formation of low-molecular-mass products. The rate of bond cleavage is determined first of all by the structure rigidity. It increases on going from flexible-chain polymers to more rigid ones, especially to polypeptides, which comprise peptide bonds in the backbone and a thick network of hydrogen bonds. The mechanical cleavage of the covalent bonds in poly(amino acids) (polyalanine, polyleucine, polyvaline), fibrous proteins (trypsin, subtilisin) and oligopeptides (gramicidin, bacitracin) has been studied.[19–22] The rate of free radical formation in proteins is higher than in linear synthetic polymers. The enhanced rigidity of the former leads to mechanical destruction to comparatively low-molecular-mass compounds, namely, cyclic peptides containing only 10–12 amino acid residues.

When preparing this review, we did not intend to survey all papers on the mechanodestruction of polymers as individual compounds but analyzed only the most important processes that occur in polymers upon mechanical impact.

## 2. Mechanical impact on low-molecular-mass organic compounds

### a. Hydrostatic compression

The effect of mechanical impact on molecular crystals under hydrostatic compression was studied in relation to a number of low-molecular-mass organic compounds. It was noticed that treatment of a crystal of deuterio-oxalic acid induces its deformation in such a way that of three hydrogen bonds in its structure two are contracted.[23]

A comparative study of the effect of hydrostatic pressure on the structures of paracetamol and phenacetin was carried out. The deformation was found to be anisotropic, which is caused by the presence of different sorts of intermolecular interactions (van der Waals forces and hydrogen bonds).[24–27]

When hydrostatic pressure is applied to paracetamol crystals, the compression of hydrogen bonds is accompanied by a change in the conformation of the molecule: the angle between the acetamide group and benzene ring planes decreases and the intermolecular hydrogen bonds OH···O and NH···O are shortened. The hydrostatic pressure on acetaminophen induces only minor changes in the intermolecular bond lengths, while the angles and intramolecular hydrogen bonds change to a greater extent.[28–36]

In a study of the effect of pressure on the glycine crystals, a phase transition in γ-glycine was found. In the new structure, the glycine zwitter-ions are hydrogen-bonded to form layers, which are connected in pairs.[37–41]

The effect of pressure on the structure of a series of amino acids and 4-hydroxyacetanilide molecules was studied.[42–49] It was shown that an increase in pressure to 8.6 GPa induced a phase transition in L-serine, whereas in DL-serine no phase transition occurs. The phase transition is possible as a result of rearrangement of hydrogen bonds to give zwitter-ions. Several phase transitions were observed in DL-cysteine at 0.1, 1.5, 2.0, and 5 GPa. In 4-hydroxyacetanilide, an increase in pressure results in rearrangement of intermolecular hydrogen bonds and decrease in the intramolecular angles between the benzene ring and acetamide group planes.

A study of the structural changes in the molecular crystals upon hydrostatic contraction has shown that the hydrogen bond lengths change and the contractability of crystals depends on not only the type of bond but also on its environment and molecular packing in the crystals.[50–56]

A study of the mechanical action on organic dimers (arylindanedione dimers were used as models) demonstrated that shear strain at high pressure is accompanied by dissociation of the molecule, which depends on both the pressure and the shear angle.[57]

Organic peroxides decompose under the same conditions, the onset of peroxide decomposition being associated with the start of strain in the sample bulk after a certain pressure has been attained. As investigation subjects, benzoyl, lauryl, cumyl, succinic acid and benzyldimethylsilyl peroxides were ised.[58]

**b. Planetary ball milling**

A specific feature of mechanical activation of low-molecular-mass organic compounds during planetary ball milling is their rather fast transition from crystalline to amorphous state. This was shown for ampicillin trihydrate,[22] sulfanilamides,[59] cephalexin, cephalotin and clonidine.[60] For most organic compounds studied, disorder of the crystal structure is related to violation of the system of intermolecular hydrogen bonds. Yet another specific feature of low-molecular-mass organic compounds under mechanical impact is their ability to undergo polymorphic transformations. These transformations induced by mechanical treatment were observed for indometacin[60] and sulfathiazole.[61] It is assumed with quite a substantiation that the polymorphic transformations occur on mechanical impact through a disordered amorphous state rather than directly from one form to the other.

Mechanical activation of barbituric acid in the trioxo form for 24 h gave rise to a new phase, which was identified as the trihydroxy isomer.[62] The new phase was formed as a result of tautomeric shift of the methylene group and two hydrogen atoms of the N—H groups. In solution, the trihydroxy isomer is immediately converted to the trioxo form.

The mechanical activation of partly amorphized bisphenol A polycarbonate has shown that the degree of crystallinity of the final sample obtained by recrystallization of the mechanically activated amorphous precursor depends on the degree of sample crystallinity prior to the mechanical treatment.[63]

Changes in the physicochemical properties of biopolymers chitin and chitosan as a result of mechanical treatment (dispersion) in a ball mill have been considered.[64]

### 3. Mechanical impact on complex compounds with organic ligands

The studies of the effect of hydrostatic contraction on complexes were started from compounds $[Co(NH_3)_5NO_2].Cl_2$.[65–72] It was shown that two NH···O hydrogen bonds are contracted unequally, the longer bond being contracted to a higher extent. As a consequence, the nitro ligand rotates, bond lengths between the cobalt atom and the ligands change. The NH···Cl bond lengths behave in different ways following the pressure gain. The *cis* $NH_3$···Cl bond is monotonically contracted, while one of the two types of hydrogen bond in the *trans*-position is stretched.

On the mechanical treatment of the crystalline complex $[Fe(Phen)_3](NCS)_2 \cdot H_2O$ (Phen is phenanthroline), amorphization takes place, which can be detected by X-ray diffraction and IR spectroscopy. The amorphized complex compound is recrystallized at 406 K.[73,74]

## III. Mechanochemical synthesis of organic compounds

Studies of the effect of shear strain at high pressure on the solid monomers have shown that under these conditions, polymers are formed at high rates.[75] It is noted in numerous publications that this method can be used to prepare polymers of the following classes of organic compounds:[76]

a) compounds with one C=C bond:

— hydrocarbons (ethylene, styrene, α-methylstyrene, *etc.*),

— esters (alkyl acrylates, alkyl methacrylates),

— acids (acrylic, methacrylic, crotonic acid, *etc.*),

— anhydrides,

— amides,

— imides,

— nitriles,

— chloro-compounds (dichloro and trichloropropene);

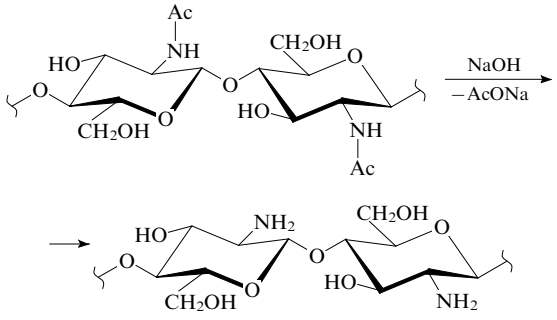
b) compounds with conjugated double bonds (butadiene, cyclopentadiene);

c) compounds with triple bond (acetylene and diacetylene derivatives, nitriles);

d) heterocyclic compounds (trioxane, hexamethyltrisiloxane, thiophene, pyridine);

e) aromatic compounds (benzene, naphthalene, anthracene, *etc.*).

The systematic research in this field was started with graft polymerization. The initiation of chemical reactions in the polymer–monomer system is due to the presence of radicals formed upon cleavage of macromolecular polymers subjected to mechanical treatment. The surfactant properties were enhanced by grafting polar monomers to some polyamides and polyesters.[77–81] The mechanical grafting was also performed in the polymer–polymer[12–14] systems. The solid-state solvent-free mechanochemical modification under combined action of high pressure and shear strain was proposed as a promising method for deacetylation of a natural polymer, chitin, in order to produce chitosan. Chitosan obtained under extrusion conditions was found to be almost indistinguishable from chitosan obtained by the traditional method as regards its important characteristics such as the solubility and the degree of deacetylation.[82–84] For example, in the presence of alkali under optimal conditions of mechanochemical treatment, deacetylation degrees of up to 0.98 are attained.[85–88]




Since chitin is a rigid-chain non-melting polymer insoluble in any available solvent, all of the known methods for the synthesis of its derivatives suffer from common drawbacks: the necessity to use large amounts of deleterious reagents, long duration of the processes, large numbers of process stages, and the need for waste water disposal. Development of an economic and environmentally safe mechanochemical method for chitin modification is a promising trend in the modern polysaccharide chemistry.

### 1. Mechanochemical synthesis of organic acid salts

The synthesis of organic acid salts is one of the simplest and most widely employed reactions of organic compounds under mechanical activation. The neutralization of benzoic, salicylic, citric, sebacic and other organic acids with metal (M) hydroxides, carbonates and hydrogencarbonates was carried out in a planetary ball mill. It was shown that this gives the salts.[89]

$$RCOOH + MOH \longrightarrow RCOOM + H_2O,$$
$$RCOOH + M_2CO_3 \longrightarrow RCOOM + H_2O + CO_2,$$
$$RCOOH + MHCO_3 \longrightarrow RCOOM + MHCO_3.$$

The reaction was monitored by following the variations in the IR spectra and X-ray diffraction patterns of the mechanically activated mixtures. On the basis of NMR and differential thermal analysis data, it was suggested[89–91] that neutralization is an autocatalytic process and is related to the formation of a 'mobile' microphase: water–carbonate (hydrogencarbonate, hydroxide)–reaction product.

The neutralization of organic acids with alkali [β-(4-hydroxy-3,5-di-*tert*-butyl)phenylpropionic acid + KOH] upon uniaxial compression of their mixture considered in a number of studies[92,93] is explosive, the reaction front propagating over the tablet from the periphery to the centre.

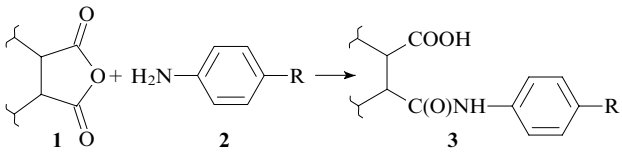
These reactions carried out by joint grinding of the organometallic complex $[Fe(\eta^5\text{-}C_5H_4COOH)_2]$ with a large number of solid bases: 1,4-diazabicyclo[2.2.2]octane ($C_6H_{12}N_2$), 1,4-phenylenediamine [$p$-$(NH_2)_2C_6H_4$], piperazine [$HN(C_2H_4)_2NH$], *trans*-cyclohexane-1,4-diamine [$p$-$(NH_2)_2C_6H_{10}$] and other give adducts such as $[HC_6H_{12}N_2][Fe(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]$, $[HC_6H_8.$ $.N_2][Fe(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]$, $[H_2C_4H_{10}N_2].$ $.[Fe(\eta^5\text{-}C_5H_4COO)_2]$, $[H_2C_6H14N_2][Fe(\eta^5\text{-}C_5H_4COO)_2]\cdot$ $\cdot 2\,H_2O$, *etc*. The solid-state process is described in terms of molecular diffusion with destruction and restoration of hydrogen bonds and proton transfer from the acid to the base.[94,95]

The supramolecular adducts $[N(CH_2CH_2)_3N]-H-[OOC(CH_2)_nCOOH]$, where $n = 1-7$, were prepared by mechanochemical reaction of dicarboxylic acids having various chain lengths $[HOOC(CH_2)_nCOOH]$ with solid 1,4-diazabicyclo[2.2.2]octane. The intermolecular hydrogen bonds between the acid and the base were studied.[96,97]

## 2. Acylation

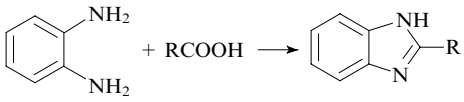
The mechanochemical approach proved useful for the study of acylation. The acylation of 2-sulfanylamidothiazole with phthalic anhydride was carried out under activation in a planetary ball mill.[98] The dependences of the reaction rate on the conditions of mechanical treatment of the mixture (drum rotation speed, ball diameter and number) were studied. A decrease in the ball diameter resulted in a pronounced acceleration of the reaction for ball weight below 50 g; however, an increase in the weight of grinding bodies to 200 g entailed an opposite effect.[99,100] In a later study,[101] it was soundly assumed that the transfer of phthalic anhydride through the gas phase and the reaction of its vapor with the sulfathiazole crystals are the key processes determining the course of the synthesis.

The acylation of amines was studied for a broad range of initial compounds.[102] The mechanochemical acylation rate was found to decrease upon introduction of the electron-withdrawing $NO_2$ group to the carbonyl component. The acylation with succinic anhydride occurs faster than with phthalic anhydride. Electron-releasing substituents ($NH_2$, OMe, OH) in the nucleophilic reagent increase the reaction rate, as in the liquid phase, whereas electron-withdrawing substituents (COOH, $SO_2NH_2$, $SO_3H$, $NO_2$) decrease the rate.



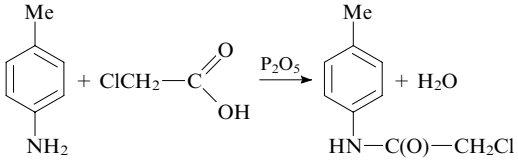

**1** is phthalic, 4-nitrophthalic or succinic anhydride;
R = $NH_2$, OH, OMe, COOH, $SO_2NH_2$, $NO_2$, *etc*.

The mechanochemical acylation can be used to prepare amides. The solid mixtures of aromatic amines with carboxylic acids react to give amides.[103] *o*-Phenylenediamine reacts with carboxylic acids to give the corresponding benzimidazoles.




The studies showed that in this case, the process selectivity substantially changes, while its efficiency depends on the nature of the acid. The results of calculation of the rate constants for the transformations led to the conclusion that the reaction rate of the formation of amides and the synthesis of benzimidazoles on mechanical impact (in this particular case, shear strain at high pressure) is tens of thousand times higher than in the melt.

The acylation of *p*-toluidine with solid carboxylic acids,[104] in particular, the mechanochemical N-acylation of *p*-toluidine with monochloroacetic acid at an equimolar reactant ratio in a ball mill, was studied. The ball diameter, the drum rotation speed, and the ratio of the amounts (weight) of the reactants and balls were varied. To prevent the formation of salts, phosphorus pentoxide was used as a water absorption agent.




The acylation of chitosan and cellulose in the solid state with carboxyl-containing compounds, higher fatty acid (stearic), dicarboxylic acids (oxalic, malonic and succinic acids) and dicarboxylic acid anhydrides (phthalic, maleic and succinic anhydrides), was studied. In the cellulose acylation and chitosan O- and N-acylation with dicarboxylic acid anhydrides, the reaction rate depends on the temperature and depends little on the chemical reactivity of the anhydride. The activity of maleic anhydride with respect to the activity of other anhydrides was so high that in the temperature range of 50–100 °C, the acylation degree reached 100%. The reactions of acids with chitosan afford ammonium salts. In the case of dibasic acids, the salt formation occurs as an intramolecular reaction with the formation of cyclic products and as an intermolecular process to give cross-linked products. Polyacylamides are formed in small amounts. A typical feature of this process is its sensitivity to the chemical reactivity of the acid and insensitivity to the acid melting points and the reaction temperature (50–100 °C).[105–107]

## 3. Exchange reactions

### a. Halogen atom exchange

Halogen atoms located in the side chain of organic compounds are relatively active; therefore, they are replaced rather easily. These exchange reactions were also carried out using the mechanochemical method with aromatic[89, 91, 108–112] and aliphatic compounds.[113, 114]

$$RHal + M(Hal)' \longrightarrow R(Hal)' + MHal,$$

Hal = Br, I; Hal′ = F, Cl, I; M = Li, K, Na, Cs.

### b. Metal ion exchange

The possibility of mechanochemical metal ion exchange between halides and cyclopentadienides of various metals was studied.[115] It was shown that mechanical treatment of mixtures of solid alkali metal cyclopentadienides and chlorides of s-, d- and f-metals (Mg, Ni, Co, Fe, Zr) gives rise to exchange reaction yielding cyclopentadienyl derivatives of the corresponding metals.

Exchange reactions were carried out upon vibrating ball mill activation of mixtures of solid 3d-metal chlorides (Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn) with sodium acetylacetonate; the reactions gave acetylacetonates of these metals.[116] A later study[117] deals with the key regularities of this mechanochemical reaction, dependences of its characteristics on the mechanical treatment parameters (vibration amplitude and frequency, the size of the activating packing, the packing to useful load mass ratio, the degree of reactor filling with the packing, and duration of treatment).

The possibility of mechanochemical synthesis of chromium(III) acetylacetonate derivatives substituted at the carbonyl group by the reaction of chromium(III) chloride with sodium acetylacetonimine was studied.[118, 119]

Upon mechanical activation of mixtures of cobalt(II), iron(III) or chromium(III) chloride with the salt $Tl_2(1,2\text{-}C_2B_9H_{11})$, the exchange reaction takes place with hydrogen evolution and formation of the corresponding metallocarboranes.[120]

The mechanism of mechanochemical synthesis of borane ($BH_3$) adducts with organic nitrogenous Lewis (L) bases is similar to the exchange mechanism

$$L\cdot HCl + MBH_4 = L\cdot BH_3 + MCl + H_2,$$

L = $Et_3N$, $Me_3N$, $Me_2NH$, $MeNH_2$, $Et_2NH$, Py; M = Li, Na, K.

These mechanochemical reactions were carried out in a vibrating mill. The reaction rates increase with increase in the reaction vibration frequency.[121]

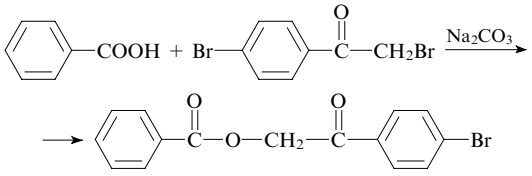
## 4. Dehalogenation reactions

The mechanical treatment of mixtures of organic halogen compounds with alkali and alkaline-earth metal hydroxides, oxides or hydrides gives halides of these metals and leads to decomposition of organic compounds. It was found that activation of a mixture of chloroaromatic compounds with calcium hydride yields non-aromatic products, and a mixture of poly(vinyl chloride) with calcium hydride (calcium oxide, potassium hydroxide) is converted to the corresponding chloride and a polymer with double bonds.[122]

It was suggested[123, 124] that the radical mechanism plays an important role in the destruction of organic halogen compounds. Upon mechanical impact, the electrons from the oxygen atom of CaO pass to organic compounds, and the organic radical anions thus formed effectively dissociate with cleavage of the H—Hal bond. The mechanochemical dehalogenation in the presence of metal oxides and hydroxides has been studied for a broad range of organic compounds: 1,2,3-trichlorobenzene, monochlorobiphenyl, aromatic polyamides, polytetrafluoroethylene, polyvinylidene fluoride, *etc.*[125–129]

## 5. Esterification and hydrometallation

The mechanochemical reaction of carboxylic acids with alkyl halides resulted in esters.[89] For example,




Also, alkylmetals were prepared by mechanical activation. The reaction occurs in two steps, the first step giving activated aluminium

$$Al + M \longrightarrow (AlM_x)$$

M = Ni, Ti,

which reacts with alkenes in the second step

$$3\,RCH{=}CH_2 + (AlM_x) + \frac{3}{2}H_2 \longrightarrow (RCH_2CH_2{-}M)_3Al.$$

The mechanochemical reaction of a butene mixture with lithium hydride affords butyllithium.[130]

## 6. The formation of solid solutions and molecular complexes

The mechanochemical approach was used for the formation of molecular solid solutions. For example, solid solutions of pentaerythritol and pentaglycerol were obtained.[131]

Solid solutions are also formed upon joint activation of 2,2,4,5,5-pentamethyl-3-imidazoline-1-oxyl 3-oxide with urea.[91]

The mechanochemical method can be used to synthesize also molecular complexes. The joint mechanical activation of α- and β-cyclodextrins with acetylsalicylic, benzoic and hydroxybenzoic acids affords inclusion compounds. The properties of the guest molecule are changed due to interaction with the host molecules. For example, the dimers that form aspirin crystals decompose to polar monomers upon the formation of the inclusion compounds.[60] They are formed through polymer amorphization stage followed by dissolution of the crystals in the amorphous medium. Hungarian researchers[132] obtained an inclusion compound upon grinding a mixture of γ-cyclodextrin with fullerene.

Molecular complexes of β-glycyrrhizic acid with acetylsalicylic acid, orthophen or butadione were prepared by the mechanochemical method. The chemical structure of the starting reactants was found to remain unchanged upon mechanochemical treatment. The IR spectra of the complexes synthesized by liquid-phase and mechanochemical methods were identical.[133] Composites of more complex composition (ascorbic acid + calcium carbonate + β-glycyrrhizic acid monoammonium salt, ascorbic acid + calcium carbonate + liquorice phenolic components, ascorbic acid + calcium carbonate + native β-glycyrrhizic acid, ascorbic acid + calcium carbonate + neutralized β-glycyrrhizic acid) were also prepared; they comprise both molecular complexes and mechanocomposites without chemical interaction between the components.[134]

The reactivity of the mechanochemically produced fullerene adducts with 9-substituted anthracenes towards the Diels–Alder reactions was estimated. As model compounds, 9-hydroxymethylanthracene and 9-methoxymethylanthracene were used.[135]

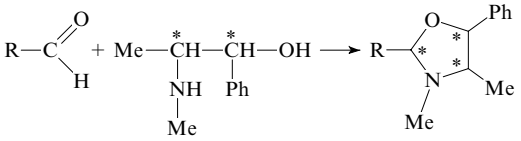
### 7. Mechanochemical synthesis of complexes with organic ligands

It was shown [136] that solid-state mechanochemical reactions with dimethylglyoxime ($H_2$dmg) and nickel(II) salts or copper(II) acetate can proceed to give compounds of three types: $[Ni(Hdmg)_2]$, $[Ni(H_2dmg)_2]X_2$ (X = Cl, $NO_3$) and CuOAc(Hdmg).[136]

The complex $[Fe(Phen)_3]Cl_2 \cdot n\,H_2O$ is formed upon mechanochemical reaction of ferrous chloride crystal hydrate with 1,10-phenanthroline (Phen) in a planetary ball mill. The initial blend is completely amorphized during the treatment, and an N–Fe–N bond is found in the product by IR spectroscopy. The Mössbauer spectra also attest to the formation of a complex compound.[137]

### 8. Miscellaneous mechanochemical reactions with organic compounds

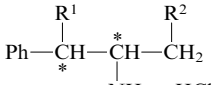
Oxazolidines were prepared from organometallic aldehydes in the solid phase



R = $\eta^5$-$C_5H_4Mn(CO)_3$, $\eta^5$-$C_5H_5FeC_5H_4$.

The stereochemical outcome of the reaction (predominant formation of one of the diastereomers) was the same in the solid phase and in solution, *i.e.*, when chiral amino alcohols were used, the solid-phase reaction was stereoselective.[138]

The solid-state reaction of organometallic aldehydes (ferrocenecarbaldehyde and ruthenocenecarbaldehyde) with optically active primary β-hydroxy amines **4**–**6** was studied.



**4**–**6**

**4**: $R^1$ = H, $R^2$ = OH, $n$ = 0;
**5**: $R^1$ = $R^2$ = OH, $n$ = 0;
**6**: $R^1$ = OH, $R^2$ = H, $n$ = 1.

The reaction affords mixtures of imines and stereoisomeric oxazolidines (three-component mixture for amines **4**, **6** and five-component mixture for amine **5**) (Scheme 1).[139]

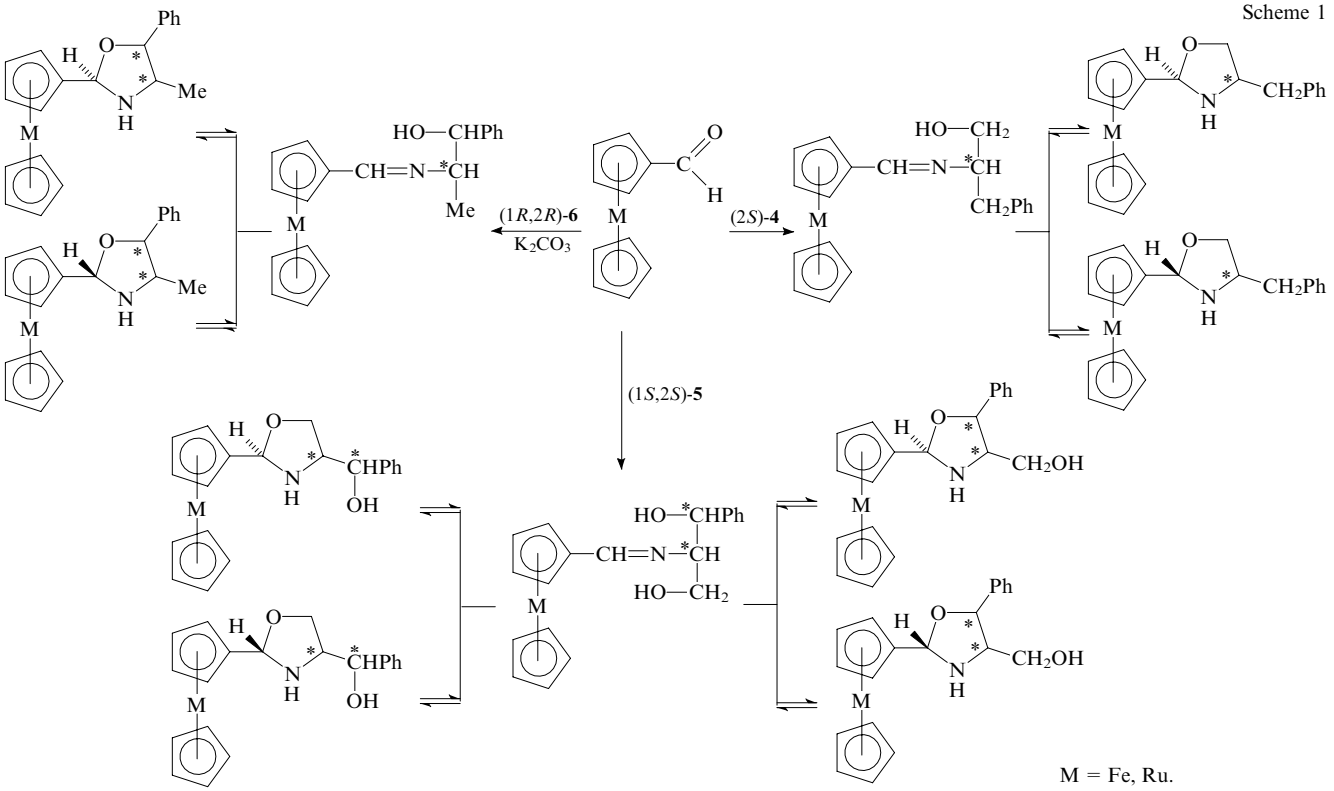
The advantages of performing organic chemical reactions in the solid phase were considered in the literature.[140–142]

## IV. Mechanochemical method for composite production

Analysis of the published data showed that during mechanical activation of organic compounds, both intermolecular and intramolecular bonds are cleaved. This affords radicals and the substance becomes susceptible for reactions with other compounds to give composite structures with chemical bonds between the components. Oxides (both simple and complex) are used most often as the inorganic components of the composite structures.

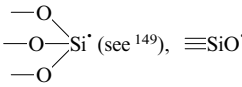
The structural rearrangements induced by the mechanical impact on the oxides have interested researchers for a long time, which was reflected in many publications.[6, 143–147] The attention was focused on silicon oxide. Butyagin *et al.*[148] found for the first time by EPR that the destruction of quartz in a mill under inert atmosphere

Scheme 1



M = Fe, Ru.

results in the appearance of paramagnetic centres. Several types of paramagnetic centres were found to exist:




(see [149]), ≡SiO• (see [149–152]), =Si•• (see [153]).

It is obvious that the chemical reactivity of other oxides will also increase during mechanical treatment. Thus NiO,[154] ZnO,[155,156] MgO (Ref. 157) and $Al_2O_3$ (Ref. 158) were considered.

The chemical reactivity of the oxides of metals having several valence states increases to even a greater extent because in this case, active sites for all valence states are formed.[159–176]

On fine grinding of natural silicates in air, the initial crystal lattices are disordered due to displacement of layers and networks relative to one another. Thus in the kaolinite structure at 1 : 1 ratio of tetrahedral and octahedral layers, the $Si-O-Al^{VI}$ and $Al^{VI}-O$ bonds in the octahedral layer are mainly disrupted, while the Si—O bonds in the tetrahedral layer are retained.

In lepidolite (2 : 1 ratio of tetrahedral and octahedral layers), the structural disruptions are mainly concentrated in the interlayer space and in the octahedral layer. For silicates with 2 : 2 ratio of tetrahedral and octahedral layers (chlorite), no predominant sites for structural disruption were revealed.[177]

More recent investigations of kaolinite and talc demonstrated that during mechanical activation, hydrogen bonds between the tetrahedral and octahedral layers are first to be cleaved, resulting in the formation of acid and basic surface sites able to react with other substances.[178]

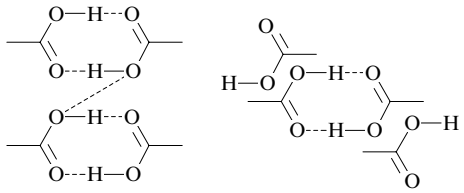
The mechanical action on inorganic compounds also gives rise to various types of active sites. Therefore, by selecting appropriate pairs of compounds, it is possible to perform mechanochemical reactions between organic and inorganic compounds that react with difficulty if at all under traditional chemistry conditions, for example, reactions of organic compounds with layered silicates.

## 1. Organic compound/silicate mechanocomposites

It is known that oxygen- and nitrogen-containing organic molecules are linked by hydrogen bonds. During mechanical activation of individual compounds, the intermolecular hydrogen bonds are cleaved but are rapidly restored after removal of the load. In the case of activation of mixtures of organic compounds with other compounds in which functional groups able to react with the functional groups of organic compounds have also been formed upon mechanical treatment, a chemical reaction takes place at the contact surface.

The mechanochemical formation of composites of organic acids with layered silicates was studied.

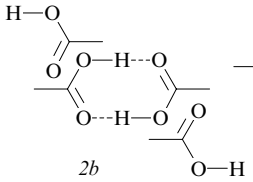
Organic acids are known to be dimerized and to form cyclic pairs with very strong hydrogen bonds between the carbonyl and hydroxy groups of the two molecules. The cyclic pairs of monocarboxylic acids contact with one another by electrostatic interaction between the hydroxyl oxygen atoms, thus forming planar networks with motifs *1*. The packages of such networks are held together by interplanar bonds of two types, *2a* and *2b*.



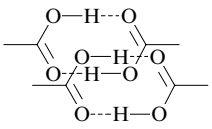

*1*



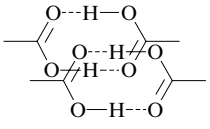

*2a*




*2b*



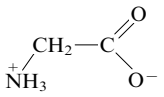

*3a*




*3b*

The aromatic acids form a planar packing motif in which the carboxyl groups of the dimers are located near the benzene ring at a C—H···O distance of 3.5 Å, and, hence, their molecules are not only hydrogen-bonded to form rings within the plane but also form chains due to the 'side' hydrogen bonds; as a result, the acids have layered crystal structure. These bonds provide a close packing. These acids are characterized by interlayer contacts of types *3a* and *3b*.

The mechanical activation of individual higher carboxylic acids (in particular aromatic) does not result in any changes in the crystal or molecular structure.[179,180] Such a behaviour was also observed for dicarboxylic acids, unsaturated and hydroxy acids.[181,182] A somewhat different situation is found for low-molecular-mass amino acids, which are considered for α-glycine as an example.[183] Its molecules existing as zwitter-ions




are linked by two relatively short and, therefore, rather strong N—H···O hydrogen bonds and form antiparallel layers. In view of IR spectroscopic data, one can suggest that the bonds between double antiparallel layers are disordered.[184]

In the presence of natural silicates, all the studied acids behave in a different way. Their mechanical activation together with kaolinite results in a relatively fast decrease in the intensity of the carboxyl IR bands: $\nu(OH) = 2750-2450\ cm^{-1}$, $\nu(C{=}O) = 1710\ cm^{-1}$ and $1650\ cm^{-1}$ and also the bands related to the hydroxy groups: 1430, $1300\ cm^{-1}$ ($\delta(OH + CO)$ bending vibrations). Simultaneously, a broad smeared $\nu(OH)$ mode for a water molecule appears at $3550-3300\ cm^{-1}$ with a bending mode at $1650\ cm^{-1}$. The bands at $\sim 1590$ and $\sim 1460\ cm^{-1}$ appear; in view of the decrease in the intensity of the OH bands, these bands can be assigned to antisymmetric and symmetric stretching vibrations of the carboxylate ion, respectively.

Similar changes occur in the IR spectra of kaolinite mixtures with other solid organic acids. Note also that after a certain time of activation of a kaolinite + acid (up to 20 mass % of organic acid), the bands corresponding to the carboxyl group disappear almost completely and sharp $\nu(OH)$ and $\delta(OH)$ bands for the water molecule ($3550-3300$, $1650\ cm^{-1}$) and $\nu_{as}$, $\nu_s$ bands (1590, $1460\ cm^{-1}$) for the carboxylate ion appear instead. Since the surface sites of basic nature are formed on the newly

exposed surface of kaolinite upon mechanical activation, while mechanical activation of organic acids may induce depolymerization, then joint mechanical treatment of these compounds results in neutralization of the surface hydroxy groups of kaolinite by the acid protons, mechanochemical grafting of the acid anion to the kaolinite surface and the formation of the kaolinite–organic acid anion mechanocomposite.

This type of behaviour of solid organic acids was observed upon their joint activation with talc, pyrophyllite and other layered silicates.[179–182,184–188] In this case, the anion is mechanochemically grafted to the silicate surface; this is indicated by the fact that after joint activation, the crystal structure of the silicate is retained, and that of the organic acid is not retained, while the molecular structure of the organic anion can be recorded by IR spectra. The X-ray diffraction patterns of the initial mixture of succinic acid with talc and the samples after activation carried out for different periods of time are shown in Fig. 1. After 1-minute treatment, only reflections of talc are recorded. The IR spectra of the products of mechanical activation of organic acid–silicate mixtures exhibit absorption bands of the carboxylate ions (Fig. 2).

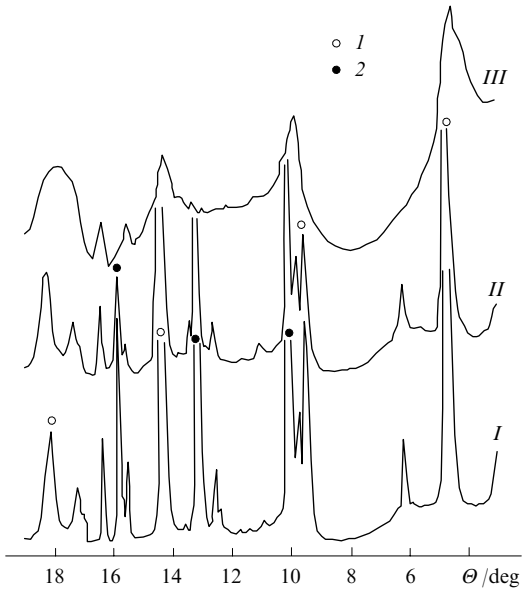



**Figure 1.** X-Ray diffraction patterns of the initial succinic acid/talc mixture (*I*) and that after activation for10 s (*II*) and 1 min (*III*); (*1*) talc, (*2*) succinic acid.

Mechanocomposites of the same type are formed between layered silicates and higher alcohols. Alcohols, like organic acids, form polymeric associates through hydrogen bonds, which are destroyed on dispersion and are restored after removal of the load, which is confirmed by almost invariable IR spectra and X-ray diffraction patterns. On mechanical activation of a mixture of kaolinite with cetyl alcohol, the intensity of the diffraction reflections of the latter sharply decreases, and the IR spectra show the formation of a new chemical bond similar to a bond in acoholates,[182] *i.e.*, not only carboxyl but also hydroxyl groups of organic compounds can react with the surface active sites formed on the kaolinite. On joint activation of kaolinite with hydroxy acids, for example, with tartaric acid, having both the carboxyl and hydroxyl functional groups, the chemical bond between kaolinite and the acid was noted to form through the carboxyl group.[182]

A similar mechanochemical interaction of layered silicates was also observed with salts of organic acids.[188]

Other layered silicates, for example, montmorillonite, can not only add various organic compounds to the lateral surface like kaolinite or talc but also accommodate them in the interlayer space (so-called intercalation). Non-ionic pyrrole was directly intercalated without a solvent by mechanochemical method into non-modified montmorillonite and polymerized in the interlayer space.[189] Polyaniline,[190–194] urea and some organic dyes[195–198] were also intercalated into montmorillonite by the same method.

Silicon oxide appears promising for the formation of organic and inorganic composite structures. Its mechanical activation gives rise to several types of active sites able to undergo chemical reactions. However, few studies have yet been published along this line. Senna and co-workers[199] obtained the indometacin/$SiO_2$ composite and demonstrated that a Si–O–C bond is formed at the interface between these phases. It was proposed to use $SiO_2$ as an inert support in composite dosage forms.

Vorsina *et al.*[200] studied the reaction of $SiO_2$ with various organic acids (monocarboxylic, dicarboxylic acids, hydroxy acids, *etc.*). It was shown that composite structures are formed through hydrogen bonding.

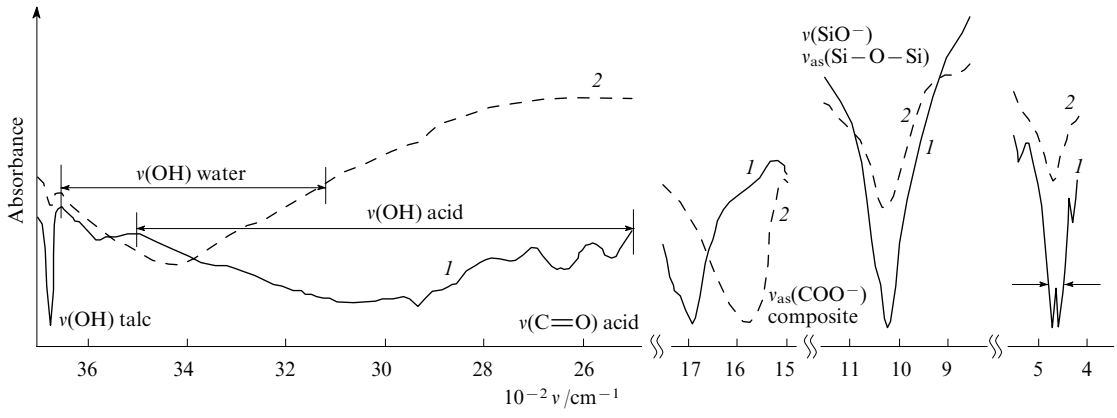



**Figure 2.** IR absorption spectra of the initial succinic acid/talc mixture before (*1*) and after mechanical activation for 10 s (*2*) and 1 min (*3*).

Highly dispersed silicon oxide, Aerosil (particle size 3–5 nm), is an excellent support for solid dyes, both organic and some inorganic ones, which also react through hydrogen bonding.[201]

## 2. Organic compound/other support mechanocomposites

Owing to its set of physical characteristics and biological properties, the hydroxyapatite/silk fibroin composite [202–207] obtained by mechanochemical method is suitable for bone tissue implantation. The same method was used to design composites of low-molecular-mass organic compounds with natural (cellulose and its derivatives, cyclodextrins, proteins, pectins, chitosan) and some synthetic [poly(ethylene oxide), poly(vinylpyrrolidone)] polymers. It was shown by IR spectroscopy that the molecules of benzoic, salicylic and acetylsalicylic acids and hexobarbital form C═O···HOR hydrogen bonds with cellulose or oligosaccharide molecules; barbituric acid derivatives form NH···O(H)R bonds with the hydroxyl groups of polymers.[22]

By joint mechanical activation of microcrystalline cellulose and piroxicam, graft complexes (with the drug substance being grafted to ultradisperse cellulose particles) distinguished by enhanced dissolution rate of the drug component were obtained.[208]

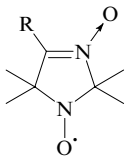
Upon grinding of 2-(4-isobutylphenyl)propionic acid (ibuprofen) with poly(ethylene glycol), the formation of hydrogen bonds between the ibuprofen carboxyl groups and the polymer hydroxyl groups and van der Waals interaction between the polymer molecules and the ibuprofen aromatic rings were established.[209]

Chitosan mechanocomposites with piroxicam and ibuprofen were obtained. According to IR spectroscopy and spectrophotometry data, these composites are formed through hydrogen bonding between these compounds owing to the presence of hydroxyl and amino groups in the chitosan structure.[210–214]

The cellulose–chitosan films and powders were prepared under shear strain conditions in a Brabender mixer, extruder and by mechanical mixing.[215–218] According to IR spectroscopy data, strong adhesive interaction of the composite components is attributable to the fact that this treatment changes qualitatively the hydrogen bonds between the polysaccharide hydroxyl groups and amino groups, indicating that the polysaccharides are mixed at the molecular level.[215] The materials thus obtained have enhanced sorption capacity.

The mechanochemical synthesis of chitosan composites with carboxyl-containing porphyrins,[219] polyethylene,[220] poly(vinyl acetate),[221] titanium oxide[222] and other compounds[223–225] has been studied. These composites are promising for the design of biodegradable polymeric materials.

The mechanocomposites formed upon grafting of low-molecular-mass compounds to the natural polymers were studied.[226, 227] An attempt was made at mechanochemical solid-state introduction into cellulose of spin traps, namely, stable imidazoline nitroxide radicals, 4-R-2,2,5,5-tetramethyl-3-imidazoline-1-oxyl 3-oxides.



R = Me (**7**), COOH (**8**), $CH_2Br$ (**9**).

The purpose of the work was not only to obtain spin-labelled cellulose samples but also to quantitatively estimate the possibility of solid-state mechanochemical grafting of monomeric organic residues to cellulose. The studies were carried out by EPR. Several compositions were investigated.

1. Joint mechanical treatment of microcrystalline cellulose and radical **7** in order to attain intercalation and adsorption of the radical by cellulose and holding it by intermolecular interactions.

2. Joint mechanical treatment of microcrystalline cellulose and radical **8** to form an ester bond between the radical carboxyl group and the cellulose hydroxyl groups.

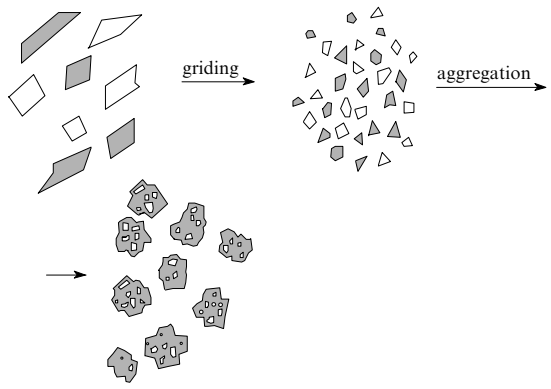
3. Joint mechanical treatment of microcrystalline cellulose and radical **9** in the presence of sodium hydroxide to form ether bond between the methylene group of the radical with the hydroxyl groups of cellulose.

The lowest concentration of the paramagnetic centres was obtained for radical **7**. The highest concentration of the grafted spin trap was attained when conditions for covalent binding of stable radical (radicals **8** and **9**) and cellulose were created. A simple calculation has shown that for radical **8**, the number of strongly bonded paramagnetic centres is roughly equal to the number of monomer units in the chain cellulose molecule, *i.e.*, one spin trap per unit is approximately present. In the case of radical **9**, the degree of modification is somewhat lower. In all of the considered cases, the EPR spectral pattern attests to a uniform distribution of the grafted paramagnetic centers in the cellulose macromolecule.

The introduction of bulky substituents disrupts the hydrogen bond systems of the cellulose hydroxy groups. The appropriate changes are observed in the IR spectra in the frequency range of 3000–3900 $cm^{-1}$ corresponding to the hydroxyl stretching vibrations. The minimum of the band shifts to higher frequency and the contour of the band changes. The mechanochemical reaction of cellulose with radical **7** does not induce pronounced disruption of the hydrogen bond system; the introduction of a substituent into radical **9** is accompanied by a decrease in the number of hydroxyl groups incorporated in the hydrogen bond system.

The mechanocomposites based on organic low-molecular-mass can also exist without the chemical grafting of components. The reaction of acetylsalicylic acids with sodium and calcium carbonates was studied. It was shown by electron microscopy that even at an early stage of activation, composite aggregates are formed. As the mechanical treatment time increases their density increases and the crystallite size of acetylsalicylic acid decreases.[111, 228–231]

Schematically this can be represented as follows:




A structure with a very large contact surface area between the initial components is formed.

Nanocomposites of Mg—Al-hydrotalcite with poly(ε-caprolactone) were prepared. Poly(ε-caprolactone) and magnesium and aluminium double hydroxides modified by organic compounds were subjected to joint mechanical treatment in a high-energy ball mill (the amount of the inorganic material in the treated mixture was 0 mass % – 6 mass %). It was shown that 12-hydroxydodecanoates add to the inorganic layer.[232]

A fairly broad range of composites have now been synthesized by the mechanochemical method. Energetic composite systems (*i.e.*, the systems able to react with evolution of a large amount of heat) organic compound/metal, such as aluminium/Teflon, magnesium/Teflon, were developed.[233–236] Polymer/oxide composite structures (for example, polytetrafluoroethylene/highly dispersed oxides[237–241]), which can be used, in particular, to reinforce polymer articles, were produced.[242]

A sort of mechanocomposites are formed upon mechanochemical extraction of organic compounds with inorganic solids. The process developed for this purpose involves mechanical treatment of mixtures of powdered plant raw materials and solid sorbents of different chemical nature. According to this process, biologically active compounds were isolated from plant raw material, for example, diterpene alkaloid lappaconitine and cardiac glycosides. The suitable solid sorbents include silica gel, aluminium oxide and other oxides, salts, solid organic acids and their salts and carbohydrates, including sucrose, starch, cellulose.[243, 244]

Non-waste mechanochemical processing of silver fir needles to a biologically active agent containing water-soluble forms of triterpene acids suitable as a plant growth regulator was developed.[2, 245–252]

It was shown that biologically active compounds affecting plant growth and development can be recovered from peat by mechanochemical extraction with water-soluble solid sorbent. The biological activity of the extracted compounds was studied and enhancement of proliferation of the rape tylosis tissue, acceleration of alfalfa shoot and root development, cytokinin type activity in shoot regeneration and stimulation of wheat germination were found.[253–255] Other mechanocomposites involving peat were produced and studied. In all cases, increase in the reactivity of the key peat complexes was observed.[256, 257]

Mechanocomposites were used as intermediates in the production of carboxymethylcellulose.[258] The influence of mechanical activation on oil residues and their mixtures with carbon[259–261] and the possibility of using mechanocomposites with plant raw materials for enhancement of oil recovery[262, 263] were investigated. Composites with organic polymers and fibres have found use as construction material.[264]

* * *

The review of published data demonstrates that many organic syntheses can be carried out by the mechanochemical method; however, systematic research in this field is barely carried out and can hardly be expected in the near future.

Since for attaining high rates of any heterogeneous reactions, great contact surface areas and withdrawal of the product with surface renewal are also important, presumably, the use of mechanical activation is most promising for the syntheses involving low-melting components. Most often, organic compounds have relatively low melting points, therefore, it is quite easy to select pairs where one component would melt under mechanical treatment. This component will wet the surface of the other component, spread over the surface, thus creating a contact surface much greater than that created in a solid-phase synthesis. However, these factors were not analyzed.

On the basis of the available published data, it can be stated that the mechanochemical approach is promising for the design of composite structures, most often, for nanocomposites. These composites can either be made by chemical grafting (for example, layered silicates and organic acids) or merely have a great contact surface area between the components (for example, acetylsalicylic acid + sodium carbonate composite). They can constitute the base of the dosage and cosmetic forms and serve as convenient starting components for the subsequent heterogeneous chemical reaction with liquid and gaseous agents.

Mechanocomposites with plant products (for example, phytosterols) can be used in cattle and poultry breeding; triterpenes and composites involving them are useful in crop growing.

The authors believe that the design of composite structures is the most promising trend of development of mechanochemical processes, which are currently among the most environmentally safe processes.

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