

Improving the reliability of road materials based on micronized sulfur composites

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Abstract. The work contains the results of a nano-structural modification of sulfur that prevents polymorphic transformations from influencing the properties of sulfur composites where sulfur is present in a thermodynamic stable condition that precludes destruction when operated. It has been established that the properties of sulfur-based composite materials can be significantly improved by modifying sulfur and structuring sulfur binder by nano-dispersed fiber particles and ultra-dispersed state filler. The paper shows the possibility of modifying Tengiz sulfur by its' fragmenting which ensures that the structured sulfur is structurally changed and stabilized through reinforcement by ultra-dispersed fiber particles allowing the phase contact area to be multiplied. Interaction between nano-dispersed fibers of chrysotile asbestos and sulfur ensures the implementation of the mechanical properties of chrysotile asbestos tubes in reinforced composite and its integrity provided that the surface of chrysotile asbestos tubes are highly moistened with molten sulfur and there is high adhesion between the tubes and the matrix that, in addition to sulfur, contains limestone microparticles. Ability to apply materials in severe operation conditions and possibility of exposure in both aggressive medium and mechanical loads makes produced sulfur composites required by the road construction industry.

1. Introduction

The potential approach to the improvement of sulfur composites is based on synergetic interaction effects at the phase boundary. In reinforced, frame and matrix composites and materials of interpenetrating structure types the greatest potential for positive change in their properties is based on the modification of binding agents themselves [1].

Negative properties of sulfur such as fragility and low hardness are revealed as a result of polymorphic transformation as it is cooled down from melting. As polymorphic transformation takes place - structural changes at which sulfur abruptly changes its properties happen. The strength of sulfur-containing materials is determined by the allotropic form of the sulfur modification, the structure's variety - evidently or latently - crystal, sizes of sulfur particles. It is known that at - temperature lower than 95,5 °C - monoclinic sulfur is transformed into a rhombic shape thus it is re-crystallized resulting in integrity damage. That is the major obstacle to wide application of sulfur as binding element.

Necessary condition allowing the expenditure of the field of application of sulfur-based materials is the decrease of the scale level of sulfur heterogeneity down to nano-level where the concept of allotropic sulfur modifications loses its significance.



Taking it into consideration, study of the possibility of production of nano-composites through modifying the sulfur by nano-dispersed fiber-type particles in order to eliminate any internal stresses and embrittlement of sulfur seems promising. The solution is focused not only on reduction of size of the particle, but also on the special properties that are inherent to nano-layers, nano-crystals and nano-particles and related to so-called size effects [2,3]

2. Sulfur composites

2.1. Materials

Sulfur is a by-product of the refining of the Tengiz field's associated oil gas. Sulfur density: 1.92-2.07, g/cm³; melting temperature: 103-119°C; specific surface: 1.04-2.61m²/g; hydrogen sulfide content: 8.2-45.6 mg/kg; sulfur dioxide content: 4.5-5.2 g/kg.

Chrysotile asbestos has been applied as a reinforcing agent. The developed technology uses chrysotile asbestos's unique property of splitting into very thin elastic, durable tubular fibers with cross dimensions of less than one micrometer. Asbestos density: 2.4-2.6 g/cm³; porosity: 5-6 %; water absorption: 3-4%; hygroscopic moisture removal temperature: 100-120°C; tensile strength: 800 MPa; specific surface: 20m²/g; module of elasticity: 80-100 GPa.

Limestone has been applied as mineral filler. Limestone density: 1.4 -1.8 g/cm³; density: 2.41-2.61g/cm³; porosity: 11.5-40%; water absorption: 8-20%; compressive strength in dry state: 54-98.3 kg/cm²; compressive strength in water-saturated state: 40.5-78.5 kg/cm²; strength loss after freezing tests: 10.8-46.9%.

2.2. Optimization of sulfur composites

In order to develop sulfur micronization methods composites with the sulfur/limestone ratio varied in Range 2 : 3, asbestos content: from 3-9% were studied. Properties of reinforced composites significantly depend on the properties of the components' composition and relative positions, peculiarities of their interaction at interphase boundary, diffusion of the matrix and fibers' components, which means that a certain ratio shall be kept between fibers and matrix and their selection shall be well-reasoned. When developing the methods of reinforcing the micronized sulfur with fiber materials there has been studied the influence of the extent to which the composite is filled with the reinforcing component to form a microstructure in which each asbestos tube is surrounded with the binder matrix layer to ensure the highest adhesion. The results of the study of quantity of the binding component in sulfur composite showed the optimum content of asbestos to be 7% (Figure 1).

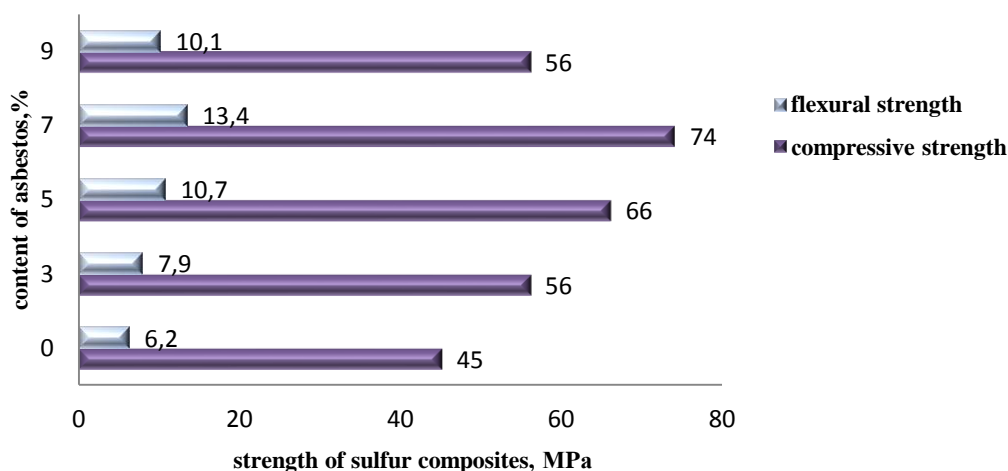


Figure 1. Dependence of the strength of sulfur composites from asbestos content.

3. Optimization of technology of sulfur composites processing

Sulfur micronization implies breaking down the particles into nano-size ones, involving high power consumption to increase the boundary surface. The micronization can be carried out by: restoring the sulfur from polysulfide solutions; ultrasound dispergation; mechanical dispergation. When sulfur is restored from polysulfide solutions it is difficult to produce dimensional samples due to very thin sulfur layers on the surfaces. Sulfur in ultrasound dispergator shall be dispergated in water medium and then dried, which significantly complicates the process. Mechanical dispergation of pure sulfur: it cannot be ground in any breaker due to high electrostatic charging and its aggregation.

Sulfur was grounded in vibrating mill in two ways - together with filler and binding component and separately. When grounded separately sulfur was found to be sticking to the mill walls and the grinding balls. It has been established that sulfur dispergation requires application of desintegrators or planetary mills as well as modern ultra-fine grinding equipment with mechanic-chemical activation and deagglomeration effects. Solution is in development of the method of sulfur micronization through grinding it in dry state together with the composite components being limestone and asbestos.

The optimum sulfur composite heat processing parameters have been determined based on changes in their strength characteristics. Molten sulfur was produced at 130-140°C, but attempts to introduce reinforcing fibers into the molten sulfur were unsuccessful as significant viscosity of the molten sulfur does not allow distributing fibers even with nano-dimensions. As the result, components were ground together, which allowed them to be distributed evenly. The sulfur composite properties investigation results are shown in Figure 2.

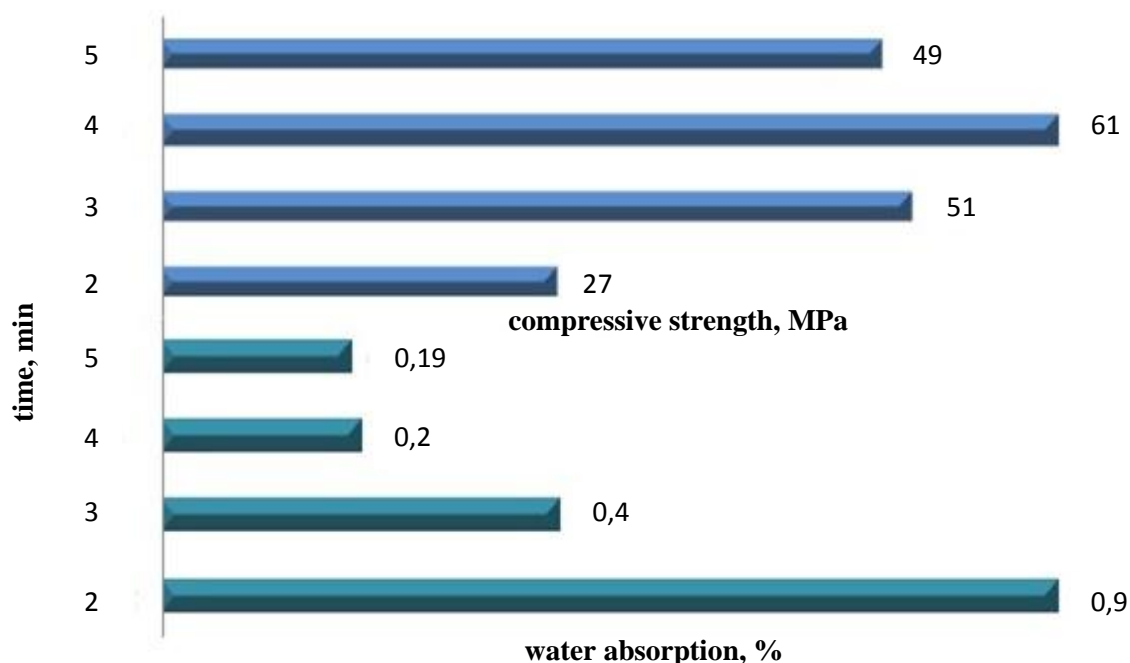


Figure 2. Dependence of the sulfur composites properties from heat-treatment duration.

The results of comparative tests of sulfur composites and cement concretes have shown that by physical and mechanical properties the sulfur composite is not inferior to the traditional concrete and by some indexes it is superior. For instance, sulfur composites' strength characteristics are 20-30% higher, water absorption is 3 times lower, frost resistance is twice as high and wearability is 30% lower.

Stable structure of sulfur composites with binary micro-fillers (mineral and fiber) is characterized by improved operational strength and deformation parameters. Durability of nanostructured sulfur

composites is determined by the character and value of forces of interactions of relations occurring on the modified binding filler boundary surface.

4. Discussion of results

Elimination of electronic insufficiency through introducing stabilizers is required in order to stabilize polymer sulfur molecules that have unsaturated electronic structure resulting in instability. Regulation of their quantity and melting temperature mode allows production of sulfur binding agent with stable physical-and-mechanical properties [4].

Applying filler for the sulfur composite in quantities comparable to the sulfur content creates prerequisites for heterogeneous primary nucleation when crystallized on hard particles [5]. As the result, filler has structure-forming effect on the sulfur matrix. When applying limestone as filler in the sulfur composite matrix calcite microcrystals are found. They have perfect cleavage extracted from limestone when ground and make the sulfur composite matrix highly durable (Figure 3a). Filling the molten substance with the fiber filler results in forming of foliated-and-flaky sulfur composite structure and the tubular structure of chrysotile asbestos, when using a capillary suction method, retains the molten sulfur in a form of ultra-thin particles. Joint grinding sulfur with fillers allows to form an optimal fine-grained homogeneous dense structure that ensures high properties of sulfur composites. Microstructure of sulfur composite represented by tightly bound particles fillers and filling the pore space of plasticized sulfur, which is a single matrix with numerous jumpers (Figure 3 b).

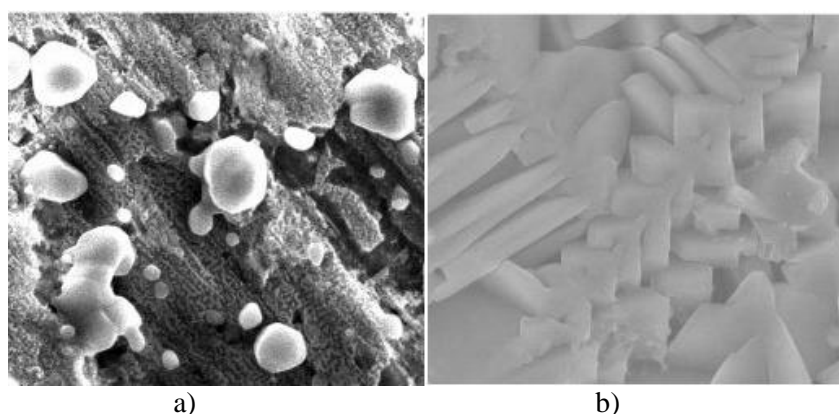


Figure 3. Microstructure of sulfur composites: a) sulfur composites filled with milled limestone; b) sulfur composites filled with milled limestone and chrysotile asbestos.

During process of create of sulfur composites formed the homogeneous nanostructure of limestone and nano-tubular structure of chrysotile asbestos. In the result occur fragmentation of melt sulfur in the form of drip inhomogeneous nano-particles of possible amorphous structure from which then be forming ultrafine sulfur crystals. Distributed within a carbonate-chrysotile matrix sulfur crystals pass and the matrix in turn takes on deformation of the crystal lattice at polymorphic restructuring of the metastable monoclinic sulfur in a stable orthorhombic modification.

Theoretically dense packing is not possible as each fiber has to be surrounded by a layer of the matrix to ensure the highest adhesion of fibers to transmit mechanical forces between the reinforcing fibers and the matrix and for the achievement maximum monolithic composite. In addition, the high adhesion of the composite components shall be maintained in operational conditions under active external influences on sulfur composites including moisture, corrosive fluids, high mechanical loads, thermal processes [6, 7]. Minimum change in the properties of the reinforcing fibers under the influence of matrix components or operating conditions, which is typical for asbestos in the studied parameters of operation, is of fundamental importance.

The size of the microparticles of the original components affect the strength and elasticity of sulfur composites as the seal the composite occur in the initial stage as the result of rapprochement of sulfur particles and fillers, and then creation of a monolithic structure as the result of the penetration of particulate sulfur in the micropores of porous natural-fibrous fillers. The sulfur is stabilized and immobilized in the microporous cavities carbonate-asbestos matrix, providing permanence of properties.

Creation of fragmented structure of the sulfur composite allows explaining the improvement of his properties in relation to the characteristics of the original components. Such method of micronization original particles sulfur composites refers to the so-called matrix isolation nano-particles of sulfur in the massive body of the nanocomposite [8]. Feature of the synthesized matrix is its porous-fibrous microstructure. A uniform distribution of sulfur in the space of the matrix occurs in during co-grinding components, at the heat treatment the sulfur does not form massive layers and sulfur particles fragmented in the chrysotile-carbonate matrix.

The sulfur in the molten state has a very low surface tension. The maximum reduction in viscosity of sulfur allows to perform capillary effect and the walls of filled tubes in turn will prevent crystallization of sulfur in the form of large crystals that reduces the brittleness of the composites and allows plasticity which is not peculiar to traditional sulfur-containing materials. Manifestation of this effect in the sulfur composites promotes synergy of its physical and mechanical properties.

The improved properties are obtained not by chemical interaction of the components of sulfur composites, but by creation of three-dimensional nanostructured systems. Superdispersed mineral fibers form the bulk structure with enormous internal surface area. High adhesion properties of the fibers to nanostructured sulfur makes the framework almost inseparable from the sulfur binder, which excludes destructurization even in the case of sufficiently strong and corrosive effects on the surface of composites

At the transition on nanotechnology with decreasing grain size crystalline sulfur increasing the volume fraction of intergranular material and the surface of grain boundaries prevent to the dislocation motion. For small nanoscale grains the increase of strength occurs due to the low density of existing dislocations and the difficulty of formation of new dislocation, i.e. the formation of nanosized structures based on sulfur allows obtaining materials with high properties

Thus, the nanostructuring of the sulfur particles provides uniform microstructure with insulation particles of sulfur by the nanofibres chrysotile asbestos and ultrafine particles of carbonate. Uniform distribution of the components in the spatial structure during the heat treatment prevents the formation of massive layers of sulfur, which is fragmented in carbonate-chrysotile matrix, compensating the internal stresses, and provides the high properties of sulfur composites.

5. Conclusions

Modification of properties sulfur compositions is caused not by the chemical interaction of the composite components, but by creation of three-dimensional nano-structured system where synergistic effect is manifested. Special role in the formation of the microstructure sulfur compositions belongs to the fillers and reinforcing components, triggering the phenomenon of capillary suction, which has stabilizing effect on the physical and mechanical properties sulfur compositions.

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