

## Mechanochemical modification method used in the development of new composite materials based on epoxy binder and natural minerals

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**Abstract:** This article highlights the results of a mechanochemical modification method of epoxy composite materials and coatings on their base. It proves the mechanochemical activated components of composition to be the most acceptable for structuring when producing composite materials. It also states the increase of mechanical properties of epoxy heterocomposite coatings with mechanically activated particles by 25%–40%.

**Key words:** Composite materials, mechanical activation, mineral fillers, modification, helio technology, polymer materials, functional and active groups

### 1. Introduction

Modern polymer composite materials are heterophase compositions with new combinations of properties that differ from the properties of initial components, but still keep the individuality. The combination of filler containing polymers allows the obtaining of materials with absolutely new technological and operational features, which are distinguished, first of all, by their good mechanical stability. Composition is a disperse system, which consists of a polymer matrix with distributed hard particles of fillers. The properties of such a system are defined not only by properties of polymers and fillers, but also by the distributing character of particles in the volume of the matrix and interactions at the interphase border.

Nowadays, composite materials are widely used in various fields of industry and manufacturing. Particularly, application of composite polymer materials and coatings for operational devices of cotton cleaning machines and mechanisms would bring a significant decrease in mechanical damages of cotton, thus saving its natural qualities. High elasticity of the surface micro- and sub-microimperfections helps prevent deep micro-cuttings in fiber with sharp peaks of imperfections, so the fiber meshing weakens.

However, the antifriction composite polymer materials and coatings are not being widely used in cotton cleaning technological machinery due to the deficit and high cost of some composition material components, as well as the absence of effective coating technologies for surfaces of bulky equipment with suitable structures and properties.

The mechanochemical activation of components is one of the most effective structuring methods used for heterocomposite materials with local minerals, ensuring their high thermodynamic compatibility.<sup>1,2</sup> Special at-

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tention here should be paid to the physicochemical and mechanical phenomena observed on the surfaces between the phases connecting the fillers, which ensure guaranteed composition qualities via specific regulation.<sup>3,4</sup>

Gibbs studied thermodynamic aspects of the surface phenomena; he accounted surface layer as the surface of a new phase with properties different from properties of volume phase specified by energy potential.<sup>5</sup> The current theory is also applicable to our condition: the analysis shows that to achieve a thermodynamic equilibrium in heterocomposites, it is necessary to decrease the free energy of the surface layer, which mainly adsorbs the substances reducing the free energy of the surface layer. The mechanochemical activation was applied herein to provide a sustainable structure of composite materials.

At the present time, there are various technological methods of managing structures and properties of composite polymer materials (CPMs) and composite polymer coatings (CPCs) used in surfaces of technological equipment. Physical methods are considered to be the most efficient, that is,  $\gamma$ -exposure, magnetic, and ultrasonic treatments. However, it should be noted that full effect of structure formation of CPMs in magnetic and ultrasonic fields can be achieved during the sufficiently long and difficult contiguous processing of these fields' effect until the full formation of coatings. In the laboratory, it can be reached by treating composite coatings based on thermoreactive polymers in the conditions of cold curing. In the conditions of hot curing and treating composite coatings based on thermoplastic, it becomes difficult, because of the absence of universal equipment that allows synchronous combination of technological processes of physical modification with the thermotiming regime of coating formation. Currently, CPC cannot be treated by known methods of physical modifications because of the large dimensions of the working components of the technological equipment.

Based on the above, we are doing our research on improving the properties of CPC using a solar-technological activating method, i.e. producing a coating from previously mechanically and chemically activated heterocomposites under solar radiation in a specially constructed desktop, constantly directed to the sun.

At the present time, experts are doing research on the accessible and cheap monomers and other raw materials for manufacturing composite materials. We therefore decided to use mechanically activated local natural minerals: Angren kaolin (produced at the Angren Kaolin Concentration Plant) and Kuytash wollastonite (produced at the Kuytash Wollastonite Concentration Plant), as well as gossypol resin (GR; a waste of the oil industry) as plasticizer and structure formatting agent. Utilization of available raw materials, such as GR, makes it possible to get polymers based on epoxy and nitrogen compounds. The molecules of gossypol contain an aromatic core, which gives it a high thermal and chemical stability. Phenol, hydroxyl, and aldehyde groups in the molecules of GR cause its great reactivity to get complex compounds with mechanic activated natural minerals.<sup>6</sup>

The fact that gossypol is a multifunctional product, and several multiple functional groups are synchronously involved in its interaction, facilitated the development of the coatings based on the activated wollastonite and kaolin with a various dispersion in an epoxy matrix plasticized by dibutyl phthalate (DBP) and GR, cured by polyethylene-polyamine (PEPA) under the impact of direct solar radiation (30 MJ/m<sup>2</sup>).

## 2. Experimental

### 2.1. Reagents

Thermoreactive oligomer is used as a polymer binding, cured with PEPA. Conventional DBP is used as a plasticizer. Angren kaolin and Kuytash wollastonite are used as fillers, and GR is used as a polyfunctional structuring agent for mechanochemical modification of composite materials.

## 2.2. Apparatus

Microhardness of coatings was studied with the help of a PMT-3 device, which has a diamond pyramid indenter. The hardness rate was calculated as a ratio of the load on the indenter to the area of the pattern:  $H_M = 1854 \check{G}/d^2$ , where  $d$  is a diagonal of the pattern. The load on the P indenter varied from 0.05 H to 5 H. The measurements were done up to  $d \leq 300 \mu\text{m}$ . Ten experiments were carried out for each point, and the average value was calculated.

The rate of cross-linking was determined by an extraction method; acetone was used as solvent.

Dispersal analysis of mechanical fillers with and without mechanical activation was done on the particle size analyzer device (SediGraph).

The mechanical activation of local natural minerals like Angren kaolin and Kuytash wollastonite was done on mechanical activation device (Kompozit 2000), which is based on collisional and smearing impact, providing mechanic activation both by means of enlarging specific surfaces of particles and by forming heterogeneous polarized dipole moments on the abrasion surface with following chemical activation and addition of the polyfunctional structure formatting agent, GR. The rotation speed is  $n = 2800 \pm 10 \text{ rev/min}$ ; the desktop power is 18.5 kW. The duration of mechanical activation is  $t = 0.5\text{--}3.0 \text{ min}$  for selected minerals.

## 3. Results and discussions

We examined the mechanism of epoxy composite curing for various compositions, both in the sun and in the laboratory at an indoor temperature of  $25 \pm 2 \text{ }^\circ\text{C}$ , as a pilot study. The research was done in the city of Tashkent in August, with average open air temperature of  $42 \pm 2 \text{ }^\circ\text{C}$  (Table 1). Solar radiation intensity was  $710\text{--}750 \text{ W/m}^2$ .<sup>7</sup>

**Table 1.** Degree of epoxy composites' curing depending on time of exposure to solar treatment.

Sample types	Compound of epoxy composites	Surface structuring conditions			
		Baseline	In the sun (t, min)		
		(t = 25 min)	5	15	25
1	ED-20 - 100 g, PEPA - 8 g, DBP - 10 g (GR - 10 g)	7.22	6.24	11.63	12.42
		8.21	7.23	11.94	12.64
2	ED-20 - 100 g, PEPA - 10 g, DBP - 10 g (GR - 10 g)	17.4	16.3	23.5	26.5
		19.0	18.2	24.7	27.7
3	ED-20 - 100 g, PEPA - 12 g, DBP - 10 g (GR - 10 g)	21.7	19.8	50.5	52.5
		22.1	21.1	52.8	54.5
4	ED-20 - 100 g, PEPA - 14 g, DBP - 10 g, (GR - 10 g)	22.3	20.3	51.8	53.8
		25.6	23.5	54.4	56.1
5	ED-20 - 100 g, PEPA - 16 g, DBP - 10 g (GR - 10 g)	23.1	21.1	53.6	54.7
		26.4	23.9	55.6	58.4

Note: Gossypol resins in brackets.

Table 1 shows how the curing reaction of epoxy composites after treatment in the sun accelerates by 1.7–2.4 times depending on the amount of curing agent; a high degree of curing is achieved when the surrounding temperature is  $42 \text{ }^\circ\text{C}$  and the composition contains  $\geq 12$  mass of PEPA.

This happens due to the following circumstances: compared to the composition in shadow, the viscosity of composition decreases under the impact of solar energy. Additionally, a decrease of viscosity promotes an increase of flow ability and therefore more even distribution of molecules of the curing agent and orientation of

their functional group. The increase of PEPA to 16 g/h does not significantly affect the degree of curing; thus, we recommend an optimal PEPA concentration level of 10–12 g/h.

Meanwhile, we can notice that the effect of composition cross-linking with the increase of curing agent composition is much greater than in the GR composition. This is explained by the existence of reaction active carbonyl and carboxyl groups in GR.

It is well known that luminous and ionizing radiation actively affects polymers and leads to some chemical conversions in them, which strongly change physical and chemical properties of polymers.<sup>8</sup> In carbohydrate polymers, hydrogen atoms from molecular chains of a polymer form free radicals in it. Further on, these radicals are stabilized by recombination, which leads to formation of branched and net structures.

Research results show that solar radiation significantly increases the curing process of thermoreactive polymers and the level of macromolecular chain cross-linking followed by enhancement of physicochemical properties of polymer materials and polymer coatings.<sup>9</sup>

The effect of surrounding temperature on the microhardness of polymer coating was studied for determination of optimal ratios of plasticizer components and solar treatment radiation regimes (Table 2). The epoxy component containing 12 g of PEPA was chosen for this purpose. Solar radiation treatment time was 1800–72,000 s (from 0.5 to 20 h).

**Table 2.** Time impacts of solar treatment on microhardness of coatings with different ratios of GR to DBP.

Microhardness of coatings $N_M$ , MPa					
GR:DBP ratio, g	Solar treatment time $\tau$ , c				
	1800	3600	18,000	36,000	72,000
20:0	82	132	151	192	202
15:5	78	126	150	182	196
10:10	74	122	149	176	185
5:15	65	107	132	164	176
0:20	61	104	126	158	163

The results show that due to the effective impact of solar energy, not only does the initiation of polymer net curing reaction followed by intensive increase of cross-linking ratio (Table 1) take place, but the epoxy material hardness is also enhanced as a result of CPM structure improvement, especially with GR. Hence, the more solar energy stream (solar treatment time), the greater the microhardness of coatings with the same composition.

The above research results lead to the conclusion that a solar radiation treatment of polymer composition is an effective way to control curing reaction; it saves energy during the preparation of high viscous epoxy composites using GR with DBP in the ratio of 10:10 (g).

Experiments have shown that the treating by mechanical activating device of wollastonite concentrate for 3–5 min forms ground wollastonite with dispersion of  $d \leq 10 \mu\text{m}$ . Under such conditions, the anisotropy coefficient ( $\kappa_a$ ) of these particle sizes ranges from 1.0 to 1.2, which in form (structure) become a usual granular filler.<sup>10</sup>

Another economically important structuring mineral for composite polymers is kaolin. Preliminary mechanic activation of Angren kaolin and wollastonite in the range from 0 to 30 g was done on a mechanical activating device for 3 min, and then GR and DBP were added at 10:10 and mixed in a ball grinder for 600–900 s, sufficient for obtaining a homogenous mechanically and chemically activated mass.

Table 3 shows that the increase in mechanic activation time of mineral fillers causes the growth of epoxy mineral microhardness by 25%–40%. This can be explained as follows: transition metal oxides existing in natural minerals form polarized dipole moments during mechanical activation, which can form complex compounds with lateral functional groups of a binder and GR modifier, mainly consisting of stearin, oleic, and palmitic acids, which in turn create auspicious conditions for formation structures of heterocomposites by their polyfunctional properties.<sup>11</sup>

**Table 3.** Time impact of mechanic activation on microhardness of coatings at different ratios of kaolin to wollastonite.

Microhardness of coatings $N_M$ , MPa						
Kaolin to wollastonite ratio, g	Mechanic activation time, c					
	30	60	90	120	150	180
30:0	158	175	186	210	215	217
25:5	165	187	193	212	218	220
15:15	178	192	198	212	224	225
5:25	211	216	232	242	251	258
0:30	234	248	254	266	270	272

Metal ions, formed by mechanic activation of minerals on the device, play a role in structuring, together with gossypol's polyfunctional groups of GR, which increases the adhesion between the filler and a binder, not just for an increase of the specific surface of mechanic activated mineral, but also for the increase of ionized focus for complex compounds with carboxyl gossypol groups.

The research results show that with similar amounts of mechanical activated mineral fillers, better mechanical properties are observed when wollastonite is introduced into the process. This significant difference of properties of epoxy heterocomposite coatings during the introduction of activated kaolin minerals and wollastonite can be explained by their structure construction. Granular or spicular wollastonite particles form more strong interactions in interphase layer filler–binder than kaolin particles with layered structure.<sup>12</sup>

#### 4. Conclusions

Based on the research analysis, we can summarize that the new proposed activating solar technological method ensures necessary structuring and physicochemical properties of epoxy heterocomposite materials and coatings that can be applied on surfaces of bulky cotton cleaning technological machines.

Mechanochemical activated components of compositions are the most acceptable for structuring during the production of composite materials. Therefore, epoxy heterocomposite coatings with mechanical activated particles have mechanical properties increased by 25%–40%.

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