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Short-term aging characterization of asphalt binders using gel permeation chromatography and selected Superpave binder tests

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Abstract

Both the rolling thin film oven test (RTFOT) and the short-term oven aging (STOA) methods are used in the laboratory to represent the aging of an asphalt binder during plant mixing, transportation and paving. The RTFOT is conducted at 163 °C for 85 min, and the recommended STOA methods are to heat the loose mix in a forced draft oven either at 135 °C for 4 h or at 154 °C for 2 h dependent on the asphalt binder's stiffness. The actual time of short-term aging in the field varies depending on hauling distances or paving times.

This research was initiated to compare the aging effects of the RTFOT and the STOA methods using the gel permeation chromatography (GPC) and selected Superpave binder tests. For this study, nine asphalt binders were prepared, and five aging periods were used for the RTFOT and four aging treatments were selected for the STOA. Loose asphalt mixes were obtained from six field projects. The results of GPC test showed that the RTFOT method has less aging effect on the binders than the STOA methods for asphalt mixtures prepared in the laboratory. Given the limited number of samples from the field, it was difficult to find any correlation of short-term aging between the laboratory and the field. The longer the aging time in the RTFOT led to an increase in the high temperature viscosity and the high failure temperature of asphalt binders, the only exception being the rubber-modified binders. The GPC was effective in evaluating the aging effect of rubber-modified binders using different RTFOT aging times.

Keywords: Asphalt binder; RTFOT; STOA; Aging effect; Aging time; GPC; LMS

1. Introduction

1.1. Background

The properties of binders in asphalt mixtures change over time during mixing, transportation and construction. As time increases, the binders become more stiff and brittle. Both the rolling thin film oven test (RTFOT) and the short-term oven aging (STOA) methods in the laboratory are intended to represent the aging of an asphalt binder during hot-mix asphalt (HMA) production and construction. The RTFOT measures the effect of heat and air on a moving film of semi-solid asphaltic binder [3]. The aging time of 85 min in the RTFOT is expected to produce aging effects comparable to average field conditions, although given the number of variables, the aging in the field is often different from that of RTFOT [12]. For asphalt mixtures, the recommended laboratory procedure for short-term aging is to heat the loose mix in a forced draft oven for 4 h at a temperature of 135 °C [10], while for the stiffer mixes, short-term aging of 2 h at 154 °C is commonly used. The actual time of short-term aging in the field varies and it is dependent on hauling distances or paving delays.

This aging, in general, results in a change in the molecular size distribution of an asphalt binder. Specifically, an increase in the large molecular size (LMS) results in an increase in the viscosity and stiffness of an asphalt binder. This viscosity change is predicted well by gel permeation chromatography (GPC) [5,6,8]. Also, previous research

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[9] introduced a method that collects a selected amount of an asphalt mixture sample, and not just an asphalt binder, and subsequently dissolves it in tetrahydrofuran (THF) for the GPC test, demonstrating the possibility of estimating the viscosity of an asphalt binder directly from the asphalt mixture without binder recovery. This method is utilized to test sample mixtures which were short-term aged either in the laboratory or in the field.

1.2. Research objectives

The overall objective of this research was to investigate the aging difference between the rolling thin film oven test (RTFOT) and the short-term oven aging (STOA) methods in the laboratory. The specific objectives are as follows:

(1) To compare the aging effect of the RTFOT and the STOA of binders either in the laboratory or in the field using the gel permeation chromatography (GPC).
(2) To evaluate the effects of five aging times (70, 85, 100, 115, and 240 min) using the RTFOT to simulate the short-term aging of asphalt binders in the laboratory.

2. Experimental program

2.1. Materials

A total of nine binders, three types each from three different sources, were used in this study. Three binders (PG 64-22) were designated as control binders, three SBS-modified binders of PG 76-22 as SM binders, and three rubber-modified binders as RM binders. The control and SM binders were collected from three binder sources designated as A, B and C. Binder A was a mixture of several sources that could not be identified by the supplier, binder B was from a Venezuelan crude source, and binder C was from a Middle Eastern source. The RM binders were made by adding a specified amount of rubber to the control binder, mixing with a stirrer (700 rpm) at 177 °C for 30 min [14]. Each binder was graded in accordance with AASHTO M320 to verify the performance grade. Table 1 shows the properties of the control binders, SM binders, and RM binders. The experimental design procedures used in this study are shown in Fig. 1.

One granite aggregate source was used for preparing samples. Hydrated lime, used as an anti-strip additive, was added at a rate of 1% by dry mass of aggregate according to the specificaion of the South Carolina Department of Transportation (South Carolina DOT). A nominal maximum size 9.5 mm superpave mixture was used for the mix design in this study. All mixtures used an identical aggregate structure to distinguish the influence of the binders.

2.2. RTFOT and STOA

The RTFOT for the nine asphalt binders was conducted at 163 °C for 85 min to simulate the short-term aging of an asphalt binder (ASTM D2872). For the STOA in the laboratory, the aggregate was heated at 180 °C for a minimum of 6 h before being mixed with an asphalt binder. The hot aggregate and the asphalt binder were mixed for 90 s, using a mechanical mixer, and the asphalt mixture in the loose condition was artificially aged in a conventional oven at a specified temperature and for a specified amount of time. The aging treatments used in this research are listed below:

- 135 °C oven aging for both 2 h and 4 h.
- 154 °C oven aging for both 2 h and 4 h.

2.3. Short-term aging in the field

Loose asphalt mixes were obtained from six paving sites around South Carolina. Table 2 details the field conditions including the paving location, the mixture types, the binder sources and grades.

Table 1
Properties of all binders used in this study

Aging states	Test properties	Binder sources								
		A			B			C		
		Con	SM	RM	Con	SM	RM	Con	SM	RM
Unaged binder	Rotational viscosity at 135 °C (Pa s)	0.430	1.475	1.155	0.703	1.862	2.513	0.472	2.025	1.357
	$G^*/\sin\delta$ at 64 °C (kPa)	1.279	–	–	2.413	–	–	1.468	–	–
	$G^*/\sin\delta$ at 76 °C (kPa)	–	1.388	0.744	–	1.313	1.808	–	1.522	0.669
RTFO aged residue	$G^*/\sin\delta$ at 64 °C (kPa)	2.810	–	–	6.075	–	–	2.579	–	–
	$G^*/\sin\delta$ at 76 °C (kPa)	–	2.508	1.596	–	3.060	4.010	–	2.518	1.661
RTFO + PAV aged residue	$G^*\sin\delta$ at 25 °C (kPa)	4074	4372	2359	3352	3613	2005	3575	4103	2325
	Stiffness at −12 °C (MPa)	217	212	142	141	142	129	232	233	148
	m-Value at −12 °C	0.307	0.310	0.322	0.359	0.370	0.336	0.321	0.319	0.324

Con: control binder; SM: SBS-modified binder; RM: rubber-modified binder.

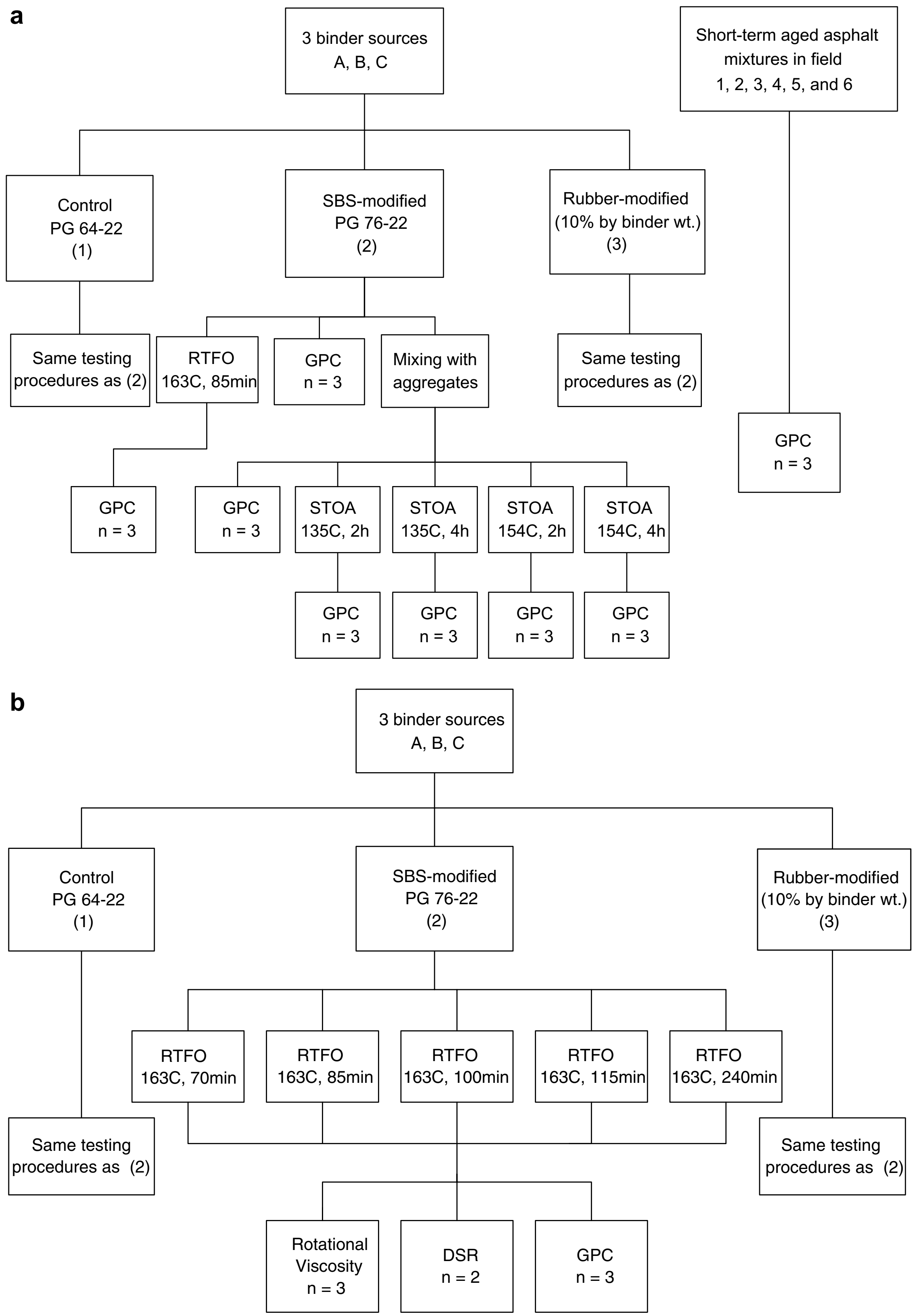

Fig. 1. Flow chart of experimental design procedure for (a) evaluating the aging difference between RTFOT aging and short-term oven aging (STOA) in the laboratory and field, and (b) evaluating the effect of aging time in the RTFO test.

Table 2
Field paving information

	Test section 1	Test section 2	Test section 3	Test section 4	Test section 5	Test section 6
Asphalt type (source)	PG 64-22 (B)	PG 76-22 (B)	PG 76-22 (B)	PG 64-22 (A)	PG 64-22 (A)	PG 64-22 (A)
Mixture type	Binder course	OGFC[a]	Surface course	Surface course	Surface course	Surface course
Location	Greenville, SC	Charleston, SC	Spartanburg, SC	Greenville, SC	Clemson, SC	Seneca, SC

[a] OGFC: open graded friction course.

2.4. Variation of aging time in the RTFOT

To evaluate further the effect of aging time in the RTFOT, five aging times (70, 85, 100, 115, and 240 min) were used. The aging temperature of the RTFOT was kept at 163 °C.

2.5. Gel permeation chromatography

The RTFOT and the short-term aging in the laboratory or in the field were then analyzed using GPC to measure the molecular size distribution of the asphalt binders. Waters GPC equipment was used for chromatographic analysis, a differential refractive index meter (Water 410 detector) as a detector, and a series of two columns (Waters HR 4E and HR 3) for separating constituents of an asphalt binder by molecular size were utilized. The specification of the columns is shown in Table 3. For the results to be valid, a sample must be kept at a constant temperature, achieved by keeping the columns constant at 35 °C in a column oven, while all processed data collections are controlled by a computer software.

For mixtures, the specified quantity of asphalt mixture was randomly collected from the short-term aged mixture and was dissolved into THF in a beaker. To keep the concentration of the dissolution in all testing the same, 0.5% by weight, the binder content of the mix had to be obtained. The ignition oven test was used to accomplish this for the mixture passing 4.75 mm sieve. For binders, the specified quantity of binder was randomly collected and was dissolved in THF at the same concentration rate (0.5% by weight).

Each sample dissolved into THF was filtered through a 0.45 μm syringe filter prior to the injection. Each test took approximately 30 min and elution started at approximately 11 min from injection and ended at 21 min. Each test was repeated three times and then the average value of large molecular size (LMS) was reported.

Table 3
Pore size and effective molecular weight range

Column	External length (cm)	Pore size (Å)	Effective molecular weight range (ps)
Styragel HR 3	30	1000	500–30,000
Styragel HR 4E	30	Mixed bed	50–100,000

Typical chromatograms of a virgin asphalt binder (unaged) and a short-term aged binder (154 °C oven aging for 4 h) are shown in Fig. 2. The area under the curve represents 100% of the binder molecules injected into the GPC system [8]. The asphalt binder constituents are usually classified into several groups [5,7,16]. For this study, a chromatogram profile was partitioned into 13 slices and three parts: large molecular size (LMS; slices 1–5), medium molecular size (MMS; 6–9) and small molecular size (SMS; 10–13) (Fig. 2). Several researches have shown that the LMS of binder had good correlations with asphalt binder properties than other sizes [5,6,16]. Therefore, only the front part of the LMS value from the quantitative data of the chromatogram was used to evaluate the aging effects.

2.6. Rotational viscometer and dynamic shear rheometer

Superpave binder specifications include a maximum viscosity requirement (3 Pa s) for an unaged binder. In this study, rotational viscosity test [2] was used to verify the high temperature viscosity change as the aging time in the RTFOT increased.

Dynamic shear rheometer (DSR) test [1] was conducted on two replicate samples for each experimental trial of the RTFOT. The values of rutting resistance factor ($G^*/\sin\delta$ and high failure temperature) were measured and recorded. With respect to rubber-modified binders, the plate gap is modified with 2 mm considering the rubber particle effect [11,13].

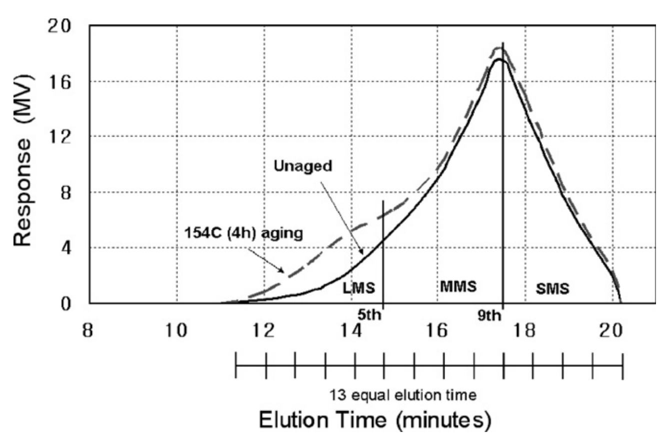

Fig. 2. Typical chromatograms of a virgin binder (unaged) and a short-term aged binder (154 °C oven aging for 4 h).

3. Results and discussions

3.1. Aging differences between the RTFOT and the STOA in the laboratory

Table 4 shows the measured values of the LMS obtained from the GPC test. Also, Fig. 3 shows the average increase of LMS ratios (LMS ratio = LMS value after aging/LMS value before aging) of nine asphalt binders after the RTFOT and the four STOA treatments. Since the original LMS contents are different from one another, it is appropriate to use LMS ratios in the analysis. The RTFOT resulted in an average increase of 21% in LMS ratios of samples, while the increase from the STOA treatments ranged from 29% (at 135 °C for 2 h) to 54% (at 154 °C for 4 h). These results indicate that the RTFOT has less effect on the aging of asphalt binders than the STOA treatments for the materials used in this study.

3.2. Short-term aging in the field

The comparison of the LMS ratios after the RTFOT, the STOA in the laboratory, and the short-term aging in the field is shown in Fig. 4. From statistical analysis, it was found that the LMS ratios of binders short-term aged at 135 °C for 4 h and 154 °C for 2 h were not significantly different at 5% level. Therefore, the average of two STOA treatments (at 135 °C for 4 h and at 154 °C for 2 h) was used as the value of the STOA. As the figure indicates, the aging effect among the binders which were short-term aged in the field varied widely (i.e., it was difficult to find a trend). The average increase in LMS ratio of six field mixes was observed to be approximately 25%. On the other hand, the laboratory aging methods (the RTFOT and the STOA) indicated a good correlation with each other. To evaluate the short-term aging of binders in the field, more data is needed in addition to information such as hauling distance, paving delays, temperature (ambient and compaction), and temperature segregation.

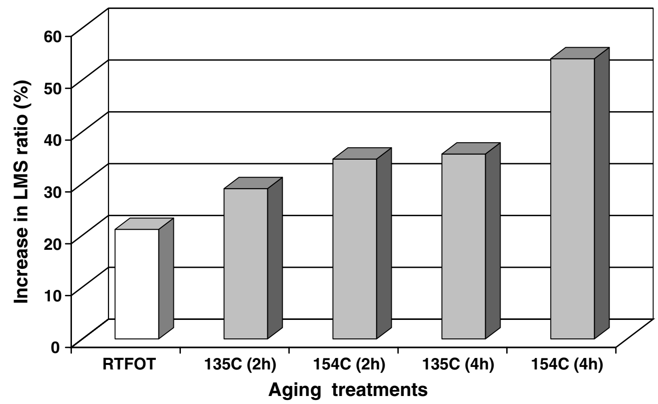

Fig. 3. Aging effect (increase in LMS ratio) by short-term aging treatments in the laboratory.

3.3. Effect of aging time in the RTFOT

The results of the GPC test indicate that the RTFOT and the STOA each have a different effect on the short-term aging of binders. In terms of the STOA, the aging time is related to the amount of binder absorbed by the aggregate as well as to the aging itself. As a result, the STOA periods of up to 2 h may be necessary to allow asphalt binder

Table 4
GPC test results; LMS (%)

Aging condition	Binder sources								
	Control (PG 64-22)			SBS-modified (PG 76-22)			Rubber-modified		
	A	B	C	A	B	C	A	B	C
Unaged	16.14	15.12	14.86	20.44	17.19	16.40	16.24	15.29	16.00
STOA									
135 C (2 h)	21.26	20.33	20.83	23.59	21.45	19.68	20.96	21.27	20.22
154C (2h)	22.56	20.34	21.87	24.24	21.57	20.79	23.32	21.59	21.64
135C (4 h)	21.95	21.27	21.67	24.87	22.60	21.44	22.68	21.86	21.14
154C (4 h)	25.47	24.56	23.68	26.71	24.15	24.81	26.21	25.56	24.96
RTFO aging									
163C (70 min)	18.12	18.98	19.31	21.13	19.54	17.53	20.60	18.21	18.81
163C (85 min)	18.94	19.29	19.86	22.90	20.09	18.33	20.84	18.45	19.51
163 C (100min)	19.47	19.71	20.12	22.99	21.04	18.61	21.50	18.59	20.57
163 C (115 min)	19.87	20.29	20.43	23.69	21.14	18.82	21.73	18.64	20.62
163 C (240 min)	22.47	23.92	23.54	25.33	23.22	20.78	24.51	20.32	–
Short-term aging (field)									
Test section 1	–	17.18	–	–	–	–	–	–	–
Test section 2	–	–	–	–	20.00	–	–	–	–
Test section 3	–	–	–	–	22.56	–	–	–	–
Test section 4	20.15	–	–	–	–	–	–	–	–
Test section 5	22.09	–	–	–	–	–	–	–	–
Test section 6	20.37	–	–	–	–	–	–	–	–

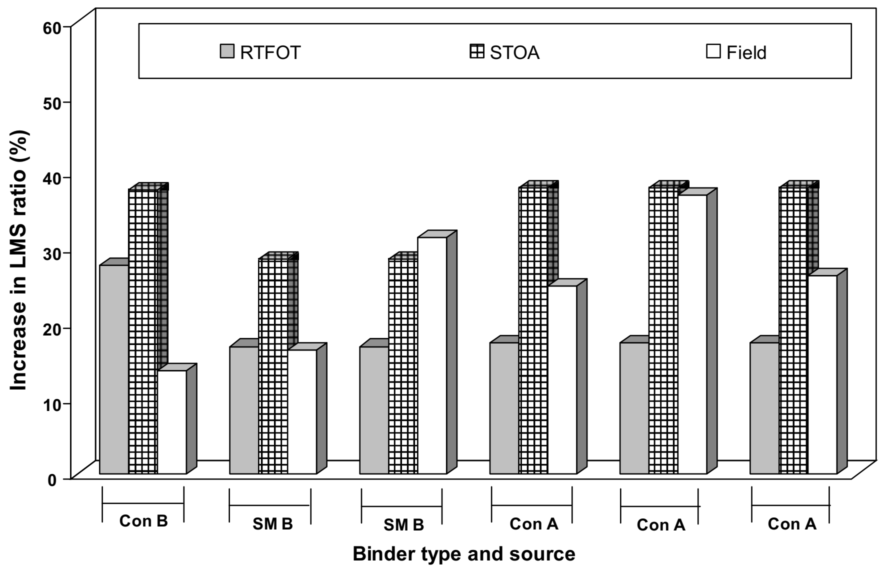

Fig. 4. Aging effect (increase in LMS ratio) by short-term aging in the field.

absorption to occur [15]. Therefore, decreasing the aging time of the STOA may not be advisable.

Table 5 shows the results of binder tests (the rotational viscosity test and the DSR test) as the aging time in the RTFOT increases. As expected, the longer aging time leads to an increase in the high temperature viscosity and in the high failure temperature of the binders tested. However, this trend was not consistent for RM binders. For example, RM A, B and C binders aged for 70 min in the RTFOT had higher viscosity than those aged for 85 min, and the RM B binder aged for 100 min had a higher failure temperature than that aged for 115 min. Ref. [4] observed that the coarse-ground tire rubber-modified binders spilled from the bottles during the RTFOT process. Ref. [11] reported that the fine rubber-modified binders exhibited unusual RTFO aging characteristics during the DSR testing. Because of the presence of rubber particles, standard superpave binder test procedures seem to have potential problems in measuring the properties of rubber-modified binders.

The rubber in asphalt binders was removed by a syringe filter in the GPC test. The increase in the LMS ratio from the different aging times in the RTFOT is illustrated in Fig. 5. RM binders exhibited higher LMS values for the longer RTFOT aging time, a trend similar to that of control and SM binders. Table 6 shows the predicted aging time in the RTFOT needed to obtain the same effect for the STOA in the laboratory. Although the limited number of binder sources and grades make it difficult to suggest the exact aging time for the RTFOT, the results obtained

Table 5
Test results of rotational viscometer and dynamic shear rheometer (DSR) of binders with different aging time in the RTFOT

RTFOT aging time	Binder sources								
	Control (PG 64-22)			SBS-modified (PG 76-22)			Rubber-modified		
	A	B	C	A	B	C	A	B	C
Rotational viscosity at 135 °C (Pa s)									
Unaged	0.430	0.703	0.472	1.475	1.862	2.025	1.155	2.513	1.357
70 min	0.647	1.070	0.623	2.412	2.569	2.313	3.094	5.663	3.069
85 min	0.660	1.160	0.660	2.688	3.063	2.544	2.175	5.200	2.101
100 min	0.712	1.322	0.673	2.912	3.244	2.607	4.675	7.857	2.500
115 min	0.740	1.350	0.705	3.263	3.663	3.038	3.950	7.500	2.487
240 min	0.941	1.724	0.930	3.649	4.112	3.357	4.641	9.882	4.014
High failure temperature (°C)									
Unaged	66.0	72.0	67.1	82.9	78.8	81.7	73.3	83.5	74.7
70 min	64.8	70.5	65.1	77.7	81.3	75.9	76.5	84.7	74.0
85 min	66.2	71.0	65.8	79.3	82.2	77.2	75.3	85.1	71.4
100 min	67.0	72.9	66.1	80.6	84.0	78.5	79.1	89.8	74.6
115 min	67.5	73.5	66.5	81.8	85.2	78.6	80.4	89.3	77.8
240 min	71.8	85.9	70.4	–	–	84.5	–	–	–

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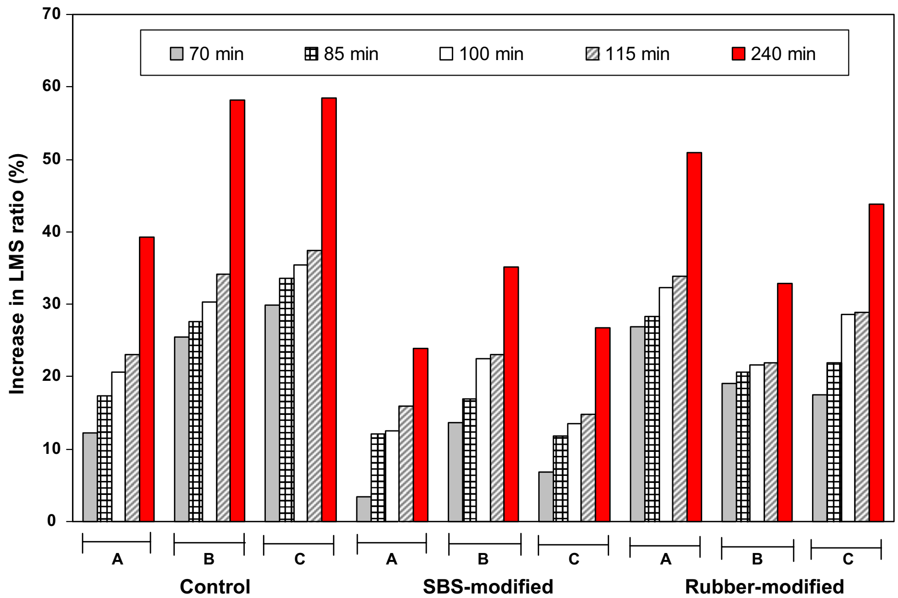

Fig. 5. Aging effect (increase in LMS ratio) by aging time in the RTFOT.

Table 6
Regression equations of aging time in the RTFOT versus aging effect based on the increase in LMS ratio (%)

Binder types	Regression equations	R^2	Predicted aging time[a] (min)
Control (PG 64-22)	$T = 0.0508(I^2) + 1.9908(I) - 0.2095$	0.99	165
SBS-modified (PG 76-22)	$T = 0.1422(I^2) + 3.8946(I) + 8.1274$	0.97	203
Rubber-modified	$T = 0.1226(I^2) + 0.5462(I) + 0.5150$	0.99	210
Total	$T = 0.0943(I^2) + 2.0099(I) + 1.0400$	0.99	189

T, aging time in the RTFOT (min); *I*, increase in LMS ratio (%).
[a] Predicted aging time in the RTFOT to simulate the aging effect of STOA.

indicate that the current aging time of 85 min at 163 °C may not effectively simulate the aging effect of the STOA in the laboratory, and, therefore, it needs to be increased.

4. Summary and conclusions

To compare the aging effect of the rolling thin film oven test (RTFOT) and the short-term oven aging (STOA) methods, nine asphalt binders (three control, three SBS-modified, and three rubber-modified binders) were prepared, and five aging times in the RTFOT and four aging treatments in the STOA were used in this study. Loose asphalt mixes were obtained from six paving fields. A series of gel permeation chromatography (GPC), rotational viscosity (RV), and dynamic shear rheometer (DSR) tests were conducted. From these results, the following conclusions were drawn:

(1) Based on the increase in the LMS ratios from GPC test, the RTFOT method (85 min at 163 °C) was found to have less aging effect on the binders than the STOA methods for asphalt mixtures in the laboratory.
(2) Since the aging effect among the binders which were short-term aged in the field varied widely, it was difficult to find any correlation of short-term aging between the laboratory and the field, but laboratory aging methods (the RTFOT and the STOA) indicated a good correlation with each other.
(3) As expected, the longer aging time in the RTFOT was found to lead to an increase in the high temperature viscosity and in the high failure temperature of asphalt binders, the only exception being rubber-modified binders. The GPC test for the crumb rubber-modified binders, in which the rubber in asphalt binders was removed using a syringe filter, was effective in evaluating the aging effect of rubber-modified binders for different RTFOT aging times.

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