Structure and physical properties of sulfur with nanoscale carbon modifiers

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Abstract. It is known that sulfur-extended asphalt is of improved operational properties. Binders with higher content of polymeric sulfur are characterized by higher operational properties. Unfortunately, many sulfur modifiers are volatile and toxic. The objective of article is to investigate the structure of sulfur with admixtures of saturated aliphatic hydrocarbon and two types of nanoscale carbon modifiers. It was shown that such admixtures lead to formation of the fine-crystalline structure of high uniformity; average size of crystals decreases in order of magnitude. Structural changes are accompanied by notable improvement of compressive strength (the values of compressive strength increases in about 3 times). The practical value of the conducted studies is due to possible application of nanomodified sulfur in road construction.

1 Introduction

As indicated by domestic and international experience, there are numerous advantages arising from modification of asphalt by sulfur [1-4]. Sulfur-extended asphalt is of improved physical, mechanical and operational properties. In particular, such asphalt is characterized by improved fatigue life under cyclic loads and increased resistance to rutting [5-9]. It is also resistant to the effects that are caused by various aqueous solutions and petrochemicals – gasoline and motor oils [10-15]. Both technical sulfur and modified sulfur, often referred to as “polymeric sulfur”, can be used for the modification of asphalt concretes. Binders with modified sulfur are characterized by high adhesion to mineral components. Pavement materials that are based on modified sulfur are characterized by improved strength and low shrinking deformation. The admixture of modified sulfur into the composition of asphalt concrete leads to a decrease in internal stresses arising during the process of cooling of a laid pavement.

Various admixtures can be used to obtain stable modified sulfur that exists under normal conditions [16]. In particular, as stated in RU patents 2196787, 2076843 and 1483836, admixtures of several organic compounds (stabilizers) with multiple chemical bonds in molecular structure (dicyclopentadiene, hexachloroparaxylene, p-alkylphenol, 2, 6-di-tert-butyl-4-methylphenol, trioxybenzene, m-dihydroxybenzene, etc.) are efficient. In case of such admixtures, the mechanism of modification is the binding of stable structural elements containing 6; 7; 8; 10; 12; 18; 20 and 30 sulfur atoms. Binding occurs due to the

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opening of double bonds in the molecules of the organic stabilizers. Moreover, such stabilizers also lead to changes in crystalline structure of sulfur. Namely, there is a formation of new types of crystalline structures: fine-crystalline structure; fine-crystalline structure with inclusions of large crystals; structure with inclusions of products of polymerization of organic modifiers. The latter structure is typical when high molecular compounds with multiple bonds are admixed to sulfur [17-20]. The disadvantage of most organic stabilizers is that such substances are usually toxic and, often, volatile. This feature of organic stabilizers can significantly affect safety requirements during production and further processing of polymeric sulfur. Thus, it is necessary to search for alternative ways to improve the properties of crystalline sulfur.

Methods of control of structure formation starting from atomic and molecular levels are subjects of design in nanotechnology. Such methods are currently in active development; they can be implemented in various ways. Common technique of implementation of nanotechnology is the admixture of nanoscale modifiers, frequently referred to as “primary nanomaterials”. Carbon nanoscale admixtures are most common. It is known that application of nanotechnology can be quite efficient in materials science. An obvious advantage of carbon nanomaterials is that it is often enough only a small amount of nanomaterials to achieve significant improvement in quality of asphalt concrete [21].

Primary objective of the current research is to investigate the structure and structure formation of sulfur with admixtures of saturated aliphatic hydrocarbons (which are both non-toxic and can be found in bitumen) and two types of nanoscale carbon-based modifiers.

2 Materials and methods

The studies were performed for technical sulfur (RU GOST 127.1), P2 paraffin (RU GOST 23683) and two types of nanoscale carbon-based modifiers – carbon black (hereafter referred to as “CB”, RU GOST 7885) and “Taunit” carbon-based nanomaterial (hereafter referred to as “CNT”). The content of nanoscale modifiers varied in range 0...0.03%, content of paraffin varied in range 0...0.5% (by weight of sulfur). The range of concentrations for primary nanomaterials was selected in accordance to the hypothesis that was discussed earlier in [21].

The modified sulfur was obtained by two-stage process. On the first stage the nanomaterials were admixed to the melted paraffin at 120 °C and sonicated for 5 min. On the first stage melted paraffin with nanomaterials was added into the melted sulfur at 130 °C. The resulting mixtures were mechanically homogenized, filled into steel molds and cooled for 24 hours at room temperature. Each specimen was in form of cube with 2 cm edge.

Both conventional optical microscopy and informative methods of research, including X-ray tomography and Raman spectroscopy, were used to study the influence of paraffin, CB and CNT on the structure formation of sulfur. Optical images were obtained with DSLR camera and Nikon MA200 microscope. X-ray images and Raman spectra were obtained with SkyScan 1173 tomograph and Senterra spectrometer, respectively (both are from Bruker Optik). Parameters of optics during registration of Raman spectra are discussed below. Images and spectra are presented below as-is, without any processing (except brightness-contrast adjustments of images). Compressive strength was measured by Advantest hydraulic system (Controls Group) and porosity was calculated indirectly on the basis of known composition and measured value of average density.

3 Results and Discussion

It is known that unmodified bulk sulfur has a coarse-crystalline structure. This structure is specific to rhombic modification. Average crystal size of unmodified is close to 1 mm. Optical images of nanomodified sulfur are presented on Figure 1.

The analysis of figure 1 shows that admixture of saturated aliphatic hydrocarbon and nanoscale modifier significantly reduces average size of sulfur crystals. Average size decreases in order of magnitude: from about 1 mm down to approximately 100 μm .

X-ray images of cross-sections of specimens made of unmodified and nanomodified sulfur are shown on Figure 2. Optical images of central cavity are shown on Figure 3.

Fig. 1. Optical images of nanomodified sulfur: sulfur with 0.3% of paraffin and 0.02% of CB (a); sulfur with 0.5% of paraffin and 0.01% of CNT (b).

Fig. 2. X-ray images of cross-sections of specimens: unmodified sulfur (a); sulfur with 0.3% of paraffin and 0.02% of CB (b); sulfur with 0.5% of paraffin and 0.01% of CNT (c).

As it follows from Figure 2, there is a central cavity in any sample, irrespective of sample's composition. This cavity is formed due to uneven cooling. The central cavity is filled by columnar crystals (Figure 3) which are oriented parallel to heat flows (away from the enclosing surfaces of the mold). The outer layer of the sample is of structure with complex crystal orientation that is difficult to classify. Admixture of nanoscale modifiers leads to a decrease of the central cavity: additional “bridges” are formed in the material. Thus, the structure of material becomes more uniform.

Fig. 3. Optical image of central cavity (a), image of crystals in central cavity (b) and structure of sulfur crystal in central cavity (c).

Values of density and porosity of modified sulfur are presented on Figures 4 and 5.

It is obvious from Figures 4 and 5 that admixture of nanoscale modifiers does not lead to any notable change in average density and porosity. The reason for this is extensive nature of average density which depends on content and densities of components. Considering porosity, it has to be noted, though, that structure of porous space is still dependent on type and amount of nanoscale modifier; this confirms by very granular structure of crystals in central cavity (Figure 3, c).

Fig. 4. Density of sulfur: modified by paraffin and CB (a), modified by paraffin and CNT (b).

Fig. 5. Porosity of sulfur: modified by paraffin and CB (a), modified by paraffin and CNT (b).

The values of compressive strength are summarized on Figure 6.

Fig. 6. Compressive strength of modified sulfur: paraffin and CB (a), paraffin and CNT (b).

It is known [21] that compressive strength of unmodified sulfur is near to 10 MPa. Thus, as it follows from Figure 6, admixture of paraffin leads to the increase of compressive strength; admixture of both paraffin and nanoscale modifiers greatly enhances this effect. In particular, admixture of 0.2% paraffin and 0.02% of CB leads to an increase of compressive strength in 3.5 times.

Results of spectral studies are presented on Figures 7-9.

It is obvious from Figures 7-9 that no notable peaks emerge when sulfur is modified by paraffin and nanoscale admixtures (there is only a small extra peak near 96 cm^{-1}). The values of relative intensities are also unchanged.

Fig. 7. Raman spectrum of unmodified technical sulfur.

Fig. 8. Raman spectrum of sulfur, modified by paraffin and CB.

Fig. 9. Raman spectrum of sulfur, modified by paraffin and CNT.

Thus, admixture of complex modifier based on saturated aliphatic hydrocarbons and nanoscale carbon materials does not lead to noticeable formation of new compounds. Therefore, the increase of compressive strength can only be explained by the formation of the fine-crystalline structure.

4 Summary and conclusion

It is revealed during the study that admixture of complex modifier, which includes saturated aliphatic hydrocarbon and nanoscale carbon materials, leads to formation of the fine-crystalline structure. Average size of crystals decreases in order of magnitude – from about 1 mm down to approximately 100 μm (and even to the lesser values in central cavity). The central cavity decreases in volume and structure of material becomes more uniform. Such structural changes are accompanied by the improvement of compressive strength: values of compressive strength increases in about 3 times. Since there are no notable formation of new compounds, improvement of compressive strength is mostly due to fine-crystalline structure.

Thus, it can be concluded that application of nanoscale carbon modifiers together with saturated aliphatic hydrocarbons are useful from two points of view: firstly, such admixtures are non-toxic; secondly, these admixtures allow to greatly improve structure and properties of sulfur.

The practical value of the conducted studies is due to possible application of nanomodified sulfur in road construction.

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