Construction and Building Materials 117 (2016) 72–79

Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

Distribution of sulfur compounds in Brazilian asphalt cements and its relationship to short-term and long-term aging processes

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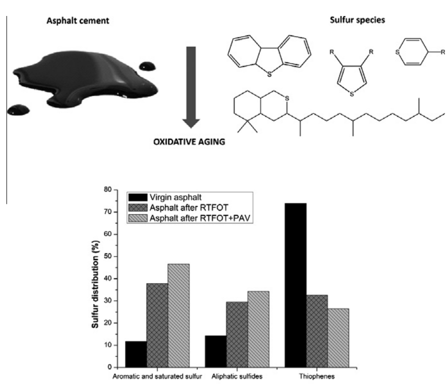
HIGHLIGHTS

- Brazilian asphalt cements were comparatively analyzed for total sulfur distribution.
- Distribution of sulfur classes was obtained from virgin and aged asphalt cements.
- Decrease of thiophenes between 17.7 and 47.5% was observed after RTFOT and PAV aging.
- Increase of aliphatic sulfides and aromatic/saturated sulfur was observed after aging.
- Sulfur speciation was studied in asphalts and their maltenic fractions after aging.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 1 June 2015
Received in revised form 11 April 2016
Accepted 26 April 2016
Available online 8 May 2016

Keywords:
Asphalt cements
RTFOT
RTFOT + PAV
Aging
Sulfur compounds

ABSTRACT

In this work, speciation analysis of sulfur compounds was carried out in asphalt cements submitted to short-term and long-term processes. The separation of sulfur classes was obtained after selective oxidation/reduction steps followed by adsorption liquid chromatography. Five asphalt cements were comparatively analyzed (virgin and aged) for total sulfur distribution, what permitted to establish a possible mechanism for sulfur transformation occurring in Brazilian asphalts. The decrease of thiophenes (17.7–47.5%) was accompanied by the increase in aliphatic sulfides (2.6–19.6%), as well as aromatic/saturated sulfur (5.9–34.9%) in its more oxidized state after RTFOT and RTFOT + PAV aging. A disruption of thiophenic rings and their subsequent conversion to saturated/aromatic sulfur compounds and cyclic/polycyclic aliphatic sulfides can be established as possible route. It showed that part of chemical changes is related to conversion of thiophenes mostly in asphaltenic fraction, since maltenes were found to be relative stable over the thiophenes distribution after aging.

1. Introduction

Asphalt cement is a very complex matrix from an analytic viewpoint, since its chemical composition depends on the petroleum source and the processes involved on its refining [1,2]. From this

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http://dx.doi.org/10.1016/j.conbuildmat.2016.04.111
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reason, the methods employed for the study and fractionation of asphalt cements are based on the chemical separation by differences on molecular weight or functional groups [1]. The separation and classification of the asphaltic matrix in functional groups allows a subsequent chemical characterization of its components. Thus, it assists in determining the influence of different molecule types on the chemical and physical properties of asphalts and how they can differ chemically from one another as well [1,3].

The heteroatoms in asphalt cements are often associated to functional groups, which interact with polar groups and strongly influence on the asphalt properties [4]. Heteroatoms, such as S, N, V and Ni, are directly related to the aging process, since the incorporation of oxygen in the asphaltic matrix is much faster in compounds containing these elements, what can lead to intra- and intermolecular association involving hydrogen bridges [5,6]. Although there is wide variety of sulfur compounds, some types preferentially occur in asphalts, such as sulfides, disulfides, sulfoxides, ring compounds (thiophenes, benzothiophenes and dibenzothiophenes) and its alkyl derivatives, beyond compounds containing oxygen and nitrogen. Fig. 1 exemplifies some typical structures containing sulfur as heteroatoms normally present in asphaltic matrices [2,7,8].

A variety of methodologies for fractioning of asphalts has been described, which are based on the principle of solubility, chemical reactivity and adsorption features, aiming to separate groups of substances similar to each other. Among the reported methodologies, liquid chromatography has been applied to the separation of: saturates, aromatics, resins and asphaltenes (SARA method) [9]; acid, basic and neutral compounds [10] by non-aqueous ionic exchange (NIELC); and macromolecular compounds according to their differences of molecular weight by gel permeation chromatography (GPC) [11]. Infrared spectroscopy (IR) has been applied very frequently for identifying functional groups (e.g. sulfoxides and carbonyls) formed after aging processes of asphalts [11,12]. Recently, atomic force microscopy (AFM) has been also applied for studying of changes in physical characteristics of asphalts due to the aging [13,14].

Nowadays, there is a wide application of asphalt cements in various industry sectors, making it necessary to perform the characterization and elucidation of reaction mechanisms that occur during the asphalt aging process, in order to improve their durability characteristics and efficiency [2]. In this context, the aging of the asphalt cement is explained by four main processes: oxidation, exudative hardening, physical hardening and loss of volatiles [15]. Beyond the formation of oxygenated compounds, polar groups already present in the asphalt cement or generated as oxidation product tend to associate, forming micelles and agglomerates of high molecular weight. Among the factors that influence these reactions and restructuring in asphalts are the maximum temperatures on summer, interactions with the aggregates and the void content of the pavement that allows more interaction between air oxygen and asphalt cement film [2,16].

In this work, major classes of sulfur compounds (aromatic/saturated sulfur, thiophenes, aliphatic sulfides and sulfoxides) were studied in Brazilian asphalt cements. The speciation analysis of these groups was obtained from virgin and aged samples, which were submitted to short-term (RTFOT) and long-term (PAV) processes. Following a comparative analysis of the total sulfur distribution within these compound classes, chemical and structural changes in each asphalt fraction could be observed in the different aging processes. The method developed by Payzant et al. [17] was adapted for Brazilian asphalt samples and allowed the separation of the respective classes according to the different oxidation states of sulfur in the matrix after selective oxidation/reduction reactions and preparative liquid chromatography (LC).Five different asphalt cements were comparatively analyzed concerning the sulfur

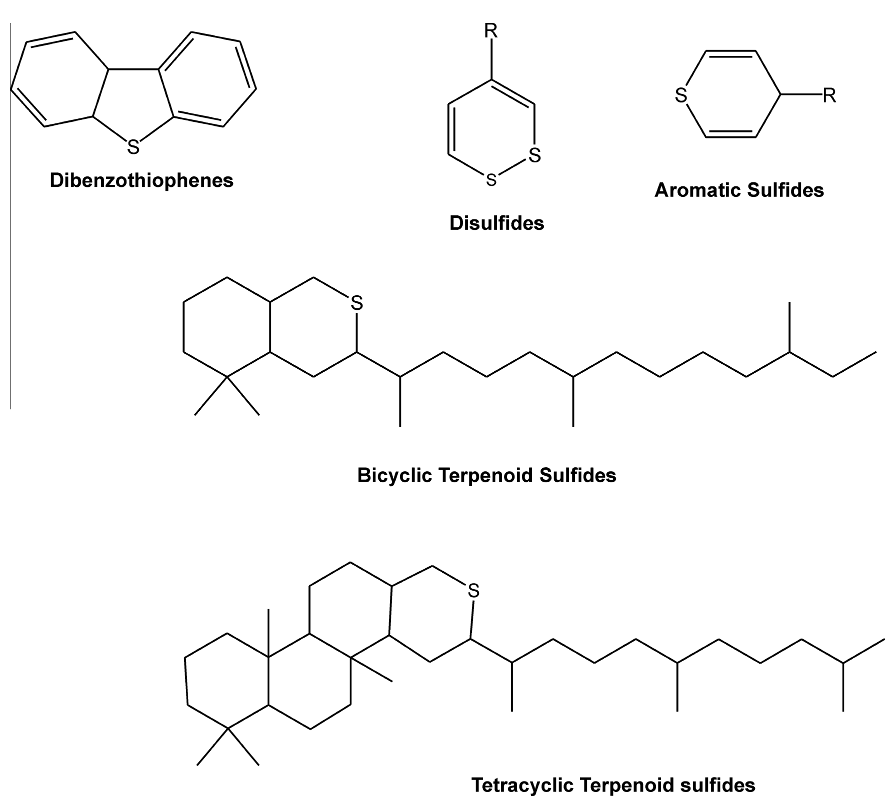

Fig. 1. Chemical structures of typical sulfur compounds present in asphalt cements.