Effect of Crumb Rubber on the Aging of Asphalt Binders

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ABSTRACT. *The application of crumb rubber in asphalt mixtures is intended to improve the binder properties by reducing the binder's inherent temperature susceptibility. This study was initiated to investigate the aging characteristics of binders due to the reaction with the crumb rubber. For this laboratory study, rubber-modified binders were produced using seven blending times (5, 30, 60, 90, 120, 240, and 480 minutes), three blending temperatures (177, 200, and 223℃), and four rubber contents (5, 10, 15, and 20% by weight of asphalt binder). To evaluate the aging difference between control and rubber-modified binders, the control binder of PG 64-22 was also mixed at seven blending times and three blending temperatures without adding the rubber. The control and rubber-modified binders were oven-aged for four periods (1, 4, 24, and 48 hours) at 177℃. Additionally, control and rubber-modified hot mix asphalt (HMA) mixtures were made in the laboratory and subjected to short-term and long-term aging treatments using a conventional oven. The viscosity of all binders was obtained, and gel-permeation chromatography (GPC) technique was used to detect molecular size distribution change of binders. The results from this study showed that 1) The GPC test was effective in evaluating the aging effect of both the control and rubber-modified binders under various blending conditions. 2) The asphalt binder with higher rubber content showed a higher large molecular size (LMS) value, and the increase in rubber content is considered to result in the additional loss of the low molecular weight in the asphalt binder. 3) After subjecting to the long-term aging, the asphalt mixtures with the control and rubber-modified binders were found to have very similar aging level.*

KEYWORDS: *blending time and temperature, GPC, rubber content, aging, LMS*

1. Introduction

1.1. *Background*

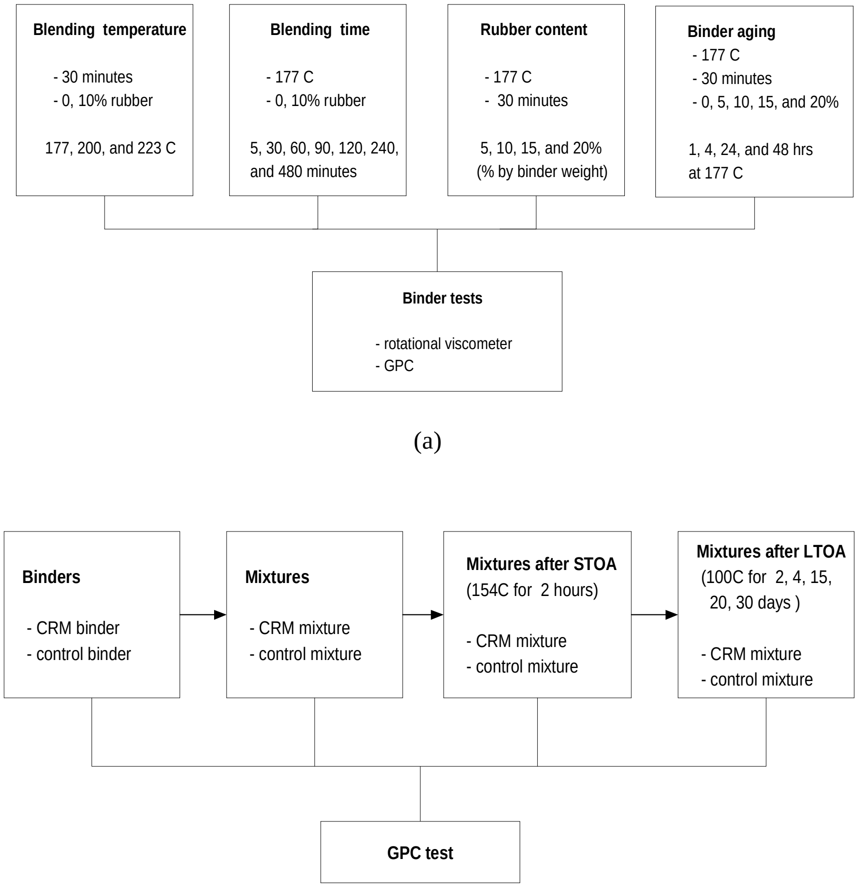
The increasing usage of crumb rubber in flexible pavements requires a better understanding of its effects on the physical, chemical, and rheological properties of crumb rubber modified (CRM) binders. In general, the addition of crumb rubber to an asphalt binder is intended to improve the binder properties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

The aging (hardening) of asphalt binder is usually associated with the loss of volatile components and oxidation of the asphalt binder during asphalt mixture construction (short-term aging) and progressive oxidation of the in-place material in the field (long-term aging) (Airey 2003). This process is attributed to the increase in the viscosity and high molecular weight molecules (asphaltenes) of the asphalt binder.

Asphalt composition, simply stated, is consisted of asphaltenes, resins, and oils. Asphaltenes are insoluble when the asphalt binder is dissolved in a nonpolar solvent such as pentane, hexane, or heptane. The component which is dissolved is called maltenes, and it is comprised of resins and oils. Vonk and Bull (1989) reported that when the rubber is added to an asphalt binder, it generally absorbs low molecular weight maltenes and leaves the residual asphalt binder containing a higher proportion of asphaltenes. Similarly, Airey et al (2002) indicated that the absorption of the lighter fractions of the binder into the crumb rubber and the subsequent changes in the rheology of the binder have a detrimental effect on the mechanical durability of the binder.

1.2. *Objectives and scope*

This study investigated the aging characteristics of binders due to the reaction with the crumb rubber. Rubber-modified binders were produced in the laboratory using seven blending times (5, 30, 60, 90, 120, 240, and 480 minutes), three blending temperatures (177, 200, and 223 °C), and four rubber contents (5, 10, 15, and 20%). The control binder of PG 64-22 was also mixed at the same condition without adding the rubber. Rubber-modified and control binders were aged at 177°C for 1, 4, 24 and 48 hours. Asphalt mixtures with rubber-modified or control binders were made and subjected to short-term (154°C for 2 hours) and long-term (100°C for 2, 4, 15, 20, and 30 days) aging treatments. The viscosity and molecular size distribution of binders after various treatment conditions were evaluated. Figure 1 shows a flow chart of the experimental design used in this study.



(a)

(b)

STOA: Short-term Oven Aging
LTOA: Long-term Oven Aging

Figure 1. *Flow chart of experimental design procedures for evaluating the effect of crumb rubber on the aging of (a) asphalt binders and (b) asphalt mixtures*

2. Experimental program

2.1. *Materials*

One asphalt binder source of PG 64-22 was used throughout the study. 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 used 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)	% retained
30 (600)	0
40 (425)	9.0
50 (300)	31.9
80 (180)	32.9
100 (150)	7.6
200 (75)	18.6

2.2. *Binder mixing*

The binder mixing used in this study was the wet process, in which the rubber is added to the asphalt binder before introducing it in the asphalt concrete matrix. A mechanical mixer was used to blend the rubber and the control binder. The crumb rubber was added to the asphalt binder at a blending speed of 700 rpm. To evaluate the aging difference between rubber-modified and control binders, the control binder of PG 64-22 was also mixed at seven blending times and three blending temperatures without adding the rubber.

2.3. *Aging treatment*

2.3.1 Binder aging

One control and four rubber-modified binders with 5, 10, 15, and 20% rubber by weight of asphalt binder were oven-aged for four periods of 1, 4, 24 and 48 hours at 177°C to simulate field applications (Shen et al. 2006).

2.3.2 Mixture aging

The aggregate was heated at 180°C for a minimum of 6 hours before being mixed with an asphalt binder. The hot aggregate and asphalt binders, at a temperature of 177°C, were mixed for 90 seconds using a mechanical mixer, and the asphalt mixture in loose condition was artificially aged in a conventional oven at a specified temperature and for a specified amount of time. The aging conditions used in this study are listed below:

- 154°C oven aging for 2 hours
- 154°C oven aging for 2 hours + 100°C oven aging for 2, 4, 15, 20, and 30 days

2.4. *Rotational viscometer*

Superpave binder specifications include a maximum viscosity requirement (3 Pa·s) for an unaged binder. In this study, rotational viscosity test (AASHTO T 316) was used to verify the high temperature viscosity change as a function of different blending times, blending temperatures, and rubber contents.

2.5. *Gel Permeation Chromatography (GPC)*

2.5.1 Sampling method

GPC test was carried out using two sampling methods in this study. For control and rubber-modified binders, a selected amount of the binder sample was collected and dissolved into tetrahydrofuran (THF). For asphalt mixtures with control or rubber-modified binders, a selected amount of the mixture sample (not the binder) was collected and dissolved into THF. Since THF is a strong solvent, the binder in the mixture was dissolved in 5 minutes with some shaking effort.

Kim et al. (2006) reported that it was possible to estimate the absolute viscosity of asphalt mixtures, including polymer-modified mixtures, directly from dissolution of RAP particles with THF without binder recovery using GPC. The coefficient of determination (R^2) of viscosity with GPC result was as high as 0.95 for the case of mixtures with a granite gneiss aggregate source and a normal binder and was ranging from 0.72 to 0.91 for polymer-modified mixtures. Additionally, two sampling methods (binder sample and mixture sample) showed no significant difference from each other at $\alpha = 0.05$ in mean difference.

2.5.2 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.

Figure 2. *GPC system used in this study*

For asphalt binders, 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. For asphalt mixtures, the specified quantity of asphalt mixture was randomly collected from the aged mixture and was dissolved into THF in a beaker. To match the concentration of the dissolution of 0.5% by weight, the mixture amount was calculated based on the binder content of the mixture, which is, in general, a known value in advance for mix design purposes.

Each GPC sample dissolved into THF was filtered through a 0.45μm syringe filter prior to injection into the injection module. A 50μl 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 large molecular size (LMS) was reported.

2.5.3 GPC result analysis

Typical chromatograms of a virgin asphalt binder (unaged) and an aged binder (154°C oven aging for 4 hours) are 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 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 aging effects. Previous research has shown that the large molecular size (LMS) of a typical binder had good correlations with asphalt binder properties (e.g., aging) than other sizes (Jennings 1980, Kim and Burati 1993, Wahhab et al 1999). The increment of LMS due to aging was known to have a good relation to an increase in the absolute viscosity value (Jenning 1980, Kim and Burati 1993, Wahhab et al 1999).

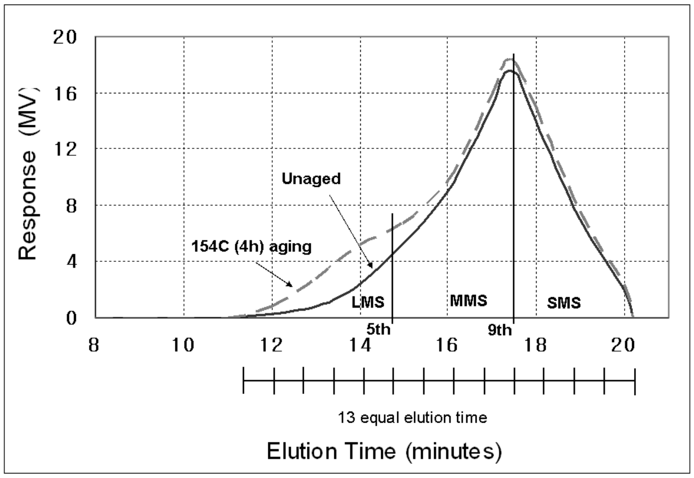


Figure 3. *Typical chromatograms of a virgin binder (unaged) and an aged binder*

3. Results and discussions

3.1. *Aging due to blending treatment*

3.1.1 Blending time

Figure 4 shows the high temperature viscosity change of the control and the 10% rubber-modified binders as the blending time, at 177°C, increases from 0 to 480 minutes. The longer blending time in the control binder was found to have little effect on an increase in the high temperature viscosity of the binder tested. The longest blending time, 480 minutes, resulted in an average increase of 6%. However, this trend was not consistent for the rubber-modified binders. Compared with the blending time of 30 minutes commonly used in South Carolina, the viscosity change ranged from -11% at 5 minutes to 46% at 480 minutes of blending time. In general, the longer blending time for production of rubber-modified binders 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.

Figure 5 shows the LMS change of the control and rubber-modified binders from the GPC test as a function of blending time. In general, the LMS values of both binders increased as the blending time increased from one time to the next consecutive time. 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 to that of control binder. From the t test results, there was no significant difference, at $\alpha=0.05$ level, between the LMS values of both binders after blending times of 60, 120, 240, and 480 minutes, respectively.

From the viewpoint of the binder aging, the viscosity at 135°C is considered not to be effective to represent the effect of different blending times. Relatively, the GPC test results showed the gradual increase in LMS values of both the control and rubber-modified binders as the blending time increased. It indicates that the GPC test is an effective tool in evaluating the aging effect of the binders as a function of blending times.

3.1.2 Blending temperature

The test results of viscosity and LMS values at three blending temperatures of 177, 200, and 223°C are illustrated in Figures 6 and 7. The effect of the blending temperatures was similar to that of the blending times. The viscosity of the control binder did not change much as a function of blending temperature. The viscosity of the rubber-modified binder increased 5% (at the blending temperature of 200°C) and 41% (at the blending temperature of 223°C), compared with the viscosity of rubber-modified binder produced at the blending temperature of 177°C. Figure 7 shows a consistent increase in the LMS values of both binders at the higher blending temperatures.

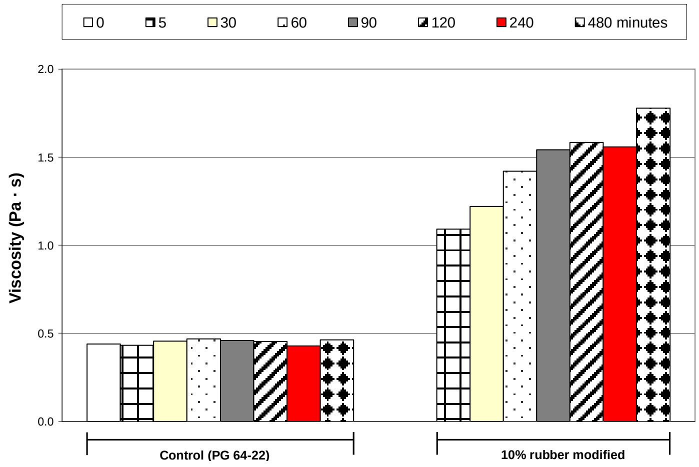


Figure 4. *The high temperature viscosity of control and rubber-modified binders as a function of blending time*

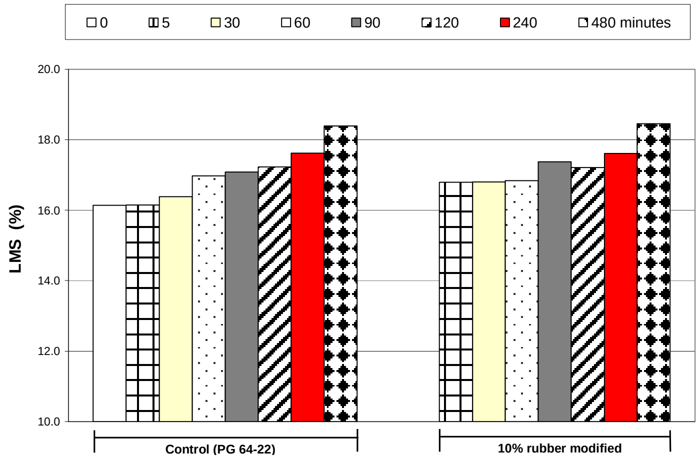


Figure 5. *The large molecular size (LMS) of control and rubber-modified binders as a function of blending time*

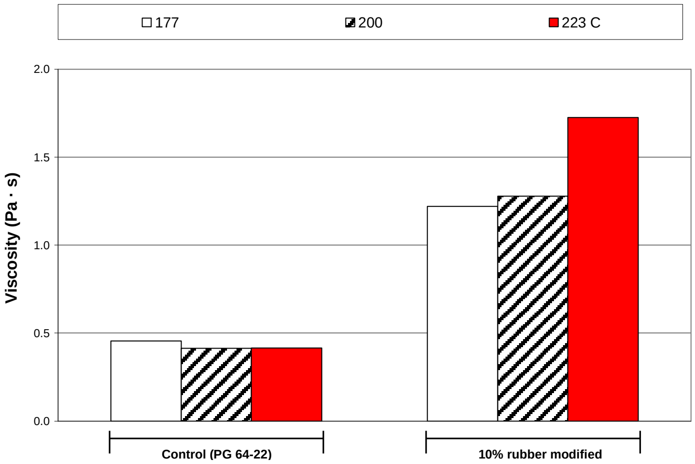


Figure 6. *The high temperature viscosity of control and rubber-modified binders as a function of blending temperature*

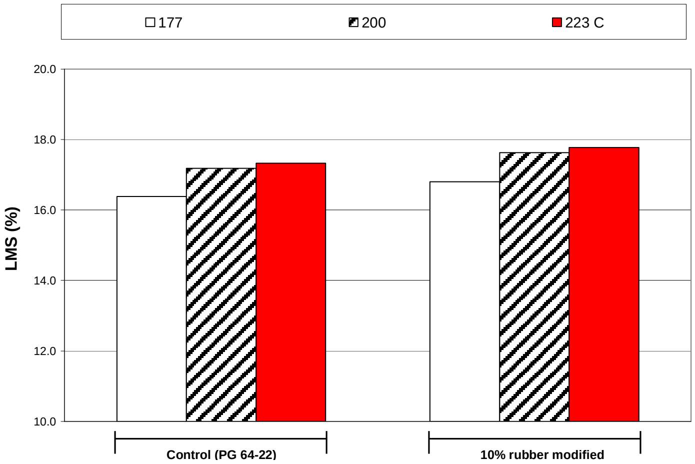


Figure 7. *The large molecular size (LMS) of control and rubber-modified binders as a function of blending temperature*

3.1.3 Rubber content

The influence of rubber content on the viscosity and the LMS values of asphalt binder are depicted in Figures 8 and 9. Figure 8 shows the significant increase in viscosity after the blending at 177°C for 30 minutes as the rubber content increases from 0 to 20%. In terms of the rubber content of 20%, the viscosity at 135°C was higher than a maximum viscosity requirement of 3 Pa·s. Compared with the rubber content of 10% by weight of asphalt binder, the 20% rubber content resulted in 479% and 7% increases in the viscosity and the LMS value, respectively.

The big difference between 479% increase (in the viscosity) and 7% increase (in the LMS) can be mainly explained with the presence of rubber particles when measuring the viscosity. Once the rubber is mixed in asphalt binder, the rubber is a cause of the higher viscosity. However, the rubber particles are removed by a syringe filter for the GPC test, and the GPC profile represents asphalt binder molecule distribution only. Therefore, while the viscosity changed significantly as a function of rubber content, the LMS value showed a slight change, as shown in Figure 9 (Kim et al. 2006).

With the same blending time and temperature maintained, the difference in LMS value between two rubber contents of 10 and 20% is thought to be the effect of crumb rubber on the binder aging. The increase in rubber content can result in the additional loss of the light oily fractions of the asphalt binder, tested for this study, during the blending.

3.2. ***Binder aging***

Figure 10 shows the GPC test results of control and four rubber-modified binders with different rubber contents as an aging period, at 177°C, increases to 48 hours. The binders with rubber contents of 0, 5, and 10% exhibited the higher LMS values for the longer aging period used in this study. In terms of 10% and 15% rubber-modified binders, the aging period necessary for the highest LMS value was decreased to 24 hours and 4 hours, respectively. It is important to note that the rate of increase in the LMS value relates to the rubber content. The results indicate that the rubber absorbs low molecular weight maltenes and leaves the residual asphalt binder containing a higher proportion of asphaltenes as other researchers previously reported (Vonk and Bull 1989).

The higher rubber content seemed to lead to the quicker increase in the LMS value at the aging condition used in this study. However, after a certain level, the LMS values of asphalt binders with relatively higher rubber contents such as 15% and 20% tended to decrease. For example, the asphalt binder with the highest rubber content of 20% showed the lowest LMS value after the longest aging period of 48 hours at 177°C (Figure 10).

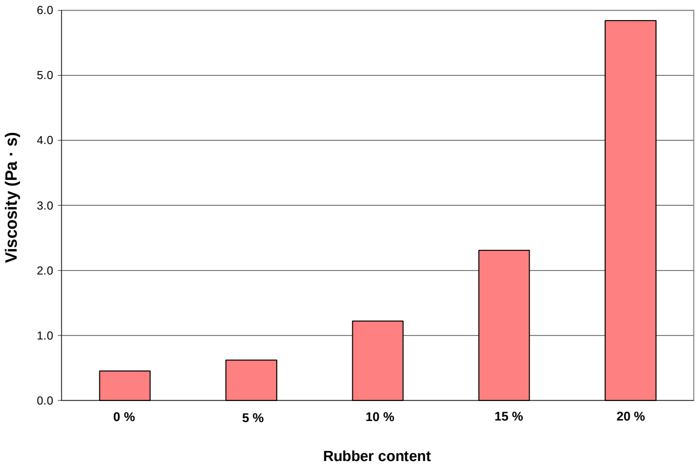


Figure 8. *The viscosity as a function of rubber content*

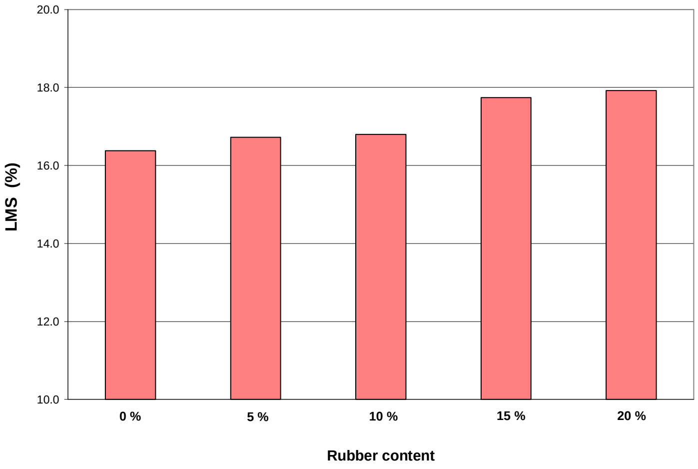


Figure 9. *The large molecular size (LMS) as a function of rubber content*

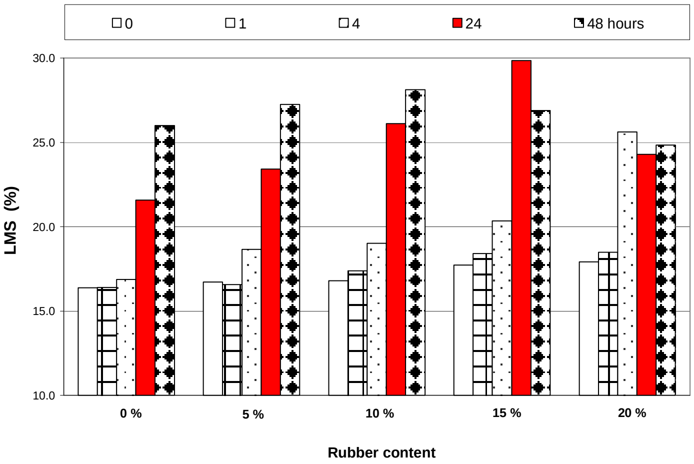
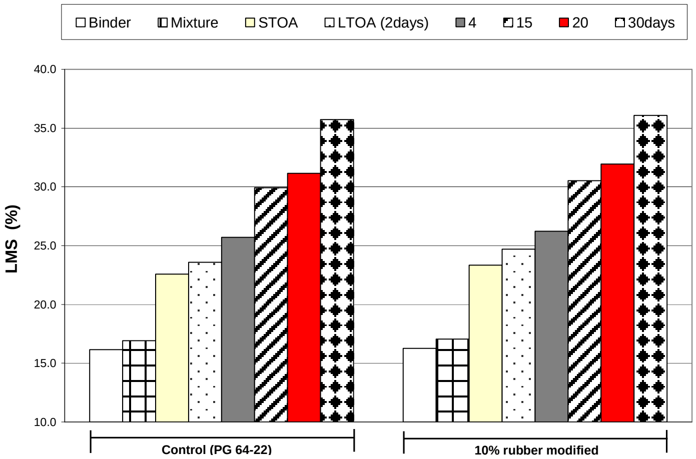


Figure 10. *The large molecular size (LMS) of control and rubber-modified binders as a function of aging period at 177°C*

3.3. *Mixture aging*

Figure 11 illustrates the increase in LMS values of control and 10% rubber-modified binders after subjecting to the STOA (short-term oven aging) and the LTOA (long-term oven aging). As this figure indicates, the asphalt binders show a very similar LMS change as a function of aging period in asphalt mixture conditions. The increases in the LMS values after the aging period of 30 days at 100°C were found to be 121 and 122% for the control and rubber modified binders, respectively.

When compared with the LMS values from the GPC test, the effect of mixture aging was different from that of binder aging shown in Figure 10. The reaction between the rubber and the asphalt binder varies depending on the temperature, viscosity, and chemical nature of both materials. The very thin film thickness of binder in asphalt mixture and the aging temperature of 100°C insufficient to make a reaction are thought to be the main reason to show no difference between the control and rubber-modified mixtures from the standpoint of the aging effect.



Mixture: binder after mixing with hot aggregate in the laboratory
STOA: Short-term Oven Aging
LTOA: Long-term Oven Aging

Figure 11. *The large molecular size (LMS) as a function of long-term oven aging period at 100℃*

4. Summary and conclusions

To investigate the aging characteristics of binders due to the reaction with the crumb rubber, rubber-modified binders were produced in the laboratory, using seven blending times, three blending temperatures, and four rubber contents. In addition, a control binder of PG 64-22 was mixed using the same blending condition without adding the rubber. The control and rubber-modified binders were aged at 177°C for 1, 4, 24, and 48 hours. Asphalt mixtures with control and rubber-modified binders were manufactured and subjected to the short-term and long-term oven aging treatments. A series of rotational viscometer and gel-permeation chromatography (GPC) tests were conducted. From these results, the following conclusions were drawn:

(1) The longer blending time and the higher blending temperature for the rubber-modified binder seemed to lead to an increase in the viscosity at 135°C, which is related to the increase in the rubber mass through binder absorption.

(2) The high temperature viscosity was found to be ineffective in evaluating the effect of blending times and blending temperatures on the binder aging. The GPC test, in which the rubber in asphalt binders was removed using a syringe filter, was effective in evaluating the aging effect of both the control and rubber-modified binders.

(3) The asphalt binder with the higher rubber content exhibited slightly higher LMS values, and the increase in rubber content is thought to result in the additional loss of the low molecular weight maltenes of the asphalt binder during the blending.

(4) In general, the higher rubber content resulted in the higher increase in the LMS value of asphalt binder under the aging conditions used in this study. With relatively higher rubber contents such as 15% and 20%, the asphalt binders showed a tendency that the LMS values decrease after a certain level.

(5) The results of LMS values of all mixtures subjected to the short-term and long-term aging indicated that the same aging level was produced comparing control sample with rubber-modified binders.

(6) It is recommended to conduct another study to evaluate the effect of the particle size and texture of rubber. Also, further study with many other binder sources may be needed to generalize the findings.

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