Reinforcing effects in elastomeric composites, filled with particles of mineral fillers, based on silicon dioxide and carbon

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Abstract. When creating elastomeric composites, structures and products made from such materials, considerable attention is paid to environmental issues, as well as to improving economic efficiency and energy efficiency in its production. In this regard, the development of new types of strengthening highly dispersed fillers for elastomeric and polymer composite materials, including those of natural origin, providing an optimal balance of mechanical properties of composites and having advantages over existing solutions, is an actual task. In the course of the work, a technology was developed for producing highly dispersed fillers by ultrafine grinding of raw materials. The obtained experimental data shows a significant reinforcement effect (up to five times) with a decrease in the average particle size of the filler. It is established, that the most effective filler, in terms of reinforcement, are particles based on amorphous silicon dioxide, obtained from rice husk processing products and shungite rock. The significant influence of the surface functionality and the carbon/silicon dioxide ratio of submicron filler particles on the mechanical properties of elastomeric composites is shown. It is established that new classes of reinforcing fillers can be recommended for practical use in the future.

1. Introduction
Elastomeric composites are one of the promising structural materials, products made of them are widely in demand and used in the automotive, aviation, space, oil refining, etc. industry. When creating elastomeric composites, structures and products made from such materials, a significant attention is paid to environmental issues, as well as to improving economic efficiency and energy efficiency in their production. In this regard, the development of new types of strengthening highly dispersed fillers for polymer composite materials, including those of natural origin, providing an optimal balance of mechanical properties of composites and having advantages over existing solutions, is an actual task.

Presented research includes the development of principles for creating composite materials based on polymer and elastomeric matrices and a new class of nanostructured mineral fillers of natural origin of various structures (for example, shungite [1], diatomite, halloysite [2], rice husk processing products, etc.), as well as the study of mechanical behaviour features and reinforcement effects in such composites in order to directly regulate their properties. New raw materials to produce reinforcing fillers for elastomeric composites differ from the existing reinforcing fillers (for example, carbon black and silica [3]) were proposed. It provides lower production costs, environmental safety and, depending on the parameters of their structure, allow to produce polymer and elastomer composites with a few unique
properties [4]. The technology to produce highly dispersed fillers by ultrafine grinding of raw materials was developed at IAM RAS [1] and applied in the given work for elastomeric composite materials. In the given study the experimental results with shungite rock and rice husk processing products as raw materials for reinforcement fillers of elastomer materials are presented.

2. Materials and methods

2.1. Physical, structural and microstructural characterization

Control of the particle size and morphology before and after grinding was performed using electron and AFM microscopy (Nanosurf EasyScan), figure 1. The structure of the particles obtained from rice husk processing products by grinding, was investigated by scanning electron microscopy (SEM) (Jeol JSM-6700F) and transmission electron microscopy (TEM) (FEI Tecnai G2 20 FEG). It includes an amorphous structure of silicon dioxide (up to 97%) and carbon impurities (3 – 5%). It is also noted that the initial particle size of rice husk processing products is about 300 microns. The initial particles have a porous layered structure. Along with the large particles on the images of figure 1, one can also see smaller particles of rice husk processing products, which indicates a wide distribution of particles by size.

2.2. Fabrication of elastomeric composites

The obtained highly dispersed fillers were introduced into elastomeric composites based on a copolymer of butadiene and styrene (SBR - 1500). Microdispersed and submicron particles obtained from rice husk processing products were used as the filler. Submicron particles were also used after surface treatment by a hydrogen peroxide. For better dispersion of filler particles in the volume of the elastomeric matrix, a coupling agent (surface modifier) organosilane TESPT (bis (3-triethoxysilylpropyl) tetrasulfide) [3] was used. Thus, the paper considers the hydrogen peroxide treatment of the surface of rice husk processing products with submicron-sized particles, the introduction of the organosilane coupling agent TESPT into the composition of the elastomeric materials. And also, the effect of double modification – combination with oxidized submicron particles of organosilane TESPT in order to increase the efficiency of the interaction of the filler with the elastomeric matrix.

The compositions of the prepared and studied samples of elastomeric composites are shown in table 1. The samples were mixed in a Haake PolyLab 300 QC mixer. The mixtures were made on the basis of butadiene and styrene copolymer (30% styrene). The mixing took two stages. The mixing temperature did not exceed 150°C.

2.3. Mechanical characterization of elastomeric composites

Elastic and strength properties of the elastomeric composites were determined in accordance with GOST 252-75 on the UTS-10 universal testing machine. The tests were carried out at ambient temperature with a constant tension rate of (500±25) mm/min. During the experiment, the stress – strain curves were determined. The obtained experimental data are presented in Figure 2 and Table 2.
3. Results and discussion

3.1 Microstructural characterization of fillers

After grinding the rice husk processing products, there is a significant decrease in the particle size (figure 1 a, b compared to figure 1 c, d), it is established that the particles are capable for strong agglomeration. The size of individual particles is several tens of nanometers (figure 1, e). The initial fraction of shungite is microdispersed particles with an average size of about 5 microns, figure 1, d. After grinding the shungite rock, there is a significant decrease in the particle size (figure 1, d compared to figure 1, e), it is established that the particles are capable of strong agglomeration. The size of individual particles is several tens of nanometers (figure 1, e). Also, using the CPS 2000 disk centrifuge, it was found that the average particle size of the obtained highly dispersed fillers is up to 700 nm.

Table 1. Compositions of elastomeric samples

| Ingredients | Sample No. / phr |
|-------------|------------------|
|             | 1 2 3 4 5 6 7    |
| 1 SBR-1500  | 100 100 100 100 100 100 100 |
| 2 Vulcanizing group | 4,7 4,7 4,7 4,7 4,7 4,7 4,7 |
| 5 Norman 346 | 3 3 3 3 3 3 3 |
| 6 Zinc Oxide  | 7 7 7 7 7 7 7 |
| 7 Technical stearin | 2 2 2 2 2 2 2 |
| 8 TESPT     | - - - - 3,9 3,9 - |
| 9 RSPP US   | - 65 - - - - - |
| 10 RSPP SUBMICRO | - - 65 - - - - |
| 11 RSPP SUBMICRO + H2O2 | - - - 65 - - - |
| 12 RSPP SUBMICRO TESPT | - - - - 65 - - |
| 13 RSPP SUBMICRO + H2O2/TESPT | - - - - - 65 - |
| 14 RSPP BLACK US | - - - - - - 65 |

In table 1:
- RSPP US – Amorphous silicon dioxide from rice husk, ultrasound treatment (microparticles)
- RSPP SUBMICRO – Amorphous silicon dioxide from rice husk, ultrafine grinding (submicroparticles)
- RSPP SUBMICRO + H2O2 – Amorphous silicon dioxide from rice husk, ultrafine grinding (submicroparticles), processed by H2O2
- RSPP BLACK US – Amorphous silicon dioxide from rice husks, ultrasound treatment (microparticles) with a carbon content of about 60%
Figure 1. Images of particles of rice husk processing products (RSPP), and shungite before and after ultrafine grinding. a, b – RSPP initial particles (SEM), c – RSPP milled, agglomerates of particles (SEM), d – Shungite initial particles (SEM), e – RSPP milled, individual particles (TEM), f – Shungite after grinding, the individual particles (AFM).

3.2. Elastic and strength properties of the elastomeric composites
The obtained experimental data (figure 2, table 2) shows first, a significant reinforcement effect with a decrease in the average particle size of rice husk processing products.
Figure 2. Stress – strain curves for samples of elastomeric composites No. 1 - 7.

Table 2. Elastic and strength properties of elastomeric composites

| Properties                  | Sample No | 1  | 2  | 3  | 4  | 5  | 6  | 7  |
|-----------------------------|-----------|----|----|----|----|----|----|----|
| Stress at 100%, MPa         |           | 0.8| 1.9| 1.9| 1.9| 3.1| 3.1| 1.9|
| Stress at 200%, MPa         |           | 1.25| 2.5| 3.8| 3.9| 11.7| 9.4| 2.5|
| Stress at 300%, MPa         |           | -  | 3.1| 5.0| 5.7| -  | 18.6| 3.1|
| Strength at break, MPa      |           | 1.5| 3.7| 21 | 17.3| 18.5| 19.5| 3.6|
| Strain, %                   |           | 243| 369| 718| 509| 265| 307| 440|

Thus, for microparticles, average strength values were obtained at the level of 3.7 MPa (samples 2, 7), while for submicron particles, other things being equal, the average strength reaches about 21 MPa (sample 3). Nevertheless, for submicron particles, there is a significant increase in elongation up to 718%. Oxidation of the particle surface leads to a slight decrease in strength and elongation (sample 4), however, the strength remains at a fairly high level for this class of fillers and is about 17 MPa. The addition of a TESPT combination agent to compositions with submicron particles (samples 5 and 6) of rice husk processing products containing amorphous silicon dioxide, mainly leads to a decrease in elongation at break and a significant increase in elongation stresses. The strength of these composites does not increase significantly, up to 19.5 MPa. A sample with an oxidized particle surface (sample 6) is distinguished by a slightly higher relative elongation and somewhat higher strength. In the case of the use of the TESPT coupling agent, oxidation of the surface of submicron particles of rice husk processing products is justified and increases the efficiency of this coupling agent in terms of the reinforcement
effect (comparison of samples 4 and 6). The use of a coupling agent in the case of non-oxidized submicron particles of rice husk processing products, on the contrary, leads to a slight decrease in strength (comparison of samples 3 and 5). These effects show a significant effect of the surface functionality of submicron filler particles on the mechanical properties of elastomeric composites with rice husk processing products. The minimum values of the strength of the composites in this experiment were obtained for filler with microparticles regardless of the composition of these particles (comparison of samples 2 and 7). Thus, in sample 2, the filler consists of 97% of amorphous silicon dioxide, and in sample 7, 60% of graphite-like carbon and 35% of amorphous silicon dioxide.

4. Conclusions
The experimental data obtained show a significant strengthening effect (up to five times) with a decrease in the average particle size. It has been established that the most effective filler in terms of reinforcement effect is a filler based on amorphous silicon dioxide obtained from rice husk processing products and shungite rock. A significant effect of the surface functionality and the carbon / silicon dioxide ratio of submicron filler particles on the mechanical properties of elastomeric composites is shown. It has been established that new classes of reinforcing fillers in the future can be recommended for practical use.

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