Effects of Chemical and Microstructural Constituents on the Healing Characteristics of Asphalt Binders

Leni F. M. Leite, Francisco T. S. Aragão, Thaísa F. Macedo, Patrícia H. Osmari, Margareth C. C. Cravo, Luis A. H. Nascimento, and Luciana N. Dantas

Abstract Self-healing of asphalt binders and mixtures during rest periods of cyclic loads is a topic that has been studied more carefully recently. To better understand the effects of the chemical characteristics on the healing behavior, this paper characterizes the chemical composition of binders based on the following tests: chemical fractionation (SARA), gel permeation chromatography (GPC), nuclear magnetic resonance (NMR), and chemical elemental analysis. In addition, the microstructural composition of the binders is also evaluated based on testing results obtained in an atomic force microscope (AFM). In such tests, the area fractions of the three main binder microstructural components, i.e., catanaphase, periphase, and paraphase, are determined. The chemical and microstructural compositional results are then compared to linear amplitude sweep (LAS) test results obtained with and without rest periods for the eight asphalt binders investigated. These comparisons indicate that the overall self-healing characteristics of the binders are related to their microscopic characteristics and this understanding may be useful for the selection and even for the fabrication of materials that are more resistant to fatigue.

Keywords Rheology · Asphalt binders · Chemical and microstructural constituents · Healing

1 Introduction

Fatigue cracking is one of the main distresses that abbreviates the service life of asphalt concrete pavements. After realizing that laboratory fatigue tests may underestimate the fatigue life of asphalt binders, researchers began to study the fatigue

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L. F. M. Leite · F. T. S. Aragão (✉) · T. F. Macedo · P. H. Osmari
Civil Engineering Program, COPPE—Federal University of Rio de Janeiro, Rio de Janeiro, Brazil
e-mail: fthiago@coc.ufrj.br

M. C. C. Cravo · L. A. H. Nascimento
Petrobras Research Center, Rio de Janeiro, Brazil

L. N. Dantas
National Department of Transport Infrastructure, Rio de Janeiro, Brazil

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characteristics of asphalt binder under more realistic intermittent loadings and identified that the self-healing is a primary source of the underprediction of the fatigue life of the binders in laboratory tests.

This healing of asphalt binders can be defined as their ability to recover the stiffness and strength lost during previous loadings [1]. During the rest periods between vehicles, asphalt concrete has the ability to self-heal, which leads to the closure of cracks and consequently causes a gain of strength and stiffness and prolongs the fatigue life of the pavements.

The linear amplitudes sweep (LAS) test (AASHTO TP101) has been proposed in the last few years as a specification test to estimate the fatigue damage tolerance of asphalt binder [2]. Later, a healing protocol based on the LAS test was established to measure the healing behavior of asphalt binders (LASH) by applying rest periods before and after cohesive failure. Based on the simplified-viscoelastic continuum damage (S-VECD) model, the percent healing (%Hs) is quantified from the healing recovery of the accumulated damage growth [2]. This protocol was used to investigate the relationship between chemical composition and performance of binders [3].

The molecular mobility, chemical and microstructural composition, and surface energy are the main internal factors influencing the self-healing capability of the binders. According to [4], the evaluation of the whole process, from damage initiation to healing recovery, is a promising approach. Recently, healing was also studied by means of rheological characteristics of asphalt binders through DSR frequency sweep tests to find out the potential optimal self-healing temperatures and the self-healing ratios of the binders at different temperatures [5].

This paper evaluates the effects of chemical and microstructural characteristics of asphalt binders on the healing potential of the materials. The experimental results obtained from distinct testing protocols are compared to LAS testing results performed with and without rest periods to identify potential correlations between the binder microscopic and rheological characteristics.

2 Materials and Methods

2.1 Binders

Eight asphalt binders were selected in order to identify the effects of mobility, microstructural, and chemical composition on the healing characteristics of the materials: six binders with penetration grade of 50/70 and one of grade 30/45 from different crude sources and process production (straight run—SR and deasphalting residue—DR), and one TLA—modified asphalt. Table 1 shows the rheological characteristics of the binders evaluated, including LAS results of final damage—Sf. This factor was defined as the area below curve of strain percentage versus number of fatigue cycles at two different strains [6].

Table 1 Rheological characteristics of the asphalt binders evaluated in this study

	A	B	C	D	E	F	G	H
Source	DR	DR	DR	SR	SR	TLA	DR	SR
PG	64-16S	64-16S	64-22H	64-22V	64-16	64-16V	64-16S	58-16
LAS -Sf	57.4	68.5	96.6	100.7	72.8	95.7	52.8	68.1

2.2 Test methods

Atomic Force Microscopy—AFM

In order to identify the microscopic constituents of the binders, i.e., catanaphase (bees), periphase, and paraphase [7–10], surface topography images were captured in an AFM using the JPK Image Processing software. To allow the comparison among images, the color scale adopted to differentiate the binder microstructural constituents was kept constant. The area fractions of these constituents was analyzed based on the procedure proposed by Osmari et al. [7] for binder samples C, E, G, and H using the software GIMP and IMAGEJ.

Thin layer chromatography—TLC

The fractions of asphalt binder were diluted, separated by liquid chromatography and then subjected to a flame ionization—FID detection procedure. This allowed the separation of the basic chemical components of asphalt binders, *i.e.*, saturates, aromatics, resins, and asphaltenes (SARA).

Nuclear magnetic resonance—NMR

NMR is an absorption spectroscopy technique. Under controlled conditions in a magnetic field, the asphalt sample can absorb electromagnetic radiation in the region of radiofrequency (MHz). The absorption of this radiation by the isotopes of hydrogen ^{1}H and by isotopes of active carbon ^{13}C produces a spectrum based on the sample structure, leading to a quantification of carbon aromatics, aromaticity factor, linear alkanes and benzylic hydrogens (alfa hydrogens).

Healing-based LAS test

The procedure adopted in this research followed the protocol proposed at NCSU. A percent healing indicator ($\%H_S$) was quantified based on the damage recovery using Eq. (1), in which S_1 and S_2 represent the measured S values immediately preceding and after the rest period, respectively, according to Fig. 1. Similarly to the time-temperature superposition principle (TTSP) application within the loading phase, the rest-damage superposition principle (RDSP) within the healing phase was proposed to unify the $\%H_S$ for a given damage level. The $\%H_S$ results from three pre-failure cases (25, 50, and 75% of S_f) that were considered to verify the RDSP and to develop the healing master curves (Fig. 2).

Fig. 1 Schematic illustration for %H_S calculation [2]

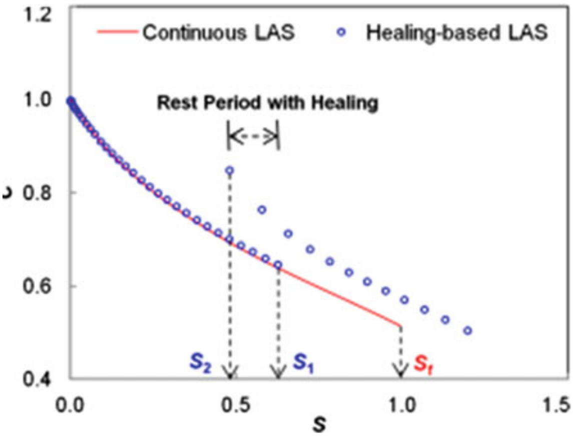
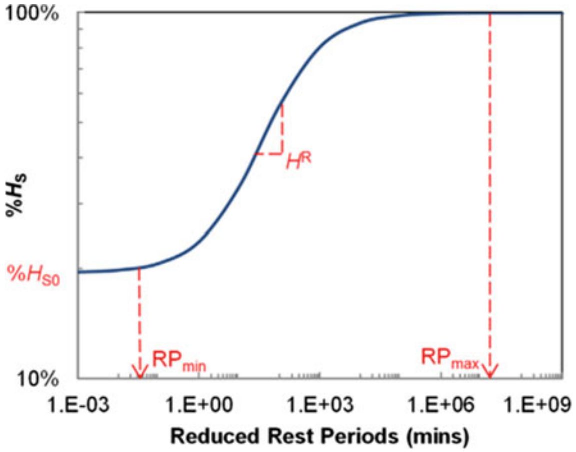


Fig. 2 Schematic illustration of candidate healing parameters from the %H_S master curves [2]



$$\%H_S = (S_1 - S_2) * 100/S_1 \tag{1}$$

Figures 3 and 4 show an example of the results obtained. As illustrated in Fig. 4, the sigmodal curves were not well represented, as the two inflection points could not be reached for the three pre-failure cases initially evaluated. Thus, it was necessary to add extra pre-failure cases (5, 10, 15, and 90% of S_f). The first three cases lead to %H_S higher than 60%, as shown in Fig. 3, and allowed the improvement of the RDSP curves, as shown in Fig. 4. Two candidate healing parameters are proposed in this study based on the constructed %H_S healing master curve: the instantaneous %H_S (%HS0) and the rate of healing (H^R).

%H_{S0} represents an instantaneous %H_S value when the duration of the rest period is significantly short. It is a constant under a single temperature and aging level for a given asphalt binder. %H_S starts to increase from %HS0 values when the rest

Fig. 3 %Hs x rest period

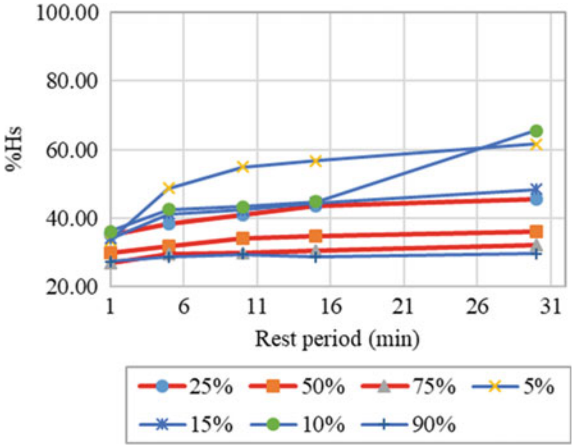
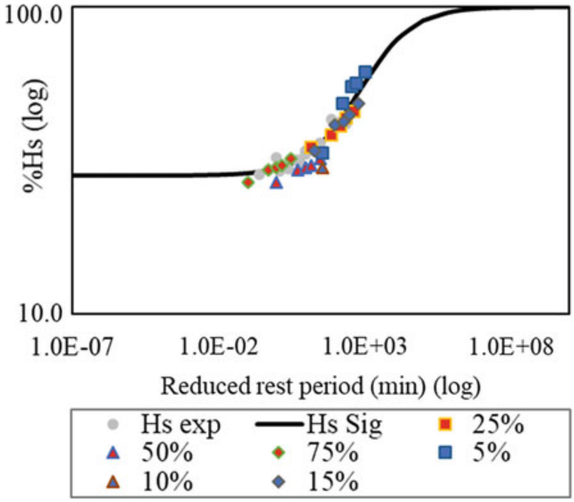


Fig. 4 %H_S master curve for neat binder



period duration exceeds a critical point, the RP_{min}. After the rest period is increased beyond the RP_{min}, the %H_S master curve eventually reaches a steady—state slope with increasing rest period duration (in log-log space). Then, the H^R index can be defined as the slope of the linear part of the increasing %H_S curve in log-log space. H^R is an indicator of the relationship between healing rate and rest period duration within the steady—state regime.

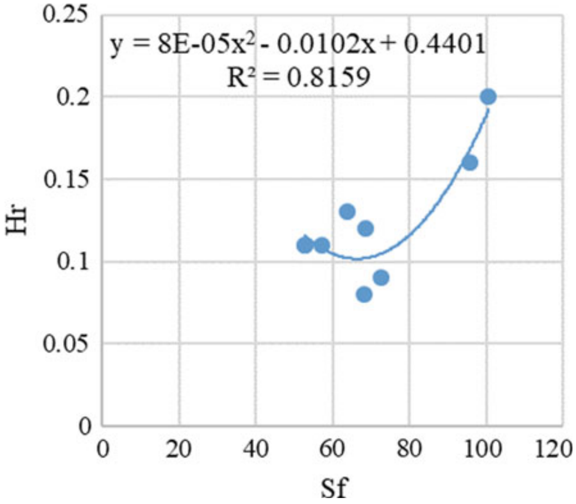


Fig. 5 Relationship between S_f and HR

3 Results

3.1 *Effects of the Chemical Composition on the Healing Potential*

Figures 5 and 6 show correlation curves between the healing parameters and the chemical composition variables obtained from the results of the eight binders evaluated in this paper. H_{so} results were in the range of 20 to 30%, whereas H^R values varied between 0.08 and 0.20. The extra pre-failure cases were essential to assure the values of H_{so} and H^R.

In general, higher values of LAS parameter S_f corresponded to the best results for the healing parameter—H^R (Fig. 5). As shown in Fig. 6, the asphaltenes play a role in the healing phenomenon and clearly increase the healing rate. The asphalt binders from the asphaltenic crudes (samples D and F) showed the highest H^R values and the best S_f results.

3.2 *AFM x Healing*

Among the binder microstructural constituent area fractions evaluated, that of the periphase was the closest related to the healing rate (Fig. 7). Additional data is currently being analyzed to facilitate a deeper understanding of the relationship between AFM binder constituents and the healing potential of the material.

Fig. 6 Relationship between H^R and asphaltenes

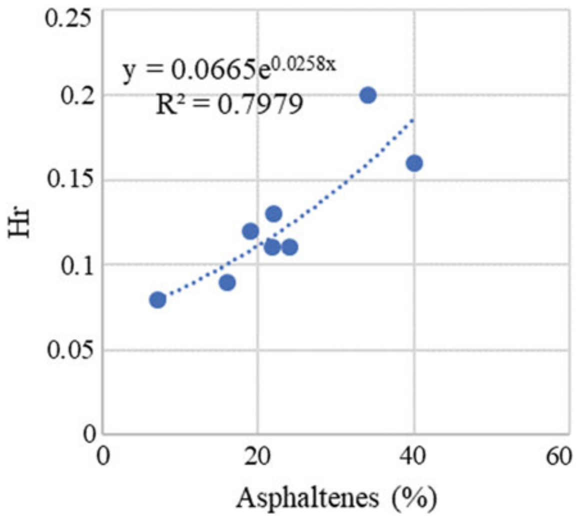
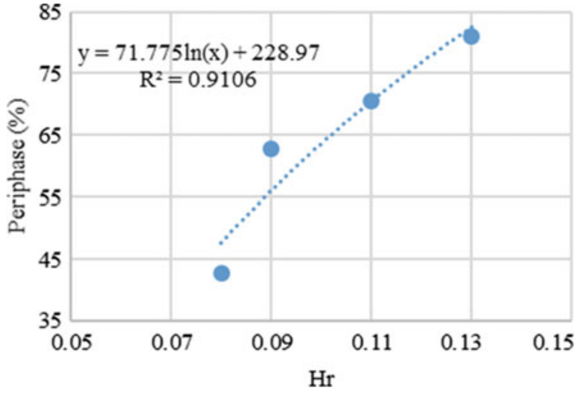


Fig. 7 Effect of the microstructural constituent periphase on the healing rate



4 Conclusions

This study evaluated the effects of chemical and microstructural constituents on the healing potential of asphalt binders obtained from different sources by means of LASH tests. The results indicated that the LASH testing protocol can be improved to provide wider and more representative sigmodal curves. For that, additional tests beyond the originally recommended S_f fractions (5, 10, 15%) should be performed, especially for stiffer binders.

Although additional analyses are necessary and are currently being conducted by the authors, this preliminary study clearly indicated that the overall self-healing characteristics of the binders are directly related to their chemical and microstructural properties. The deeper understanding on such relationship may promote the selection and even the fabrication of materials that are more resistant to fatigue.

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