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The effect of modifiers on the microstructure of road bitumen and strength of asphalt concrete: a mini-review

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This review explores the effect of bitumen microstructure on the mechanical strength and cohesive properties of modified bitumen. It is shown that the morphology of structures plays a key role in ensuring high performance properties of bitumen road surfaces. Special attention is paid to the effect of polymer, surfactant, and nanomodifiers on the size, shape, and stability of microstructures in the bulk phase of the bitumen binder. The latest data on the mechanisms of bee-like structures formation, their morphology, the correlation of structure sizes with the cohesive strength of bitumen, as well as practical aspects of modifying bitumen compositions to achieve optimal strength characteristics are analyzed.

Keywords: bitumen microstructure, bee-like structures, bitumen modification, strength of asphalt concrete

INTRODUCTION

Bitumen is a highly dispersed colloidal system widely used in road construction and waterproofing materials.

The composition of petroleum bitumen can be characterized by four classes of compounds [1]:

- Saturated hydrocarbons, correlated with the softening temperature of the material and empirically measured by the penetration index;
- Aromatic and naphthenic constituents which are partially hydrogenated aromatic compounds;
- Resins, in some cases called polar aromatic components, which contain many alkyl residues and functional groups;
- Asphaltene molecules formed by a conjugated carbon core having functional groups and heterocyclic compounds and bearing alkyl side chains grafted directly to these nuclei.

Asphaltenes are associated with highly aromatic (H/C~1.0-1.3) and high molecular weight molecules [2], while resins have a higher H/C ratio (1.2-1.7), lower aromaticity and lower molecular weight compared to asphaltenes [3, 4].

Asphaltenes are the least-soluble bitumen fraction consisting of an almost continuous spectrum of several polyaromatic molecular forms and can be extracted or separated from other fractions by precipitation using a large volume of n-alkanes to crude oil [5].

MATERIALS AND METHODS

For gathering all articles, directly corresponding to the topic, databases Scopus and Google Scholar were used. A period till 2025 was set to identify the most recent research papers. Involvement criterion was the use of keywords “bitumen microstructure” or “bee-like structures” in the title. Fourteen manuscripts were comprehensively reviewed.

RESULTS AND DISCUSSION

The mechanical properties of bitumen binders are determined not only by their chemical composition, but also by their supramolecular architecture which is formed due to the self-assembly of asphaltenes and interaction with other bitumen fractions: resins, saturated and aromatic components [6].

In recent decades, atomic force microscopy (AFM) and transmission electron microscopy (TEM) have shown that characteristic morphological elements, the so-called bee-like structures, form on the bitumen surface [7]. These structures which have a characteristic periodic relief, are associated with the orderly arrangement of asphaltene aggregates and play an important role in ensuring the strength and stability of bitumen at various temperatures and loads, which is a prerequisite for the operation of bitumen as part of asphalt concrete road surfaces.

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Modification of bitumen in order to increase its strength characteristics is one of the urgent tasks of pavement materials science. It is important to take into account how various modifiers, such as polymers (e.g., SBS), surfactants, and nanoparticles, affect the morphology of bee-like structures and, consequently, the macroscopic strength of bitumen binders.

Bee–like structures are periodic wave-like formations on the bitumen surface, observed using AFM as alternating elevations and depressions with a characteristic wavelength of 0.5-2.5 μm and an amplitude of 5-50 nm [7]. Studies by Loeber *et al.* [8] have shown that these structures are formed due to the π-π runoff of aromatic fragments of asphaltenes, leading to the formation of dense ordered aggregates at the bitumen/air or bitumen/substrate interface.

The concentration of asphaltenes plays an important role in the formation of bee-like structures: the higher their content, the higher the probability of formation of large aggregates. The ratio of resins and aromatic oils also significantly affects the microstructure of bitumen: resins stabilize dispersed asphaltene aggregates, preventing their coalescence [6].

According to Pauli *et al.* [9], bitumen with a higher degree of polarity (high content of asphaltenes and resins) exhibits more pronounced and larger bee-like structures. In contrast, bitumen with a high content of aromatic oils has less pronounced or does not exhibit these structures at all.

The size and morphology of bee-like structures have a direct effect on the cohesive strength of bitumen, i.e. on the energy required to destroy its internal structure. Loeber *et al.* [8] found that small and evenly distributed structures contribute to the formation of a stronger network of intermolecular interactions, increasing cohesive energy. On the contrary, large, sparse bee-like structures can contribute to brittle fracture due to the presence of "weak zones" in the bulk phase of bitumen. Works by Zhang *et al*. [10] on modified bitumen with SBS showed that the optimal size of bee-like structures ensures maximum resistance of asphalt concrete to fatigue failure; minimal tendency to coating cracking at low temperatures; high level of cohesive strength of the binder under prolonged loads.

Lu & Isacsson [11] found that the introduction of SBS promotes the formation of finely dispersed bee-like structures by stabilizing asphaltene aggregates. In this case, a two-phase structure is formed: a polymer grid and a bitumen matrix, where asphaltene aggregates are "embedded" in the polymer phase. This morphology of the bitumen binder leads to increased elasticity and improved cohesive strength [12].

The introduction of surfactants also has a pronounced effect on bitumen morphology by stabilizing asphaltene dispersion and preventing aggregation and formation of excessively large bee-like structures [6]. The use of cationic surfactants increases the stability of bitumen in the aquatic environment and promotes the formation of uniform fine bee-like structures; amphoteric surfactants effectively disperse asphaltenes and reduce the likelihood of flocculation. This leads to an increase in cohesive strength, especially in combination with polymer modification.

The addition of nanoparticles (SiO_2, TiO_2, nanoclay, graphene) makes it possible to significantly change the supramolecular architecture of bitumen. Xu *et al.* [13] showed that nanoparticles form a rigid framework around asphaltene aggregates. This prevents coalescence and growth of bee-like structures, contributing to the formation of a fine-grained, uniform morphology. As a result, there is a significant increase in the cohesive strength and resistance of bitumen to aging.

Modern research shows that the combined use of polymers and surfactants to modify bitumen binders makes it possible to achieve optimal morphology of bee structures: small bee-like structures; high uniformity of microstructure distribution in the bulk phase of bitumen; stability of the structure under seasonal temperature fluctuations. The synergistic effect of polymer and surface-active modifiers in bitumen provides maximum strength characteristics of the modified binder and durability of the asphalt concrete coatings being formed. So, in the work [14] it was found that the condition for achieving the minimum size of bee-like structures is the introduction of 1.0 g/dm^3 AG-4I and 1.0 g/dm^3 AS-1 into the bitumen; the average size of dispersions is 1.66 μm. In these concentration regimes, as a result of simultaneous exposure to AG-4I (polymer additive) and AS-1 (surfactant), fractions with a size of more than 4.0 μm were completely destroyed, and aggregates in the range 2.0-4.0 μm were destroyed two times; the content of fine fractions (≤2.0 μm) increased by 57.4% compared to virgin bitumen and amounted to 81.9%. A close correlation was revealed in the nature of changes in the dispersed composition of modified bitumen and the strength indicators of asphalt concrete samples. In the asphalt mixture sample made on the basis of the ternary composition "bitumen-AG-4IAS-1" (C_{AG-4I} =1.0 g/dm^3; C_{AS-1}=1.0 g/dm^3), the maximum increase in compressive strength was achieved with the smallest size of bee-like structures of modified bitumen. This shows that the modifying role of additives is in the formation of dense, durable asphalt concrete, which is achieved due to the deep disaggregation of bitumen microdispersions and their uniform distribution over the entire volume of the binder.

Thus, controlling the size and homogeneity of bee-like structures is an important factor in the design of bitumen compositions.

CONCLUSION

Thus, summarizing the results of modern research, we can conclude:

- The size and morphology of the bee-like structures of bitumen are closely related to the strength of the asphalt concrete coatings being formed.
- The optimal size and uniform distribution of bee-like structures in the bitumen binder contribute to maximum strength, resistance to deformation and aging.
- Promising areas are combined approaches to modification and in-situ microstructure monitoring to optimize asphalt concrete formulations with the required performance characteristics.

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