Infrared Spectroscopy Study of Photodegradation of Polymer Modified Asphalt Binder

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ABSTRACT: The effect of solar radiation in the aging of the asphalt binder can be considered relevant in several countries due to the high level of insulation. This article deals with the comparative aging of a conventional asphalt binder and styrene-butadiene-styrene modified asphalt binder samples under the effect of weathering. The samples were exposed to cycles of xenon radiation, moisture, and temperature. The degradation of binders was analyzed by using the technique of Fourier transform infrared spectroscopy. The C—H/C=O ratio decreased 92.5% for the conventional asphalt cement and 74% for the polymer modified asphalt after 150 h of exposure in a weathering chamber. The oxidation resistance of styrene-butadiene-styrene modified asphalt binder was higher than the conventional asphalt cement evaluated by using the weathering test and infrared spectroscopy analysis. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 125: 3275–3281, 2012

Key words: aging; degradation; FTIR; radiation; rubber

INTRODUCTION

The asphalt binder is the main binding material used in pavement, and undergoes the aging process during its mixing, application and service life. Asphalt binder is composed by hydrocarbons, but it has a complex chemical composition due to the high number of carbon atoms (40–120), and the presence of heteroatom such as sulfur and nitrogen. Its composition is a result of the manufacture process and the crude origin. Bitumen, like other organic substances, is affected by the presence of oxygen, ultraviolet radiation, and temperature variations.[1]

Asphalt binder aging involves a number of physical and chemical processes over the life of the pavement and has several causes such as oxidation, which generates an increase of the consistency of the asphalt binder, as well as the loss of volatiles. The consistency increase, especially in heavy traffic conditions, can significantly decrease the lifetime of the pavement.[2] Another cause of binder aging is moisture, which usually manifests itself by cohesion loss of the mixture and adhesion loss between bitumen and aggregate surface (stripping).[3]

Even today, the influence of ultraviolet radiation is usually ignored in the aging simulations as it is believed that it only affects the surface layers of the pavement.[4,5] The age-hardening may have two effects: increased load capacity and rutting resistance of the pavement, producing a stiffer material or flexibility reduction of the pavement, resulting in crack formations, reducing fatigue life.[6] The aging of asphalt binder due to ultraviolet radiation of the sun is one of the factors responsible for the decrease of its useful life.[4,5] This is most important in Brazil, given the fact that the sunlight level to which this country is submitted is high because of its latitude.[5] A comparison of the aging effect on a conventional asphalt binder and a styrene-butadiene-styrene modified asphalt binder allows the study of the effect of polymer addition on the binder degradation due to the exposure to xenon radiation.

According to White,[7] during the thermal and photo-oxidation of the asphalt binder, the breaking of the polymer chains occurs and this liberates molecule segments, facilitating rearrangements, which in turn, allow these segments to reach lower energy states, which is a characteristic of state balance for the material and therefore accelerates physical aging. The material changes irreversibly, and physical aging occurs together with the chemical changes.

An example of the changes in residual stress occurs in the photoaging, where the depth profile of molecular degradation falls sharply from the surface

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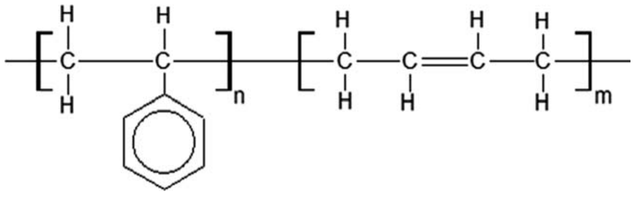

Figure 1 Chemical structure of styrene-butadiene-styrene.

of exposure. An accelerated volume of relaxation near the surface results in shrinkage and increases the residual stress. Therefore, tensions develop in the region, which becomes brittle, due to molecular degradation and increases the crack nucleation and propagation. The effect of solar radiation in the aging of bituminous binders was studied by using infrared spectroscopy.

EXPERIMENTAL

The samples of asphalt binders studied were the following:

- Asphalt cement 50/70 penetration supplied by PETROBRAS (named B samples).
- Styrene-butadiene-styrene (SBS) modified asphalt provided by Laboratoire Central des Ponts et Chaussées: LCPC in France with 3.6 wt % of SBS (named F samples). The chemical structure of styrene-butadiene-styrene is shown in Figure 1.

Plates of granite were made by cutting aggregates. They were painted with a layer of 0.6 mm binder thickness to simulate the thickness of the binder coating to aggregate surface and then placed in a Q-SUN Model Xe-1-S weathering chamber. Five granite plates were made for each asphalt binder studied. Five samples were taken from the surface of each granite plate for Fourier transformed infrared spectroscopy (FTIR) analysis.

The materials were exposed to alternating cycles of radiation and moisture at controlled temperatures. The effect of sunlight was obtained with a xenon arc lamp whose spectrum is closest to sunlight, as it includes ultraviolet, visible light, and infrared. The dew point and rain were simulated with moisture condensation and spraying of water.

The exposure conditions in the weathering chamber were according to the ASTM method D-4798. The cycles lasted 80 min: 64 min of xenon radiation and 16 min of radiation and water spray at a temperature of 60°C, and irradiation at 340 nm = 0.35 W/m^2 as shown in Figure 2. The variable power 3500–6500 W was used to maintain the intensity of irradiation. The samples were exposed for 50, 100, 150, and 200 h. The samples were photographed by using an Olympus Camera Model X 845 after exposure for 50, 100, 150, and 200 h.

After the weathering tests, the samples were analyzed by FTIR and scanning electron microscope (SEM) analysis. The asphalt binder samples were analyzed before (B0 and F0 samples) and after degradation in weather-o-meter chamber for 50 (B50 and F50), 100 (B100 and F100), 150 (B150 and F150), and 200 h (B200 and F200), respectively.

For the FTIR spectroscopy, the ABB BOMEM, model MB series equipment was used. The attenuated total reflectance diamond method was used. Spectra were obtained in units of absorbance in the range 4000–400 cm^{-1}, recorded with 16 accumulations of reading and resolution of 4 cm^{-1}, over a diamond cell.

The calculation of the peak area was performed using the PeakFitTM Program in spectra with line correction of linear base. The spectra, after applying the baseline correction (nonlinear), were normalized and the ratios of the intensities of the bands νC—H (2918 cm^{-1}) and νC=O (1703 cm^{-1}) were used to evaluate the aging.

The functional and structural indexes were calculated from the band areas measured from valley to valley. The choice was set on the areas rather than on the band heights because several vibrations of

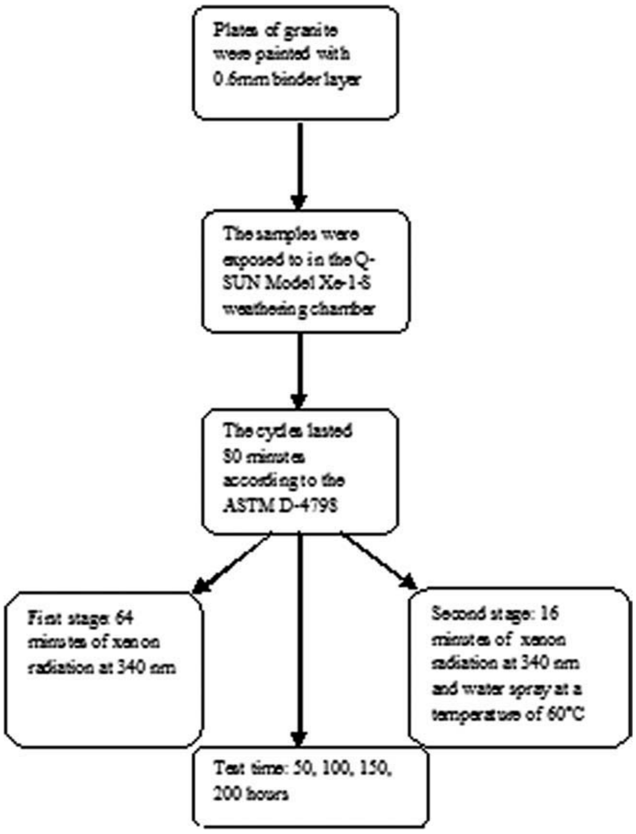

Figure 2 Environmental tests.

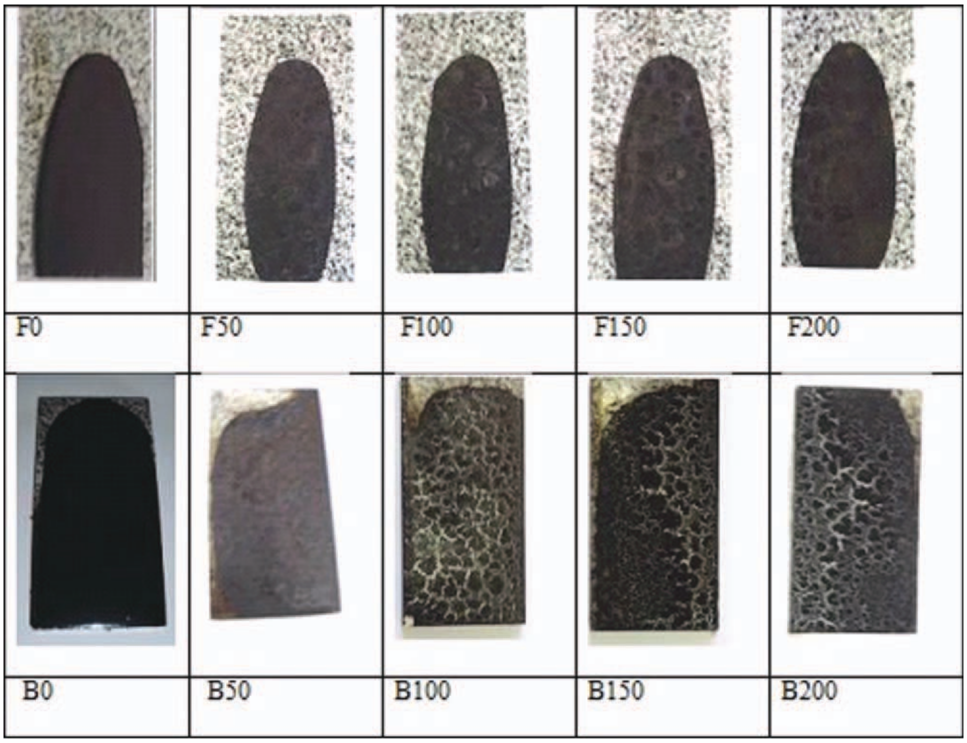

Figure 3 SBS modified asphalt binder (F) and conventional asphalt binder (B) before and after exposition in a weather-O-meter chamber for 50, 100, 150, and 200 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the same type are simultaneously taken into account (for example the C=O ester, acid, and ketone vibrations between 1753 and 1635 cm^{-1}). Several index types were set calculated with band area ratio. In fact, since bitumen, film does not have a constant thickness and since this practice does not exist, the spectra should be brought back to the same absorbent series (spectral normalization) to be compared.[8]

RESULTS AND DISCUSSION

Samples of bitumen after radiation exposure in the weathering chamber showed changes in their surface as cracks and white spots (shown in Fig. 3). SEM analysis presented satisfactory evidence to the increase of porosity in the surface caused by weathering and possible hardening of the binder, which makes the material more brittle, thus favoring the loss of filler and the appearance of cracks.[9] Analyses made by Quantikov (image analysis software) using SEM images revealed increased porosity from of 10 to 45% as a result of binder degradation followed by pullout of the filler. This result supports the theory of the fostering of cracks due to aging.[9]

The aging process produces the reduction of polymer molecular size and the inhibition of the effect of polymer on reduction of asphalt stiffness. The stiffness of the base asphalt also increases with aging, causing stress under deformation that exceeds the failure stress, leading to cracks of the hot mix asphalt despite the polymer.[10]

The conventional asphalt binder showed a more significant change in color, more cracks, and white spots on the surface after 50 h of aging than did the SBS modified binder. This result can be explained by the polymer addition to the asphalt binder. Polymer modification improved ductility and prevented cracks.[10]

Discoloration of degraded polymers was reported in literature, as suggested by Edge et al.[11] and can occur, for example, with the hydroxylation of an aromatic ring produced by the hydroxyl radicals that arise during the decomposition of hydroperoxides formed in the thermal oxidation process.

Hydroperoxide formation occurs at the ether link in the first stage of polymer degradation at temperatures below 200°C. The hydroperoxide decomposes generating an OH radical. Degradation proceeds and generates hydroxylated compounds. The OH initiated oxidation of the monohydroxy compound and lead to further oxidation of aromatic rings resulting in the formation of dihydroxy compounds.

The thermal oxidation produces the scission of the ether link with the formation of hydroxyl and carboxyl end groups and acetaldehyde. Further reactions during thermal and thermo-oxidative degradations lead to the formation of new carbonyl functionalities, ketoesters or hydroxylated ketoesters

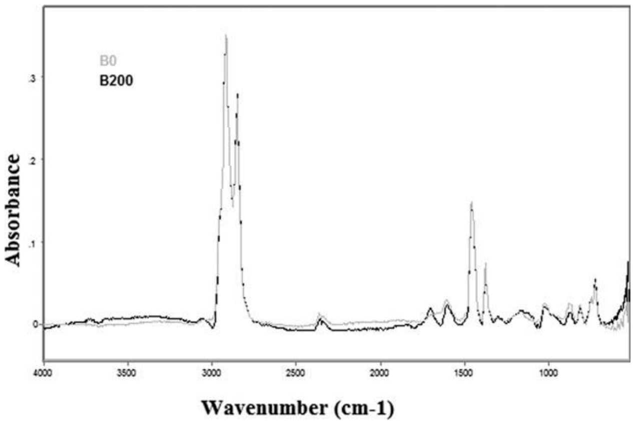

Figure 4 Typical spectrum of conventional asphalt binder before and after aging.

containing a conjugated system of double bonds. The buildup of conjugated aromatic structures is also part of the color formation process. Several possible mechanisms of formation of such aromatic networks are reported earlier in literature.[11,12] However, cumulative oxidation of these resultant species leads to more complex chromophoric systems responsible for changes in color with heating time.

Measurements were made of absorption spectroscopy in the infrared region in a diamond cell of samples of the aged binders. Figures 4 and 5 show the spectra of asphalt binder before and after the aging process. Bands at 1700 cm^{-1} are associated to C=O of carboxyl, ketones, aldehydes, ester, or amides. Bands at 1600 cm^{-1} are associated to C=C of aromatics, peaks at 1460 and 1376 cm^{-1} are related to aliphatic CH_2 and CH_3. After aging, there is a significant increase of absorbance of bands at 1700 cm^{-1} associated to C=O.

Figure 6 shows the relative intensities of C—H and C=O bands of asphalt binders before and after aging. The photodegradation process promotes chain scission and oxidation process, increasing the concentration of C=O groups. The ratio of intensities of C—H/C=O bands usually decreases as the photodegradation proceeds. For both asphalt binder samples, the ratio of intensities of C—H/C=O bands is the highest for the virgin sample (without aging), and this ratio decreased with the increase of exposure time up to 150 h of aging. After 50 h of aging, the ratio of intensities of C—H/C=O bands for the asphalt binder without polymer addition was only 26% of the original value (before aging). For the polymer modified asphalt binder, the ratio is 63% of the original value, before aging. Considering the relative concentration of carbonyl groups as a measure of degradation process, after 50 h of exposure in the weathering chamber, the asphalt binder without polymer showed a higher level of oxidation than did the polymer asphalt.

For 200 h of exposure, the C—H/C=O ratio increased in relation to the value at 150 h. Condensation of C=O groups can occur in the binder sample aged for 200 h, decreasing the concentration of carbonyl groups.[13] The classical carbonyl reactivity is cited in literature,[14] and the condensation of carbonyl is a very usual reaction, also cited in literature.[15] The action of radiation can promote the break of double bonds of carbonyl groups, and condensation of the carbonyl groups to produce new molecules, decreasing the total content of C=O groups.

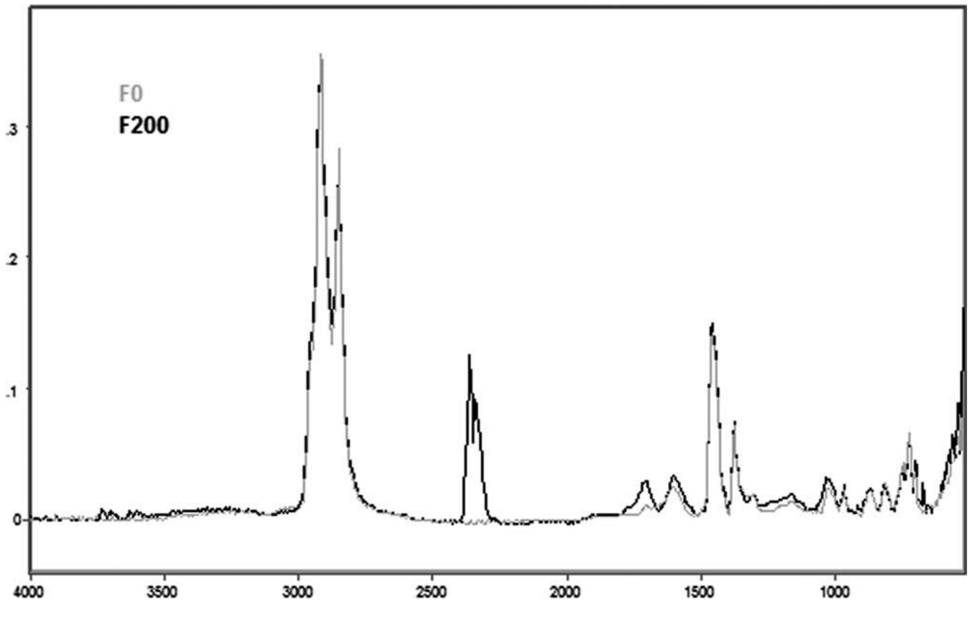

Figure 5 Typical spectrum of polymer asphalt binder before and after aging.

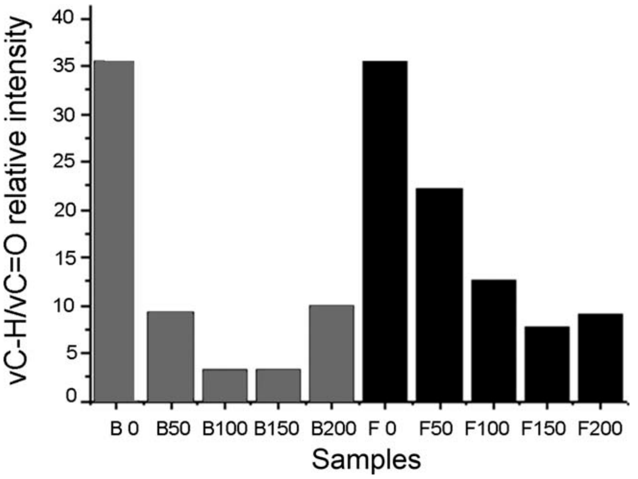

Figure 6 Ratio of intensities of CH and C=O bands of conventional asphalt cement and SBS modified asphalt binder before and after aging.

The benefit of polymer modifiers to oxidation resistance decreases as the aging proceeds and the C—H/C=O ratio was similar for both asphalt binders after 200 h of exposure in the weathering chamber. This is the result of polymer degradation. Oxidative aging degrades polymers in asphalts into smaller molecules[16] and hardens the base asphalt.[10] As a result polymer benefit diminishes with aging. For samples aged for 200 h, the oxidation behavior of SBS modified asphalt and conventional asphalt cement is similar. There are two reasons for the reduction in polymer benefit with aging: the decrease of the polymer molecule size and, as a consequence, the asphalt-polymer interaction reduces; second, the stiffness of the base asphalt increases, causing stress under the deformation that exceeds the failure stress, causing cracks of the hot mix asphalt despite polymer addition.[10]

The main bands observed in FTIR spectra of asphalt binders are shown in Table I. Bands at 1030 cm^{-1} are related to the S=O groups, produced during aging. The ratio of area of peak at 1030 cm^{-1} to the total area of peaks (sulfoxide index) for the conventional asphalt cement and SBS modified asphalt before and after aging is shown in Figure 7. The sulfoxide index for the asphalt cement did not change during exposure in the weathering chamber. However, for 150 h of aging, the sulfoxide index decreased. The increase of concentration of C=O groups generated by oxidation of binder can produce a decrease of sulfoxide index. For the SBS modified asphalt, the sulfoxide index increases with exposure time. The sample after 150 h of exposure showed the highest value of sulfoxide index, more than twice the sulfoxide index of asphalt binder aged for 200 h. It seems that the oxidation rate increases at 150 h of testing. For the polymer modified asphalt, at 150 h of exposure in the weathering chamber, the oxidation of sulfur heteroatom was higher than the oxidation of carbon atoms, and generated the increase of sulfoxide index. For the conventional asphalt binder, the oxidation of carbon was higher than the sulfur oxidation at 150 h of testing.

The aromatic index, eq. (1), is the ratio of area of peak at 1600 cm^{-1} in relation to the total area of peaks:

$$\mathrm{AI} = A(1600)/\Sigma A \tag{1}$$

The sum of the peak area is given in eq. (2):

$$\begin{aligned}\Sigma A = {} & A(1700) + A(1600) + A(1460) + A(1376) \\ & + A(1030) + A(864) + A(814) + A(743) + A(724) \\ & + A(2953, 2918, 2862)\end{aligned} \tag{2}$$

For the SBS modified asphalt binder, the aromatic content increased with the time of exposure in the weathering chamber (Fig. 8). For the asphalt cement, this behavior was observed for samples with aging up to 100 h (shown in Fig. 8). The asphalt cement sample aged for 100 h showed the highest content of aromatic compounds among all the samples tested. After 100 h of aging, the aromatic index decreased. Literature data[10] reported the decrease of aromatic content in the aged samples due to the production of resins and asphaltenes from the aromatic groups. After 100 h of aging, a production of asphaltenes

TABLE I
Bands Observed in the FTIR Spectra of Binders

Bands	Attribution	Observations
~ 1375	Deformation on plan CH_3	Aliphatic
~ 1458	Deformation on CH_3, CH_2	Aliphatic
~ 1636	Stretch C=O	Carboxyl acid and ketones
~ 2850	Symmetric stretch C—H (CH_2)	Aliphatic hydrogen
~ 2870	Symmetric stretch C—H (CH_3)	Aliphatic hydrogen
~ 2923	Asymmetric stretch C—H (CH_3, CH_2)	Aliphatic hydrogen
~ 2955	Asymmetric stretch C—H (CH_3)	Aliphatic hydrogen
~ 3450	Stretch O—H	Alcohol, carboxyl acid, and phenol

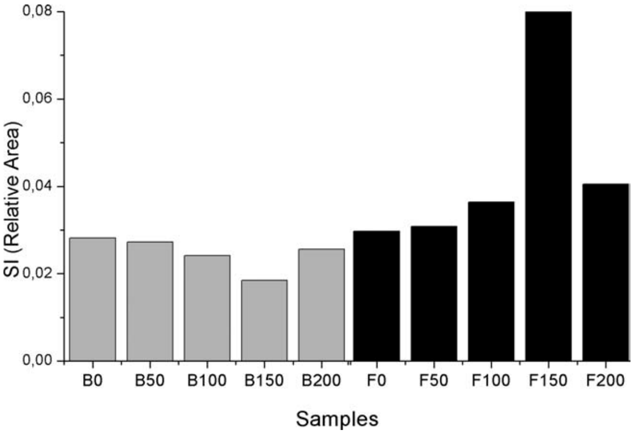

Figure 7 Sulfoxide index ($A_{1030}/\Sigma A$) of conventional asphalt cement and SBS modified asphalt binder (F) before and after aging.

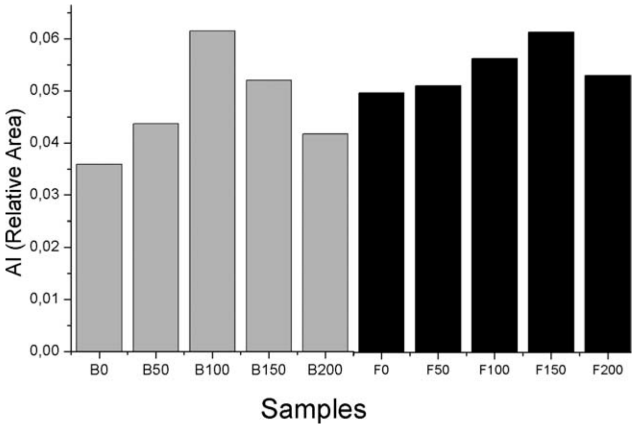

Figure 8 Aromaticity index for the conventional asphalt cement and SBS modified asphalt binder before and after aging.

from the aromatic groups occurred for the conventional asphalt cement. The results of the present work indicate that the degradation rate of asphalt binders increased after 150 h of aging. However, this result did not occur in the case of SBS modified asphalt. SBS has two polystyrene blocks that makes the polymer binder system more resistant to deformation.[13] More polar groups in the polymer mean stronger interactions between the polymer and the polar aromatic components of asphalt; therefore, it is more difficult for SBS modified asphalt to produce asphaltenes from the aromatic groups.[10]

The aliphatic index was calculated by using the eq. (3):

$$\mathrm{AS} = A(1460) + A(1376)/\Sigma A \qquad (3)$$

Figure 9 shows the aliphatic index for asphalt cement and SBS modified asphalt. The asphalt cement showed a decrease of aliphatic index with the increase of testing time. The SBS modified asphalt showed a tendency of decrease of aliphatic content with aging time. The decrease of the aliphatic index could be a result of increase of concentration of oxidized species such as C=O and S=O.

The carbonyl index represents the ratio of area of peak at 1700 cm^{-1} to the total of peak areas. The carbonyl content increased significantly for the asphalt cement aged for 100 and 150 h as shown in Figure 10. However, there was a high decrease of carbonyl groups in the binder after 200 h of weathering testing, probably to the condensation.

The reduction of carbonyl groups in the SBS modified asphalt aged for 200 h in relation to the sample aged for 150 h occurred, but in a lower degree (Fig. 10).

CONCLUSIONS

The oxidation resistance of SBS modified asphalt was higher than the conventional asphalt binder evaluated by using the weathering test and FTIR analysis. Considering the relative concentration of carbonyl groups as a measure of degradation process, after 50 h of exposure in the weathering

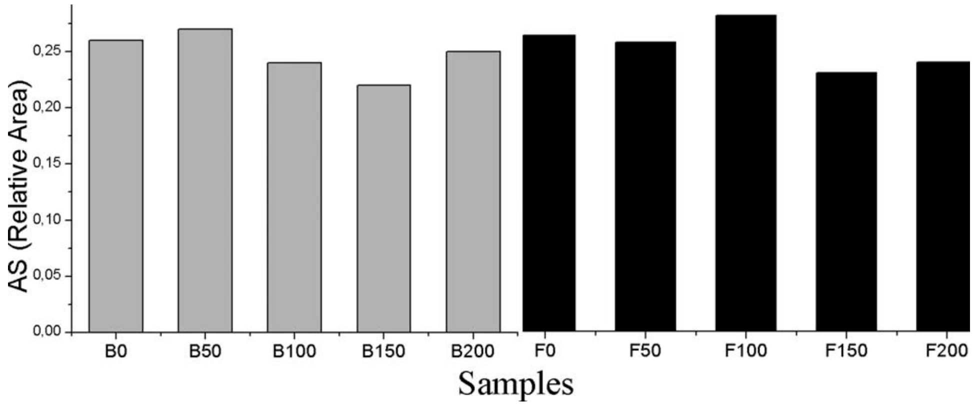

Figure 9 Aliphatic index for the conventional asphalt cement and SBS modified asphalt binder before and after aging.

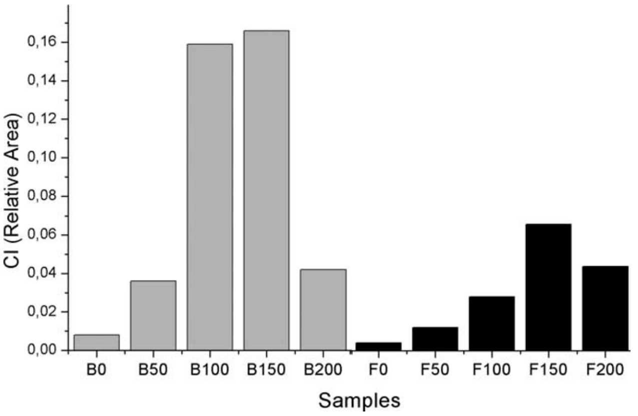

Figure 10 Carbonyl index for the conventional asphalt cement and SBS modified asphalt binder before and after aging.

chamber, the asphalt binder without polymer showed a higher level of oxidation than did the polymer asphalt. After 50 h of aging, the ratio of intensities of $\mathrm{C{-}H}/\mathrm{C{=}O}$ bands for the asphalt binder without polymer addition was only 26% of the original value (before aging). For the polymer modified asphalt binder, the ratio is 63% of the original value, before aging. Another result that corroborates the higher degradation of asphalt binder without polymer is that the conventional asphalt cement showed a more significant change in color after 50 h of aging, and more cracks and white spots on the surface than the SBS modified asphalt. The $\mathrm{C{-}H}/\mathrm{C{=}O}$ ratio decreased 92.5% for the asphalt cement and 74% for the SBS modified asphalt after 150 h of exposure in the weathering chamber, indicating a lower oxidation of the polymer modified asphalt. The benefit of polymer modifiers to oxidation resistance decreases as the aging proceeds and the $\mathrm{C{-}H}/\mathrm{C{=}O}$ ratio was similar for both asphalt binders after 200 h of exposure in the weathering chamber.

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