Layered nanostructured composites with self-healing effect based on plastic borosiloxane matrices

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Abstract. This paper presents a layered composite material with an internal self-healing matrix based on borosiloxane compounds. The effects of self-healing in materials of various chemical nature (polymers, cements, ceramics, metals and composite materials) are considered and evaluated from the point of view of their practical application and the creation on their basis of self-healing composites. The properties and characteristics of borosiloxane are described. The prospects of using of borosiloxane as an internal self-healing matrix of layered or reinforced composites are shown. The effect of self-healing of the developed layered composite at breakdown and cut is demonstrated.

Keywords: self-healing materials, borsiloxane (borosiloxane), multilayer composites, matrix.

1. Introduction
The concept of self-healing man-made materials capable of recovering their initial characteristics after damage has been appeared relatively recently - several decades ago. This area of materials science attracts the scientific community actively due to the present development of technologies of materials science as well as the opening up prospects for the application of such materials. Artificially created substances or systems capable of partially or fully restoring the initial characteristics after the caused damage would open up tremendous opportunities, especially in cases when it is necessary to support operations of materials in hard-to-reach areas for as long as possible. Ideally, recovery in such materials has to occur without any external intervention, especially of a human. There are a few successful applications of such technologies in scientific publications. Most ideas for the implementation of artificial self-healing of non-biological materials are presented as the laboratory research models [1-17].

The following definition based on the analyzed literature and authors’ own experimental data are proposed: the effect of self-healing (self-repairing) in man-made materials - a full or partial reduction of the surface area of material's damage due to mass transfer and consolidation of boundaries (bonds) with full or partial recovery of the functional characteristics of the material. This effect is observed in materials after their damage is usually accompanied by a discontinuity with increasing surface area. In such materials, the consolidation of the boundaries of damage (responsible for the concept of "healing") occurs after their drawing together, realized through mass transfer (responsible for the concept of "self"). The processes of mass transfer and consolidation of boundaries can occur autonomic (for example, due to the flow of material) or nonautonomic, i.e. healing is stimulated by external influence. An example
of external influence is temperature increase or ultraviolet radiation. The self-repair mechanisms of man-
made materials are divided into “external” and “internal” according to the method of organizing the
processes of self-healing. “External” self-healing mechanisms are based on recovering components
specially embedded in the matrix of the base material, for example, microcapsules with healing
substances. The “internal” self-healing mechanisms are not required any additional repairing
compositions [1].

The ability of artificial materials to self-repair of any properties can allow to increase their service
life, reduce the cost of maintaining them in working condition and repair, as well as increase the level
of safety of the structure or product as a whole. Based on the opening opportunities more of academic
and industrial research organizations support the development of new self-healing materials and
composite systems based on them.

The aim of this work is to determine the possibility of using borosiloxanes as a healing matrix for the
preparation of self-healing layered composites.

2. Evaluation of self-healing effects in materials of various kinds and technologies based on them

Self-healing materials are a wide class of substances and can be subdivided into conditionally “neat”
materials (polymers and semipolymers, ceramics, cements and metals) and composite materials and
systems, which are presented in various combinations (reinforced materials, encapsulated materials,
systems with hollow and filled fibers, vascular systems, laminates, sandwich panels with liquid reagents,
etc.) [1–8].

Today, self-healing in “neat” materials is most successfully implemented in oligomers (semipolymers)
and polymers due to relatively high diffusion rates because of having transverse molecular bonds which
are able to restore bonds by crosslinking of polymer chains under specific conditions. Some low
molecular weight polymers have reversible covalent bonds allowing partial or complete self-healing
when reconnected with additional heating or without it [2, 3]. Consolidation of damage boundaries,
reinstatement of bonds, directly responsible for the healing effect, can be achieved both by the use of
cova lent bonds and by non-covalent interactions. In the first case, various crosslinking reactions are
used, for example, Diels-Alder reaction. Non-covalent healing can be achieved through the formation
of hydrogen bonds and complex compounds, aromatic interaction (π-π-interaction), ionic interaction,
Van der Waals forces, etc. Materials with covalent bonds have high strength, but at the same time they
need the introduction of micro-inclusions of initiating substances and monomers, which provide healing.
Because of this, the resource of such materials is limited, because over time there is a shortage of
substance for the implementation of mass transfer. The bonds of the second type of polymers are more
easily broken and restored, which undoubtedly affects the possibility of multiple healing and, accordingly, the durability of the material, but at the same time they withstand less stress and temperature
[2-5].

Many of the developed polymers demonstrating self-healing properties are elastic materials (rubbers,
etc.) or viscous substances (resins, gels), most of which are oriented to use at temperatures from 0 to
150 °C. The type and size of the healed defects have a wide range, self-healing of disconnected surfaces
require their connection. The recovery time of properties is ranging from a few seconds to hours.
Sometimes, an increase of the temperature (relative to the exploitation's temperature) or exposure to
radiation, e.g. ultraviolet, is required to realize the self-healing of the initial parameters [1–8].

In ceramic materials to obtain the effect of self-healing processes are usually used oxidation of the
constituent parts of the ceramic matrix or additional substances introduced into it at high temperatures
(about 1000 °C). For such processes, accompanied by an increase in mass in places of defects, usually
use ceramics phase $\text{Mn+1AXn}$, where M is the transition metal, A is the IIIA element or IVA subgroup
of the periodic system, X is carbon or nitrogen (for example, the Ti2AlN phase) for processes
accompanied by mass gain in the defect areas. As a result, defects caused by wear or thermal stress are
obtained by filled bonding oxides of the A-element. Products of oxidation reactions are used to fill small
cracks (up to about 100 microns). The healing time is tens of hours and more [9, 10].

Self-healing of cement materials is also accompanied by mass of material gain in the defect areas,
mainly due to mineral components, which provide healing of cracks in consequence of hydration, calcination, oxidation or other chemical processes. The sizes of the recovered defects are in the range from several microns to mm. These processes occur in air upon contact with water, and are characterized by a long time (tens of days - months) in a wide range of temperatures [7, 11].

Self-healing of metallic materials, due to their special properties, is achieved more difficult than in most other classes of materials. One of the problems is the nature of the bond between atoms and their low mobility at working temperatures. In general, defects in metals are healed by more fusible and plastic phases introduced into the main matrix, or by the accelerated formation of agglomerates from phases dropping out of the basic material at the sites of defects under certain conditions. For example, autonomous damage recovery upon heating to 550 °C can be achieved in iron containing a small amount of gold due to creep of the precipitated phases[12, 13].

Improving self-healing characteristics of various materials is the development of composite systems based on them with introduced various fibers, materials with special properties or chemical components, allowing autonomic or non-autonomic reducing the destruction of the initial material and contributing to the faster and complete healing of the defect. For example, some elastic fibers are introduced into the polymer matrix, bring together after deformation the boundaries of the polymer's destroyed area, then this surfaces form bonds and the defect is healed by the previously described methods (autonomous action). Non-autonomous self-healing is realized by introducing into the matrix materials with special properties that are able to additionally influence under external impact, e.g. to expand and thereby reduce the size of the destroyed area. As such materials there can be various entangled fibers and materials with a “shape memory effect” (SME), expanding or contracting with increasing temperature, as well as various substances, e.g. gels, capable at several times to increase in size at a certain external impact [6, 14, 15].

There are lot of works that study self-healing composite materials, in which inert thin-walled breakable capsule with a healing substance are introduced in the basic matrix. The capsule breaks when a defect occurs, such as a crack, and the healing agent get out and spreads into the crack. At the same time, it either interacts with the matrix or the external environment or mixes with a catalyst — a solidifier pre-embedded in the material (separately from the capsules), hardens and seals the crack [1-8].

Layered composite materials (sandwich panels) are considered one of the most promising areas for creating self-repairing systems, having in its composition a layer or several layers with some kind of self-healing mechanism. In this scheme, each layer performs its specific function, and in the general system, the layered composite material is able to minimize damage and restore its original macrocharacteristics. Such sandwich panels can include various solid, viscous and liquid fillers, which react together to form a solid phase in case of material defect [6–8, 16–18]. In most cases, the healing of composite encapsulated materials is represented as the filling of the discontinuities appearing in the material with some substance other than the base material, sometimes with completely different properties from the matrix material. In fact, this is not the recovery of the original characteristics of the material, but the formation of a new material with a different structure and properties. However, self-healing in most cases means the reduction of the bulk or surface integrity of the product with the simultaneous partial or full recovery of important performance properties, such as leaktightness, strength characteristics, electrical conductivity, exterior etc.

The concept of self-healing laminated composite materials is broad and may include various self-healing mechanisms in one system, allowing to obtain for unique self-healing effects that are unattainable in other materials.

3. Properties and characteristics of borosiloxane oligomeric and polymeric compounds

Based on the analytical evaluations and characteristics of self-healing materials, borosiloxane-based materials (BS) were chosen as the main self-healing matrix of the layered composite [8, 19-22]. BS are oligomers or polymers based on elemental organosiloxanes in which the Si-O-B group is present. They have the properties of silicone oils and polymer materials, combining such characteristics as fluidity
under static load and elasticity under short-term or shock load. It is assumed that these properties determine due to intermolecular donor-acceptor interactions of boron and oxygen atoms. Thus, BS is a dilatant (non-Newtonian) fluid, which behaves like a chewing gum or elastomer when stretched, and turns into a viscous fluid, spreading over the underlayer surface in the absence of external stress [23, 24]. Mass transfer to the damaged area in borsiloxane composites occurs due to the ability to spread at low loads (Figure 1).

Figure 1 shows an experiment demonstrating the process of self-healing of disconnected boundary of BS. Two balls of the same size were made of BS, then the balls were brought into a point touch. Without external intervention the BS balls spread out under the action of gravity. The contact area of brought together balls gradually increases, in which the consolidation of boundaries is implemented. The subsequent stretching of the plate cut out from the consolidated sample shows that the place of consolidation has the same mechanical properties as the whole sample. The material is stretched, and then breaks not at the place of consolidation of the boundary (when stresses greater than the strength of the sample are applied). The experiment demonstrates the phenomenon of mass transfer with the integration of boundaries, leading to a decrease of the total surface area, and the phenomenon of interdiffusion during the consolidation of surfaces.

Thus, BS is a promising material for use as an internal self-healing matrix of a layered composite material.

4. Layered self-healing composite material with internal borsiloxane oligomeric matrix
The developed composite with internal borosiloxane matrix has a multilayer structure. The multilayer scheme has the advantage of simplicity of obtaining and is most convenient for checking the effectiveness of the selected materials for each layer of the laminated composite material. As an internal self-healing matrix, one or several BS layers with various fillers were used. Monolithic vacuum-tight silicone sheet with a thickness of 0.5–1 mm and wicker glass-fiber cloth with a thickness of 0.3–0.4 mm impregnated with silicone were chosen as materials for the outer layers. These materials showed sufficient tensile strength and satisfactory functional properties. The choice of outer layers of silicone-based materials is justified by the fact that these materials exhibit good adhesion in contact with borosiloxane caused by similar bonds.

Samples of BS used in the work were obtained by mixing polymethylsiloxane with boric acid and Lewis acid, which was a catalyst. Boric acid was taken in the amount of 4-40 weight part per 100 weight part polymethylsiloxane, Lewis acid was taken in the amount of 0.001-3 weight part per 100 weight part polymethylsiloxane. The obtaining blend compound was heated and introduced into it one additive at least
- a filler (aerosil, talc or kaolin) or a plasticizer (oleic acid). Heating was carried out by microwave radiation to a temperature of 150-250 °C for 10-90 minutes [24]. Carbon and polyamide fibers were added additionally to the BS to reinforce it. The obtained BS samples showed good flowability and consolidation of boundary at their bringing together both in the reinforced state and in the initial state.

The general manufacturing technology of the laminated composite was in the following steps:

- preliminary isothermal exposure of the BS at a temperature of about 100 °C;
- crumpling material to obtain a homogeneous mass, followed by vacuuming to remove air bubbles;
- rolling BS to a layer of a given thickness;
- successive lay-up of the BS layer with other layers of the composite;
- homogeneous distribution of the BS in the composite material until it is completely adjoining to other layers.

Some various layered self-healing composite material with an internal borsiloxane matrix with thickness of 0.5 mm, 1 mm and 1.5 mm, with and without fillers, were manufactured. A sample of a laminate self-healing composite material consisting of three layers with an internal borosiloxane matrix with thickness of 1 mm is shown in Figure 2.

![Figure 2](image2.png)

**Figure 2.** Typical cross-sectional view of a three-layer self-healing composite with an internal layer of BS.

The demonstration of the self-healing effect and the experimental determination of the healing characteristics of the produced layered composite during breakdown and cut were performed in a laboratory setup, which is a chamber with a flanged window (Figure 3).

![Figure 3](image3.png)

**Figure 3.** Laboratory setup for testing of the self-healing properties of layered composites: (a) an overpressure chamber, in the upper part of which a sample of a laminate composite with a white top layer is clamped by a flange joint; (b), (c) breakdown and cut of the composite; (d) the image of
surface defects formed by the piercers, (e) an enlarged image of the damage area on the upper layer of the composite.

Experimental laboratory setup has valves for inlet and outlet of gas creating pressure in the chamber volume, the pressure is monitored according to the installed pressure gauge. A sample of the self-healing composite material is placed in the flange window and leaktight fixed in it, an overpressure of about 0.1-0.3 atm is created in the chamber. This setup allows to study the processes of self-healing in manufactured composites after their end-to-end breakdown by any object. Evaluation of the effect of self-healing of the test sample of a layered composite and the dynamics of healing was carried out the pressure drop in the chamber, after a defect was formed in the composite with a discontinuity. The parameters of self-healing of the defect are monitored by pressure drop: when the pressure in the chamber after the breakdown decreases and then stabilizes, it is assumed that the hole from the damage was tightened and there was a consolidation of the boundaries in the BS [18]. Testing of the self-healing properties of the composite was carried out by its breakdown with pointed piercers of 0.8 mm, 1 mm, 1.5 mm and 2 mm of various diameters, as well as by a through-cut with a scalpel.

All samples of the testing layered self-healing composite with an internal borosiloxane matrix showed an effect of self-healing at the end-to-end breakdown: the holes healed almost instantly, the pressure in the chamber after the breakdown stabilized less than 1 second. Figure 3 shows the characteristic damage places on the upper layer of the composite left in the composite. A cut of about 6 mm long was formed with a through-cut of the self-healing composite by a scalpel with a blade dipping to its full length. A pressure drop of 0.03 atm was observed from the original 0.25 atm after removing the scalpel blade from the composite in the chamber. The self-healing time of the testing laminate composite was 2 seconds, after that the pressure in the chamber has stabilized.

5. Conclusion
The paper considers and analyzes the effects of self-healing in materials of various chemical nature (polymers, cements, ceramics, metals and composite materials) from the point of view of their practical application and the creation on their basis of layered self-healing composites. The properties and characteristics of BS compounds are described and the prospect of their using as an internal self-healing matrix of layered or reinforced composites is shown. An approach to the creation of a new layered composite using BS as a self-healing layer was developed. The effect of self-healing of the developed laminate composite with its through damage by breakdown and cut is demonstrated using the original laboratory setup. Damage formed from piercers with a diameter of 0.8 mm, 1 mm, 1.5 mm and 2 mm healed almost instantly, and the cut of about 6 mm long healed in 2 seconds.

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