

Effects of Reaction Time on Physical and Chemical Properties of Rubber-modified Binders

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ABSTRACT

One of the most successful methods of disposing of scrap tires is the use of crumb rubber in asphalt pavements. The time required to react the rubber with an asphalt binder is dependent on many factors including the chemistry of the asphalt binder and the rubber as well as the particle size and texture of the rubber and the reaction temperature. In this study, rubber-modified binders were produced using seven reaction times (5, 30, 60, 90, 120, 240, and 480 minutes) at the reaction temperature of 177°C. To evaluate the aging difference between rubber-modified and control binders, one control binder of PG 64-22 with the same binder source was also mixed at the same condition without adding the rubber. Superpave binder tests such as a rotational viscometer and a dynamic shear rheometer (DSR) were conducted to investigate physical properties of binders produced with different reaction times. In addition, gel-permeation chromatography (GPC) technique was used to detect molecular size distribution change of binders. The results from this study showed that 1) the longer reaction time had little effect on the increase of the viscosity and the high failure temperature of the control binder, and the properties of the rubber-modified binder were correlated with the reaction time; 2) there is no difference in the molecular size change between the control and the rubber-modified binders regardless of the reaction time.

INTRODUCTION

The increasing usage of crumb rubber in flexible pavements requires a better understanding of its effects on the physical, chemical, and rheological properties of rubber-modified binders. In general, the application of crumb rubber in an asphalt binder is intended to improve the binder properties by reducing the binder's inherent temperature susceptibility. The improvement of the properties of rubber-modified binders depends on the interaction between crumb rubber and binder where the rubber particles swell in the binder to form a viscous gel with an increase in viscosity of the rubber-modified binder (Green and Tolonen 1977, Heitzman 1992, Bahia and Davis 1994, Zanzotto and Kennepohl 1996, Kim et al 2001, Airey et al 2003).

The time required to react the crumb rubber with an asphalt binder is dependent on many factors including the chemistry of the asphalt binder and the crumb rubber as well as the particle size and texture of the crumb rubber and the reaction temperature.

This study investigated the physical and chemical characteristics of binders due to the different reaction times with the crumb rubber. Rubber-modified binders were produced using seven reaction times (5, 30, 60, 90, 120, 240, and 480 minutes) at 177°C. The rubber content was 10% by weight of the binder, and the mixing condition of 30 minutes at 177°C is the same procedure used in field application in South Carolina. The control binder of PG 64-22 was also mixed at the same condition without adding the rubber. The high temperature viscosity, rheological properties, and molecular size distribution of the binders after each reaction time were evaluated.

EXPERIMENTAL PROGRAM

Materials

One asphalt binder of PG 64-22 which was designated as control binder was collected from one binder source. Table 1 shows the properties of the control binder of PG 64-22. One

type of rubber which was produced by mechanical shredding at ambient temperature was prepared with a gradation as shown in Table 2. To ensure that the consistency of the rubber was maintained throughout the study, only one batch of rubber was used in this laboratory investigation.

Table 1. Properties of control binder (PG 64-22)

Aging states	Test properties	PG 64-22
Unaged binder	Rotational Viscosity @ 135 °C (Pa ·s)	0.430
	G*/sin(delta) @ 64 °C (kPa)	1.279
RTFO aged residue	G*/sin(delta) @ 64 °C (kPa)	2.810
RTFO + PAV aged residue	G* sin(delta) @ 25 °C (kPa)	4074.3
	Stiffness @ -12 °C (MPa)	217.0
	m-value @ -12 °C	0.307

Table 2. The gradation of crumb rubber used in this study

Sieve No.(µm)	% retaining
30 (600)	0
40 (425)	9.0
50 (300)	31.9
80 (180)	32.9
100 (150)	7.6
200 (75)	18.6

Binder mixing

The binder mixing used in this study was the wet process, in which the rubber serves as part of the asphalt binder in the asphalt concrete matrix. A mechanical mixer was used to blend the rubber and the control binder (Figure 1). The crumb rubber was added to asphalt binder using 7 reaction times of 5, 30, 60, 90, 120, 240, and 480 minutes, a reaction temperature of 177°C and a reaction speed of 700 rpm. To evaluate the aging difference between rubber-modified and control binder, the control binder of PG 64-22 was also mixed at seven reaction times and a reaction temperature without adding the rubber.

Rotational Viscometer

Superpave binder specifications include a maximum viscosity requirement of 3 Pa·s for an unaged binder. In this study, rotational viscosity test (AASHTO T 316) was used to



Figure 1. A mechanical mixer used in this study

verify the high temperature viscosity change as a function of different reaction times and a reaction temperature.

Dynamic Shear Rheometer

Dynamic shear rheometer (DSR) test (AASHTO T 315) was conducted on two replicate samples for each experimental trial of all treated binders. The values of $G^*/\sin\delta$ and high-temperature performance grades were measured and recorded.

Gel Permeation Chromatography (GPC)

GPC procedure

Waters GPC equipment with computerized software was used for chromatographic analysis of binders (Figure 2). A differential refractive meter (Waters 410) was used as a detector. A series of two columns (Waters HR 4E and HR 3) was used for separating constituents of asphalt binder by molecular size. For testing the sample at a constant temperature, the columns were kept at 35°C throughout the test in a column oven. The mobile phase was THF flowing at a rate of 1 ml /min.

The specified quantity of binder was randomly collected from the container containing the binder and was dissolved in THF. The concentration of dissolution was 0.5% by weight. Each GPC sample dissolved into THF was filtered through a 0.45 μ m syringe filter prior to injection into the injection module. A 50 μ l of dissolved sample was injected into GPC injector for each test. One test took 30 minutes and elution started at approximately 11 minutes from injection and ended at approximately 21 minutes, as shown in Figure 3. Testing for each sample was repeated three times and then the average value of LMS was reported.

GPC Result Analysis

A typical chromatogram of a virgin asphalt binder (unaged) is illustrated in Figure 3. The area under the curve represents 100% of the binder molecules injected into the GPC system (Kim et al. 2004). The asphalt binder constituents are generally classified into several groups (Jennings 1980, Jennings and Prabanic 1985, Kim et al. 1995, Noureldin and Wood



Figure 2. GPC system used in this study

1989, Wahhab et al. 1999). In this study, a chromatogram profile was partitioned into 13 slices and three parts: large molecular size (LMS; slices 1 to 5), medium molecular size (MMS; 6 to 9) and small molecular size (SMS; 10 to 13) (Figure 3). Only the front part, the LMS value, in the quantitative data of the chromatogram was used to evaluate the effects of reaction time. The research has shown that the large molecular size (LMS) of binder had good correlations with asphalt binder properties than other sizes (Jennings 1980, Kim and Burati 1993, Wahhab et al 1999). The increment of LMS due to aging was known to have good relation to increased viscosity (Jenning 1980, Kim and Burati 1993, Wahhab et al 1999).

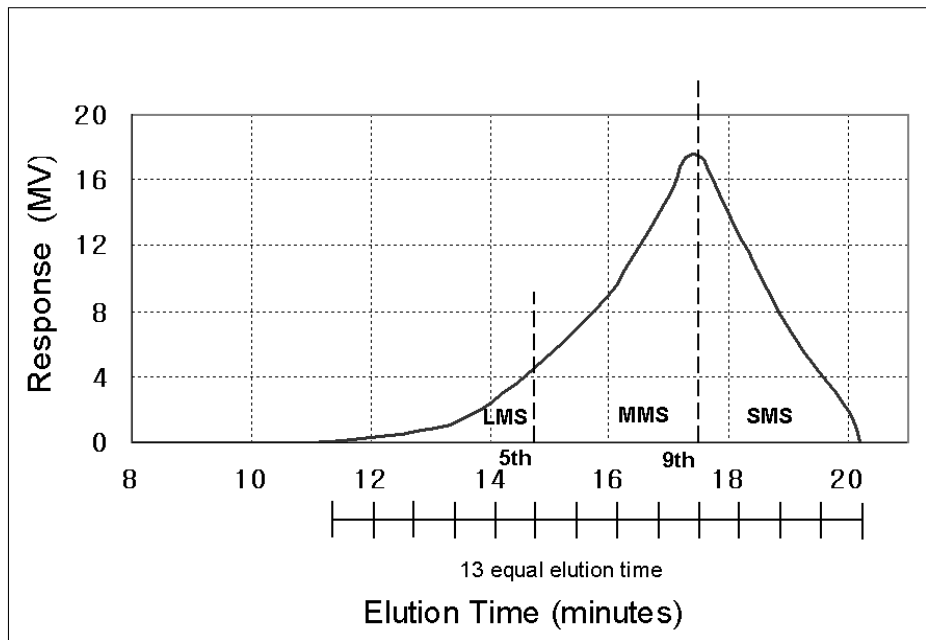


Figure 3. A typical chromatogram of a virgin binder of PG 64-22

RESULTS AND DISCUSSIONS

Rotational viscosity

Table 3 shows the high temperature viscosity values of the control and the 10% rubber-modified binders as the reaction time at 177°C increases from 0 to 480 minutes. Figure 4 shows the viscosity ratio to compare the increase in the viscosity as a function of reaction time (viscosity ratio of control binder = binder viscosity after each reaction time / binder viscosity before reaction, and viscosity ratio of rubber-modified binder = binder viscosity after each reaction time / binder viscosity after 30 minute reaction; the mixing condition of 30 minutes at 177°C using a high shear radial flow mixer (700 rpm) is used in South Carolina to produce field mixtures). The longer reaction time in the control binder almost had no effect on an increase in the high temperature viscosity of the binder tested. The longest reaction time, 480 minutes, resulted in the average increase of 6%, compared to the binder viscosity before reaction.

However, this trend was not consistent for the rubber-modified binder. Compared with the commonly used reaction time in South Carolina, 30 minutes, the viscosity increase ranged from -11% at 5 minutes to 46% at 480 minutes of reaction time (Figure 4). In general, the longer reaction time for production of rubber-modified binder seemed to lead to an increase in the viscosity. The result is thought to be associated with the increase in rubber mass through binder absorption.

High failure temperature

Table 4 shows the high failure temperature values from the DSR test as a function of reaction time. Similar to the viscosity at 135°C, the longer reaction time in the control binder had little effect on an increase in the high failure temperature. The difference of failure temperature between 0 and 480 minutes was 1.2°C. In terms of the 10% rubber-modified binder, the failure temperature at the shortest reaction time of 5 minutes was the smallest value of 73.8°C, and the longest reaction time of 480 minutes resulted in the increase of 2.9°C.

Figure 5 shows the failure temperature (FT) ratio of the binders (FT ratio of the control binder = FT after each reaction time / FT before reaction, and FT ratio of the rubber-modified binder = FT after each reaction time / FT after 30 minute reaction). As the figure indicates, the increased ratio of FT among the control binders varied; therefore, making it difficult to find a trend. With respect to the rubber-modified binder, FT ratio increased rapidly until the reaction time of 60 minutes. After 60 minutes, the binder had almost the same FT ratio regardless of the reaction time. The statistical results also indicated that the FT values of rubber-modified binders tested after 60, 90, 120, 240, and 480 minute reaction times were not significantly different at 5% level.

Large molecular size (LMS)

Table 5 shows the LMS values of control and rubber-modified binders from the GPC test as a function of reaction time. In general, the LMS values of both binders increased as the reaction time increased from one time to the next consecutive time. The LMS ratio of the binders (LMS ratio of control binder = LMS after each reaction time / LMS before reaction, and LMS ratio of rubber-modified binder = LMS after each reaction time / LMS after 30 minute reaction) is illustrated in Figure 6. The control and rubber-modified binders showed the increase of 14% and 10% in LMS ratio after 480 minutes of reaction time at 177°C, respectively.

The GPC test for the rubber-modified binder, in which the rubber in asphalt binders was removed by a syringe filter, showed the result similar with that of control binder, indicating that there is no difference between the control and the rubber-modified binders regarding the molecular size distribution after 7 reaction times used in this study.

Table 3. Rotational viscosity (Pa·s) as a function of reaction time

Binders		Reaction time (minutes)							
		0	5	30	60	90	120	240	480
Control (PG 64-22)	Mean	0.439	0.432	0.455	0.468	0.459	0.454	0.429	0.463
	St dev	0.025	0.023	0.023	0.015	0.019	0.001	0.005	0.001
Rubber-modified (PG 64-22 + 10% rubber)	Mean	-	1.092	1.220	1.421	1.542	1.583	1.558	1.779
	St dev	-	0.146	0.014	0.007	0.014	0.026	0.052	0.008

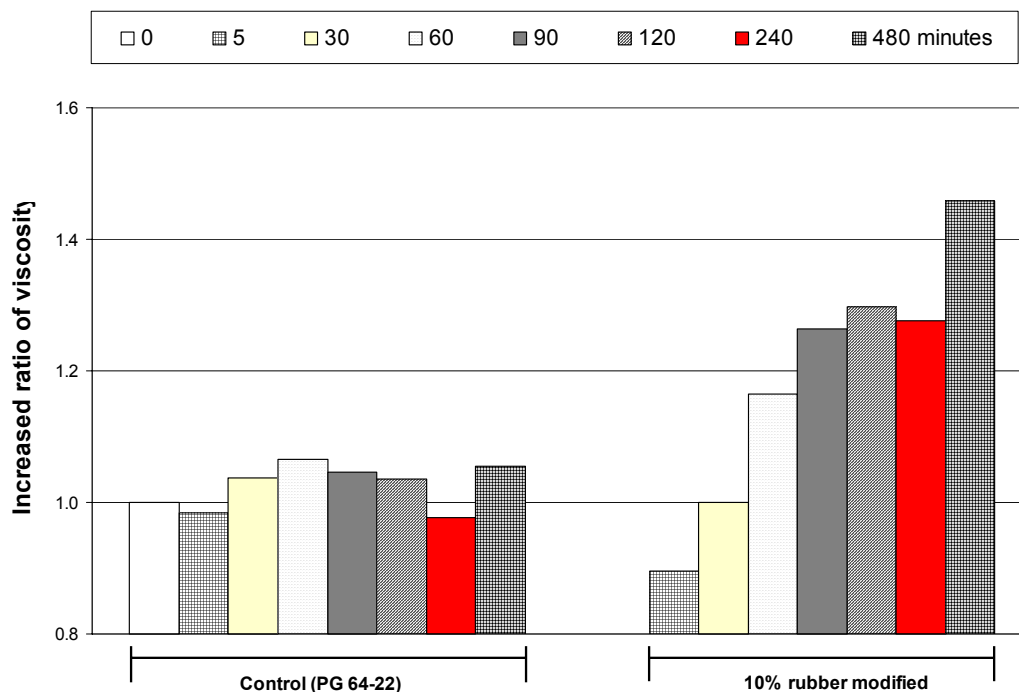


Figure 4. The viscosity ratio of control and rubber-modified binders

(viscosity ratio of control binder = binder viscosity after each reaction time / binder viscosity before reaction, and viscosity ratio of rubber-modified binder = binder viscosity after each reaction time / binder viscosity after 30 minute reaction)

Table 4. High failure temperature (°C) as a function of reaction time

Binders		Reaction time (minutes)							
		0	5	30	60	90	120	240	480
Control (PG 64-22)	Mean	66.0	65.5	67.1	65.8	66.9	67.4	66.9	67.2
	St dev	0.000	0.141	0.071	0.000	0.212	0.071	0.071	0.000
Rubber-modified (PG 64-22 + 10% rubber)	Mean	-	73.8	75.3	76.7	76.5	76.7	76.6	76.7
	St dev	-	0.071	0.283	0.566	0.071	1.131	0.283	0.424

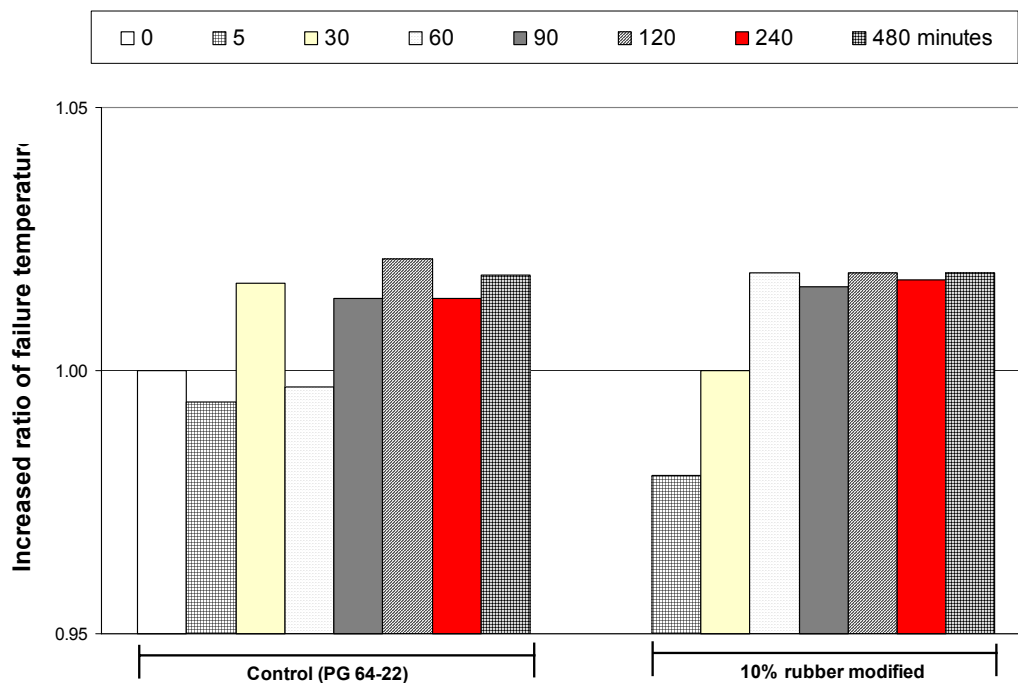


Figure 5. The high failure temperature ratio of control and rubber-modified binders

(FT ratio of the control binder = FT after each reaction time / FT before reaction, and FT ratio of the rubber-modified binder = FT after each reaction time / FT after 30 minute reaction)

Table 5. Large molecular size (% LMS) as a function of reaction time

Binders		Reaction time (minutes)							
		0	5	30	60	90	120	240	480
Control (PG 64-22)	Mean	16.14	16.15	16.38	16.97	17.08	17.23	17.63	18.39
	St dev	0.214	0.159	0.231	0.072	0.145	0.194	0.042	0.107
Rubber-modified (PG 64-22 + 10% rubber)	Mean	-	16.79	16.80	16.84	17.37	17.21	17.61	18.46
	St dev	-	0.177	0.182	0.115	0.031	0.377	0.177	0.195

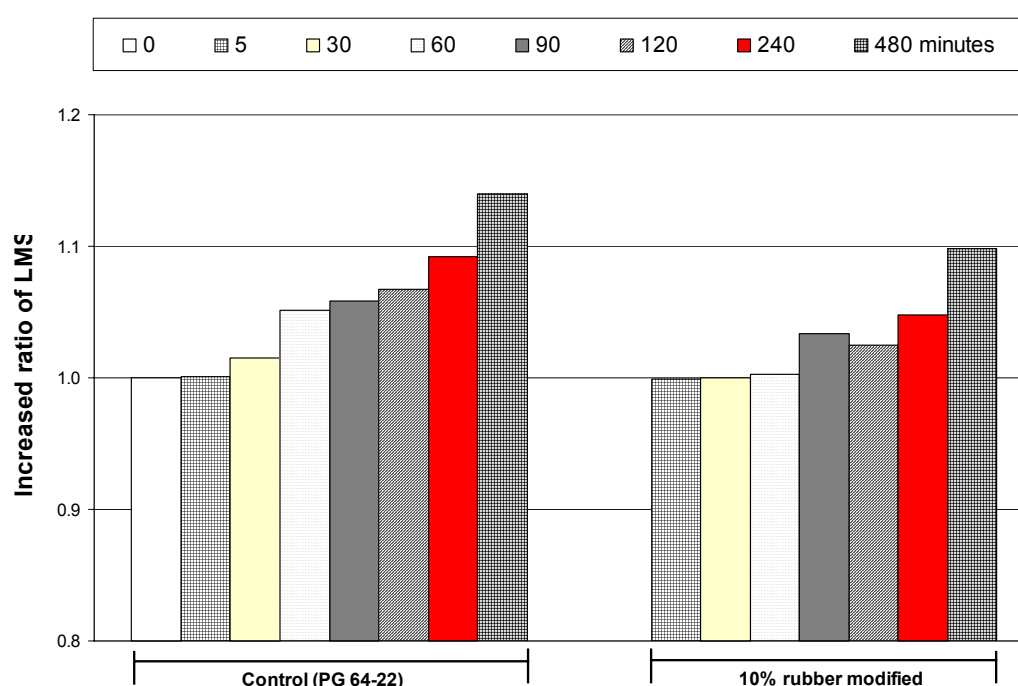


Figure 6. The large molecular size (LMS) ratio of control and rubber-modified binders

(LMS ratio of control binder = LMS after each reaction time / LMS before reaction, and LMS ratio of rubber-modified binder = LMS after each reaction time / LMS after 30 minute reaction)

SUMMARY AND CONCLUSIONS

To investigate the effects of the reaction time on the characteristics of rubber-modified binders, rubber-modified binders with one rubber source were produced using 7 different reaction times at 177°C. In addition, a control binder of PG 64-22 was mixed using the same reaction time and temperature without adding the rubber. A series of a rotational viscometer, a dynamic shear rheometer (DSR), and gel-permeation chromatography (GPC) tests were conducted. From these results, the following conclusions were drawn:

- (1) The longer reaction time was not effective in increasing the high temperature viscosity of the control binder, and in general, the longer reaction time for production of the rubber-modified binder seemed to lead to an increase in the viscosity, which is related to the increase in the rubber mass through binder absorption.
- (2) DSR tests indicated that the reaction time ranging from 0 to 480 minutes in the control binder had little effect on the increase of the high failure temperature, and with respect to the rubber-modified binder, the difference in the high failure temperature after the reaction times of 60, 90, 120, 240, and 480 minutes was not significant.
- (3) The GPC results showed that the longer reaction time seemed to lead to an increase in the LMS value of both the control and the rubber-modified binders, indicating that the LMS value of the binders is correlated to the reaction time regardless of the presence of the rubber.
- (4) It is recommended to conduct another study to evaluate the effect of the particle size and texture of the rubber and the reaction temperature. Also, further study with many other binder sources may be needed to generalize the findings.

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