Structure and properties of self-healing materials based on hydroxyl terminated polydimethylsiloxane and boric acid

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Abstract. Borosiloxane materials (BS) with self-healing properties based on polydimethylsiloxane with terminal hydroxyl groups and boric acid were obtained. BS was obtained with different viscoelastic characteristics by varying the synthesis conditions and composition. The properties of the obtained BS are characterized by the methods of synchronous thermal analysis and mass spectrometry. Self-healing and elastic properties were characterized by methods of spreading and rebound of ball from BS. The molecular and supramolecular structures of borosiloxanes obtained under various conditions explaining the difference in their viscoelastic properties are presented. It is shown that by changing the conditions of synthesis and the introduction of a plasticizer, it is possible to vary the parameters of self-healing and elastic properties of materials based on BS. The resulting materials may be interesting for various fields where the restoration of material characteristics by self-healing is required, from medical biocompatible materials to nano- and microelectronics and space technology.

1. Introduction

Materials based on borosiloxane (BS) since the first synthesis in 1943 have been attracting the close attention of developers and researchers. From the point of view of the molecular structure of BS, this is the general name for organosilicon compounds containing the R-Si-O-B group, where R is a hydrocarbon radical [1,2]. They are the reaction products between organosiloxanes and boron-oxygen compounds, most often boric acid (BA). BS-materials can have various mechanical properties depending on the structure of the molecule and the molecular weight of the initial organosiloxane, the synthesis conditions of the BS, as well as on the amount and properties of the introduced functional additives (fillers, plasticizers, thickeners, etc.). They can be both in solid and in liquid state, and also can have a viscous, rubber-like or glassy consistency [3].

BS-based materials are used in various fields. For example, the effective absorption of mechanical energy upon impact allows them to be used in sports equipment [4]. The ability of BS to self-adhesion made it a promising material for various systems with self-healing properties. Flexible conductive nanocomposites based on BS and carbon nanotubes [5,10] with self-healing
properties were obtained in [11]. BS self-healing coatings were used to protect metal from corrosion [12]. BS was used as a self-healing layer in sandwich composites in our previous works [13, 14]. Despite the fact that the unique properties of BS are well known and described in detail in the scientific and technical literature, causal relationships between the structure of BS at various scale levels and the unique viscoelastic characteristics of materials based on it are not fully disclosed [15–20].

Therefore, the aim of this work is obtaining composite materials with various viscoelastic properties, by varying the conditions of preparation with comparing the characteristics of the obtained materials and analyzing their viscoelastic and self-healing properties.

2. Experimental part

Samples of low-temperature BS (BS-LT) were obtained by mixing polydimethylsiloxane (PDMS) with terminal hydroxyl groups (molecular weight $\sim 20,000$ g/mol) with fine-grained BA (average particle size of BA was 0.075 mm) and keeping in for 24 hours at room temperature. Samples of high-temperature BS (BS-HT) were obtained by heating of PDMS with BA during 24 hours at temperatures above 210 $^\circ$C. The mass ratio of PDMS and BA upon receipt of BS-NT and BS-VT was 10:1. After synthesis, BS-HT was sequentially mixed with 1.5 wt. % of water and 1 wt. % of oleic acid (plasticizer). The amounts of water and oleic acid were selected experimentally. A scheme of obtaining of samples of BS is shown in fig. 1.

$$a = \frac{h}{H} \cdot 100\%.$$ (1)

Self-healing properties were characterized by measuring of spreading time of a ball weighing 2 grams on the surface of a glass substrate. The relative increase in diameter $b$ was determined.
by an equation (2):

\[ b = \left( \frac{D_i}{D_0} - 1 \right) \cdot 100\%. \]  

(2)

\( D_i \) is the diameter at time \( t \), \( D_0 \) is the diameter at time \( t = 0 \).

3. Results and discussion
The obtained samples BS-LT and BS-HT, in contrast to the initial PDMS, have a sufficiently high viscosity and exhibit a complex of visco-elastic properties. The character of the mechanical behavior of the samples changes with an increase of a rate of occurrence of mechanical stress in BS samples (Figure [1]). BS-LT and BS-HT are very similar to chewing gum. It is easy to do a ball from them or give any other shape to them. The samples spread over the surface. BS-HT has a full range of properties of well-known toy Silly Putty, BS-LT exhibits similar viscoelastic properties, but does not have the property of rebound. Figures 2a and 2b show DSC and TG curves of the initial compounds (PDMS and BA), and samples of BS-LT and BS-HT.

![Figure 2. a) Synchronous thermal analysis of PDMS (I), BA (II), BS-LT (III) samples, b) Synchronous thermal analysis of the BS-HT sample: after storage in air (I) and reheating of the sample without contact with air (II)](image)

The study of the initial compounds shows that PDMS is thermostable to temperatures above 400 °C, then the mass of the sample begins to decrease, which is apparently due to thermal decomposition (fig. 2a, curve I). BA shows several peaks on DSC (fig. 2a, curve II) in the region of 100-190 °C, which, apparently, is associated with the processes of evaporation of bound water, melting and sublimation of boric acid, as well as sequential decomposition of orthoboric acid to metaborate, tetraborane and boric anhydride. In the temperature range from 160 °C to 180 °C, the mass loss in the TG curve is not as large as in the initial process. Moreover, this is accompanied by a pronounced peak of heat absorption on the DSC. These facts indicate the occurrence at temperatures from 160 to 180 °C of the process of melting of the components of the resulting mixture, which corresponds to the literature data [22]. Above 180 °C, the mass loss is apparently associated with the release of residual water released during melting of BA. In fact, upon heating the BA, its sublimation is observed, with the formation of a white vapor which, apparently, accompanies the processes of dehydration of the BA. The joint occurrence of the processes of melting, decomposition, and sublimation upon heating of boric acid is confirmed by literature data [23].

The thermal stability of BS-LT samples is lower than that of the initial PDMS. The peak of decomposition occurs at \( \sim 370^\circ\text{C} \), which is accompanied by intense weight loss (fig. 2a, curve III). The decrease in thermal stability is obviously associated with the presence of boron in the
compounds. The peak on the DSC BS-LT curve at a temperature of about 150 °C, apparently, corresponds to the processes of water loss of BA, as well as the reaction between PDMS and BA with the formation of BS-HT. On the BS-HT DSC curve (fig. 2b, curves I) there is a peak, apparently related to the dehydration of the sample. This process is absent upon repeated heating (fig. 2b, curves II). It is assumed that the tendency to partial hydrolysis of BS-HT with air moisture with a characteristic turbidity of the samples is due to the hydrolysis of non-cyclic borosiloxane groups with the formation of free boric acid and OH-groups in the main chain of BS-HT. This process is reversible. When the hydrated sample is heated above 160 °C, the turbidity of the sample disappears, water is removed from the BS-HT. However, when stored in air, the sample becomes cloudy again, adsorbing moisture from the atmosphere.

Mass spectrometric analysis of the evolved gases during synchronous thermal analysis showed that when BS-HT is heated, methane is released, among other gaseous substances, even at temperatures of about 160 °C, which may indicate the addition of BA to the main PDMS circuit with the formation of lateral Si-O-B groups of a linear or cyclic structure.

It should be noted that the deformation of rubber-like materials usually consists of 3 types of deformation: elastic, plastic and highly elastic. In accordance with the principle of temperature-time superposition, the predominance of one or another type of deformation depends on the applied load and the speed of its application. An analysis of the properties of the obtained BS shows that BS-LT and BS-HT are characterized by plastic deformations, which occur, for example, during spontaneous flow under the influence of gravity. With an increase in the rate of application of stress, BS-HT is more characteristic of highly elastic deformations, which manifest themselves in rubber-like properties under tension. BS-HT is also characterized by elastic deformations, which is manifested, for example, in a good rebound of a ball rolled from a BS-HT.

Based on the presented differences in the properties of BS-LT and BS-HT, we can assume that their molecular structures are different. In fig. 3 and 4 show the proposed variants of the molecular and supramolecular structure of BS-LT and BS-HT.

It is assumed that the nature of the viscoelastic properties of BS-LT and BS-HT are based on hydrogen bonds between siloxane and BA molecules. Hydrogen bonds are responsible for a sharp increase in the viscosity of siloxanes during interaction with BA. Non-Newtonian (including self-healing) properties are due to the reversibility of hydrogen bonds. BS-LT form spontaneously at room temperature, by polycondensation of PDMS and BA molecules with the formation of three-dimensional branched products (fig. 4). BS-HT are siloxane molecules with hydroxyl groups in the side chain of the molecules. It is assumed that these hydroxyl groups can be either directly attached to the main chain of the BS-HT and be formed by six-membered cycloborosiloxane groups (fig. 4). The difference in properties between BS-LT and BS-HT is apparently due to an increase in the number of hydroxyl groups per one BS molecule. Due to this, BS-HT exhibits more pronounced elastic properties with an increase in the rate of application of an external load.

Self-healing and elastic properties of BS samples are characterized by spreading and rebound methods (fig. 5). Both types of BS have the ability to self-heal due to plastic deformations and reversibility of hydrogen bonds. Unplasticized BS-HT is fragile and has a lower rate of self-healing. Close self-healing rates with BS-LT samples were achieved by plasticizing BS-HT with oleic acid.

It should be noted that the elastic properties of BS-HT after plasticization practically did not change, as demonstrated by the rebound method (fig. 5). Thus, BS-LT and BS-HT can be used as self-healing components in composite materials or multilayer composites, and the presence of elastic properties in BS-HT can give such composites additional protective properties against damage due to dissipation of the damage energy.
Figure 3. Suggested molecular and supramolecular structures of BS-LT

Figure 4. Suggested molecular and supramolecular structures of BS-HT

R = -OH, -OCH₃, -CH₂-O-[Si(CH₃)₂-O]ₓH
Figure 5. Dependences of relative spreading from time. I - BS-HT, II - BS-LT, III - BS-HT with 1 wt. % oleic acid. A demonstration of the principle of the used spreading measurement technique is in the photographs

4. Conclusion

Materials based on BS with different visco-elastic characteristics are obtained by varying of the synthesis conditions. It was shown by synchronous thermal analysis, that the thermal stability of BS samples is lower than that of the initial PDMS, the decomposition peak falls at $\sim 370^\circ$C, which is accompanied by intense mass loss. The self-healing and elastic properties of BS samples are characterized by spreading and rebound methods. It was shown that the relative rebound of plasticized and unplasticized BS-HT is significantly higher ($> 70\%$) than that for BS-LT ($< 10\%$). The addition of only one percent of oleic acid into BS-HT allows one to achieve close self-healing characteristics in BS-LT and BS-HT. It is shown that by changing the conditions of synthesis and the addition of a plasticizer, it is possible to vary the parameters of self-healing and elastic properties of materials based on BS. The resulting materials may be interesting for various fields where the restoration of material characteristics by self-healing is required, from medical biocompatible materials to nano- and microelectronics and space technology.

Superstructures of nano- and micro-filaments formed during solidification of fibers from solutions of compositions of polystyrene with inorganic fillers can be modified essentially by regulation of combinations of tensile and compressive stresses, Dynamical flows of the polystyrene gel during solidification induces transformations of the atactic molecules and syndiotactic forms with subsequent crystallization revealed by optical anisotropy.

Qualitatively new kinds of organic-inorganic compositions have been prepared by the deformation-chemical procedures of the ball rolling: organic polymers of polystyrene introduced in the form of nano – and micro – needles into inorganic matrices of cesium iodide and potassium chloride single crystals.

Acknowledgements

The work of V.I. Mashchenko was supported by the RFBR grant No 19-07-01005 A, the work of N.N. Sitnikov and I.A. Khabibullina supported by the RFBR grant No 18-29-18095 mk.
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