

Influence of Aging on HP-GPC Profiles of Recycled Aged Rubber

Modified Binders

Junan Shen, Visiting Professor, Clemson University, 310 Lowry Hall, Clemson, 29634-0119, SC, Tel:(864)-656-0114, Fax:(864)656-2670, E-mail:junanshen@clemson.edu

Serji Amirkhanian, Professor, Clemson University, 110 Lowry Hall, Clemson, 29634-0119, SC, Tel:(864)-656-3316, Fax:(864)656-2670

Soon-Jae Lee, Graduate student, Clemson University

Abstract

The Gel Permeation Chromatographic (GPC) profiles of aged binders are well reflected by some aging process. This paper presents a study to characterize the influence of an aging process on the profile of recycled aged rubber modified binders. RTFO and PAV aging tests were used for the aging of the recycled aged rubber modified binders. The molecular size distributions of two aged rubber modified binders and one control aged PG76-22 were measured by GPC. A rejuvenator and a softer binder were selected as the rejuvenating agents to identify the aging influence of the rejuvenating agents on the chromatographic profiles. For this project, 5 and 10% of the rejuvenator and 100 and 200% of the softer binder were mixed with the aged binders. A total of 30 blends were tested using GPC. It was concluded that compositional changes of the blends were well reflected by GPC for RTFO and PAV aging. Increases in Larger molecular size (LMS) and decreases in Medium molecular size (MMS) and in small molecular size (SMS) were observed by RTFO and as well PAV aging for all the blends regardless of the type of aged binders and the rejuvenating agents.

Keywords: GPC, Aging, Molecular size, aged binder, rubber modifier

INTRODUCTION

High pressure-gel permeation chromatography (HP-GPC) separates asphalt binders into fractions of various molecular sizes. This procedure can classify asphalt molecular size into three groups according to their molecular size (i.e., LMS: larger molecular size, MMS: medium molecular size, SMS: small molecular size). An increasing number of research studies are using HP-GPC technique to analyze and characterize asphalt binders. The use of this technique to characterize asphalt binders is gaining increasing acceptance among asphalt researchers, due to a number of promising findings indicating a direct link between HP-GPC profiles of binders and pavement performance (Garrick and Wood, 1988, Wahhab et al, 1999, Glover et al, 1988). GPC has been used to determine the variations in molecular size distribution of virgin and recycled asphalt binders associated with aging. Eleni et al (1995) discussed aging influence on chromatographic profile and the relationship between selected properties of the binders and the HP-GPC parameters. Ahmed and Wood (1989) reported the variations in molecular size distribution of virgin and recycled asphalt binders associated with aging. Kim et al (1993) investigated aging properties of asphalt binders. A common conclusion among researchers is that aging of an asphalt binder causes an increase in the LMS and a decrease in the MMS and SMS. These molecular size changes could result in a drastic change in asphalt binder's consistency.

Annually, there are more than 280 million tires disposed of in the United States. Currently, approximately 67% of these tires are utilized for applications such as tire derived fuel, molded products, crumb rubber, and other applications. Crumb rubber has been used as one of the modifiers for pavement binders for many years. The rubber modified asphalt binders, which are initiated decades ago in US, have better performance properties such as rutting resistance than virgin binders. Now, the need for recycling of aged rubber modified binders is increasing because more and more of these pavements are over 10 or 15 years old in some states. The properties of the blends of aged rubber modified binders and rejuvenating agents are still not very clear due to the presence of crumb rubber.

Due to the presence of the Crumb Rubber Modifier (CRM), the rubber modified binders could not be evaluated as well as neat binders by standard Superpave binder test procedures. Several potential problems were reported during DSR testing including stiffness-related problems, plate slip, and equipment limits. Some modifications of test procedures have been attempted such as increasing the gap of the plates to accommodate high percentage and coarse particle sizes of CRM. However, there is still no Superpave protocol for rubber modified binders recommended; therefore, the evaluation of the CRM binders is still confined to using the Superpave binder tests with modifications. New method to characterize rubber asphalt binder and recycled aged rubber asphalt binder is necessary.

RESEARCH OBJECTIVES

The main objective of the study was to investigate the aging influence on compositional changes of recycled aged modified binders with rejuvenating agents, as measured by HP-GPC techniques. In addition, the possibility of using GPC results to evaluate the rubber modified binders and aged rubber modified binders were investigated. Specific objectives of this study included

- 1) To investigate whether aging process produces significant differences among HP-GPC profile of aged asphalt binders.
- 2) To determine whether significant differences exist among the recycled binders by traditional rejuvenating agents (i.e., a rejuvenator and a softer binder) as measured by GPC results.

MATERIALS AND TEST PROCEDURES

Two crumb rubber modified binders were produced in laboratory using -40 mesh (maximum size 0.475mm) ambient crumb rubber modifier and two binder sources (graded as PG 64-22) mixed at 177C for 30 minutes (Shen et al, 2005 b). An artificially accelerated aging process of RTFO+PAV was used to generate aged rubber modified binders and control PG76-22 (3% SBS mixed with PG64-22).

After being produced, these aged binders were then mixed completely with either the rejuvenator or the softer binder at several contents of 5 and 10% by weight of the aged modified binders for the rejuvenator, and 100 and 200% by weight of aged binder for softer binder (PG52-28). The properties of the rejuvenator are listed in Table-1.

GPC was used to measure the blends of the aged binders added with the rejuvenating agents, the RTFO aged residuals and the PAV aged residuals as well. The tested blend combinations are listed in Table-2. The chromatographic profiles of the rejuvenator and the softer binder are shown in Figures 1 and 2; respectively.

Table 1 Properties of the rejuvenator

Items	values
Specific gravity, 15.6/15.6C	0.98-1.02
Viscosity, 60C CST	200-500
Flash Point, COC, C	204 min
RTFO-C 163C, Weight Loss %	4.0 Max
RTF-C, Viscosity ratio	2.5 Max
Compatibility, PC/S Ratio	0.5 Min
Saturates, w%	28 Max
Chemical Compatibility	0.2-1.2

Table 2 Blend combinations

Rejuvenating agents	Aged RM A	Aged RM B	Aged PG 76-22
Rejuvenator % by wt. of aged binder	0	0	0
	5	5	5
	10	10	10
Softer binder % by wt. of aged binder	100	100	100
	200	200	200

The GPC testing equipment consists mainly of a solution injection unit connected to six silica gel porous columns through which the sample solution is pumped. The silica gel pore arrangement allows larger molecules of a sample to flow through a differential refractometer detector, followed by progressively smaller molecules. The detector continuously scales the amount of molecules flowing through as a function of time. The system is connected to a recorder that gives a continuous tracing of time versus amount of flowing molecules. The equipment used in the test is shown in photo 1.

The GPC test procedure used in the test is summarized as follows:

1. An asphalt sample is weighed on a sensitive scale and is allowed to dissolve in a tetrahydrofuran (THF) solvent. Asphalt concentration in the solvent is adjusted to be 1/400. This is achieved by dissolving 0.0080 g of asphalt binder in a 3.2g solvent.
2. The solution is drawn by an injector and then filtered with a filter of 0.45 mm to ensure the purity of the solution.

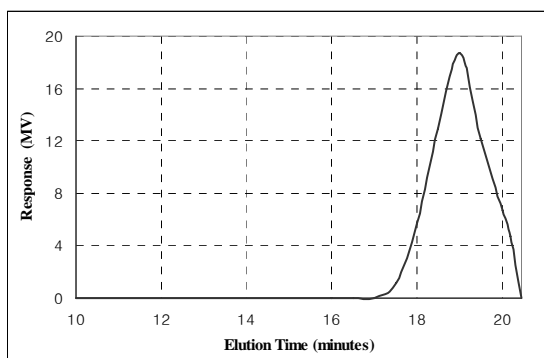


Figure 1 Profile of the rejuvenator

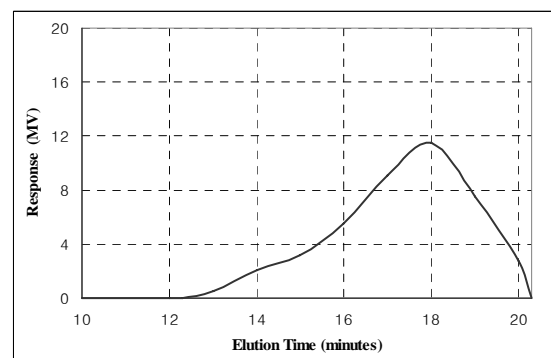


Figure 2 Profile of the softer binder PG 52-28

3. A 0.5-ml quantity of the solution is then immediately drawn by a smaller injector and injected into the GPC system through its injection unit.
4. The solution is drawn through the gel permeation columns and allowed to flow at a rate of 1 ml/min.
5. Test temperature is kept at 35C.



Photo 1 GPC set used in the study

The chromatographic profile of each asphalt sample was divided into 13 slices based on equal elution time between the starting and ending times period as shown in Figure 3 (Kim and Burati, 1993). The first 5 slices is defined as large Molecular Size (LMS). The next 6-9 slices are defined as Medium Molecular Size (MMS), the rest of the area under the curve is referred to as Small Molecular Size (SMS). All of the areas are expressed as percentage. The LMS is shown to be strongly related with the properties of the binders.

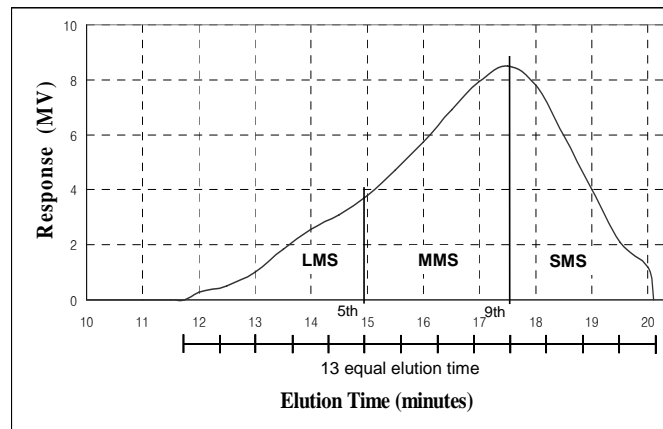
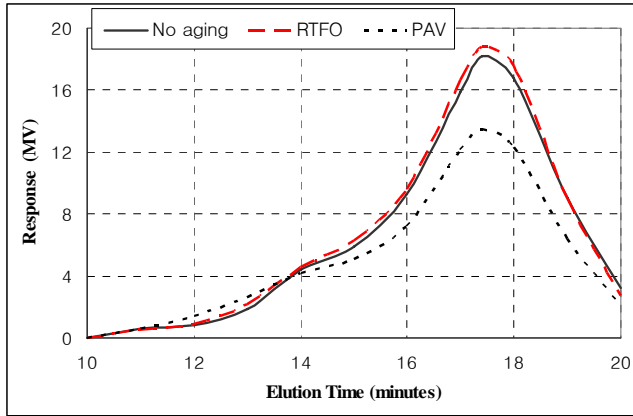


Figure 3 Methodology of Calculation of LMS, MMS and SMS

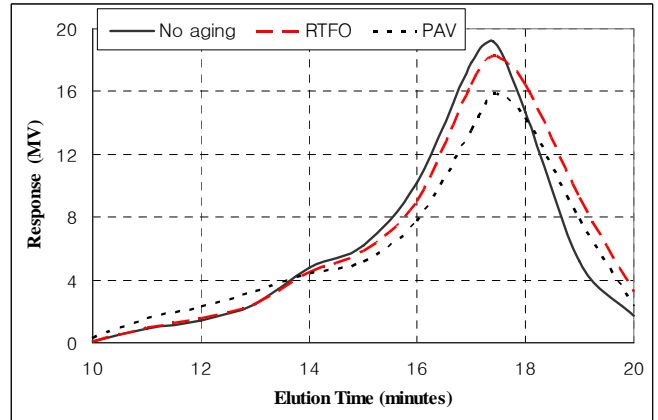
RESULTS AND DISCUSSIONS

GPC Profiles with aging

Figures 4, 5 and 6 show the chromatographic profiles of the blends of the two aged rubber modified binders and one control aged PG76-22 with softer binder at the 100% of content and rejuvenator at the 10% content; respectively. In general, it can be observed the trend that all the profiles moved to less elution time after RTFO aging and further to less elution time after PAV aging, except one case for rubber modified A containing 10% rejuvenator.

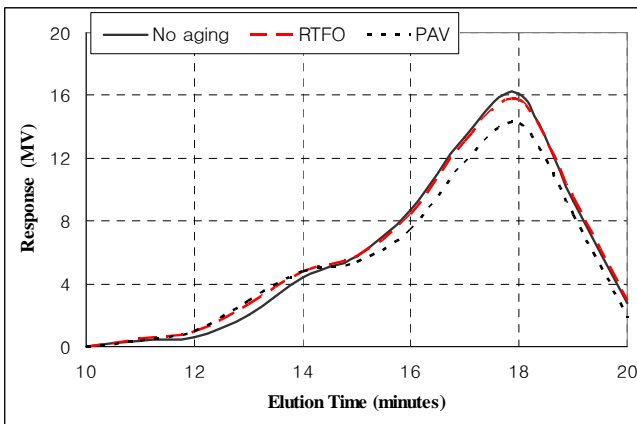


a)

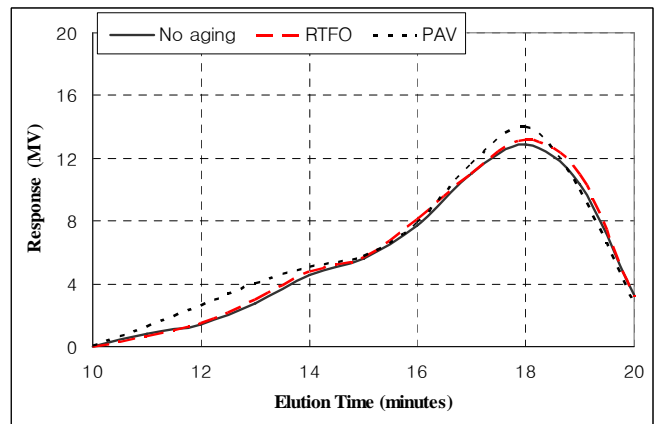


b)

Figure 4 Profiles changes of rubber modified binder A by aging with: a) 100% softer binder, b) 10% rejuvenator

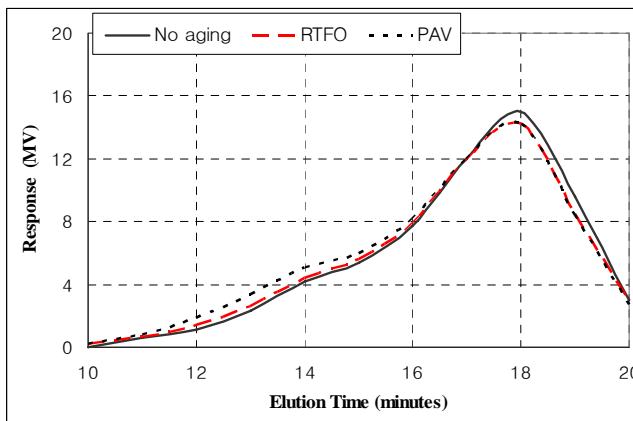


a)

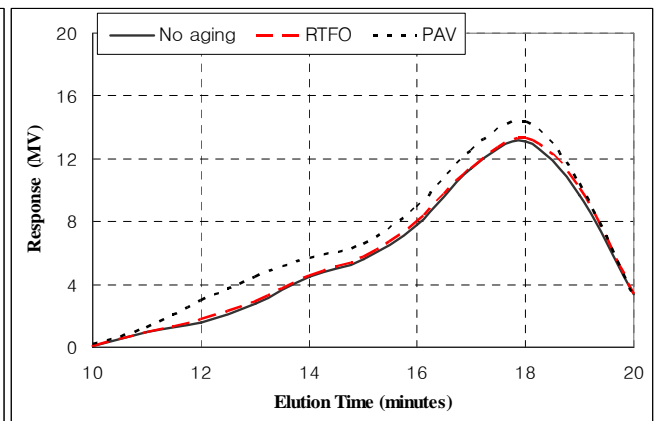


b)

Figure 5 Profiles changes of blend of rubber modified binder B by aging with: a) 100% softer binder, b) 10% rejuvenator



a)



b)

Figure 6 Profiles changes of the blends of aged PG76-22 by aging with: a) 100% softer binder 100%, b) 10% rejuvenator

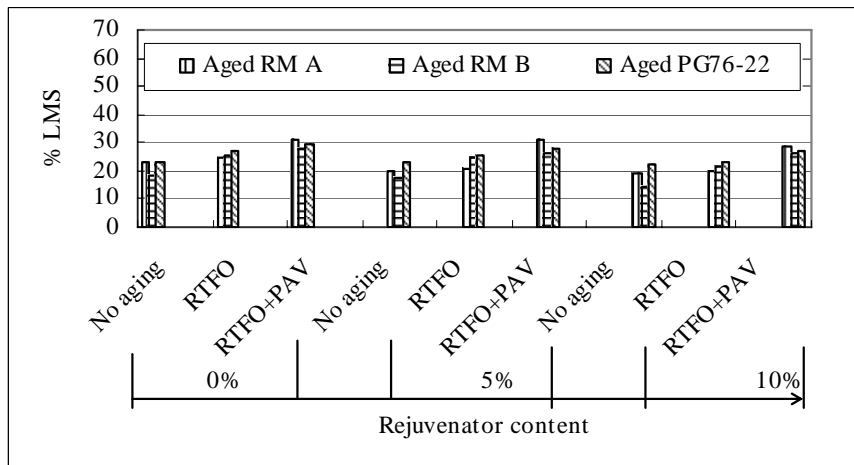
Obviously, the PAV aging produced a bigger increase in the larger molecular size (left side of the curves) than RTFO aging for all the blends. The profile changes due to the aging are similar to the two rubber modified binders and the control PG 76-22, regardless of the rejuvenating agents.

LMS, MMS and SMS of the blends

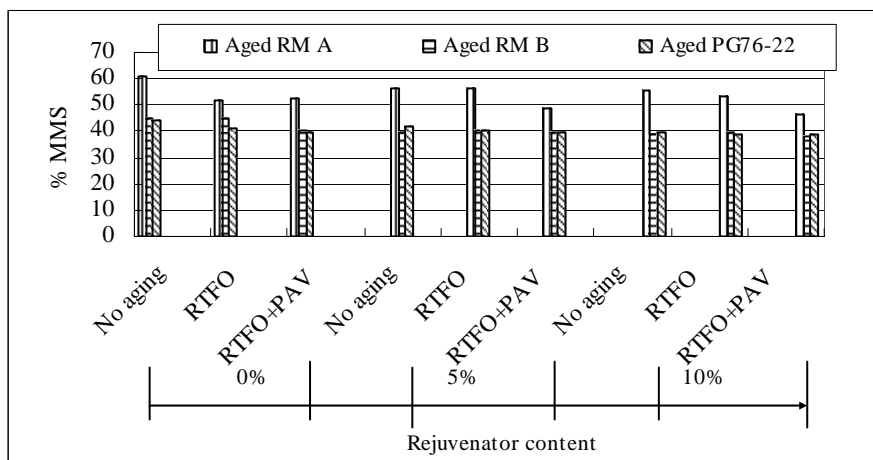
Increases in LMS of the blends by RTFO aging were observed, as shown in Figures 7 a) and 8 a) as well. This finding was true for all the blends. Further aging with the PAV caused further increases in the LMS of all blends. For some of the blends, a bigger increase in the LMS by RTFO was observed than that caused by the PAV aging.

Decreases in MMS of the blends by RTFO aging were observed, as shown in Figures 7 b) and 8 b) as well. This trend was true for all the blends.

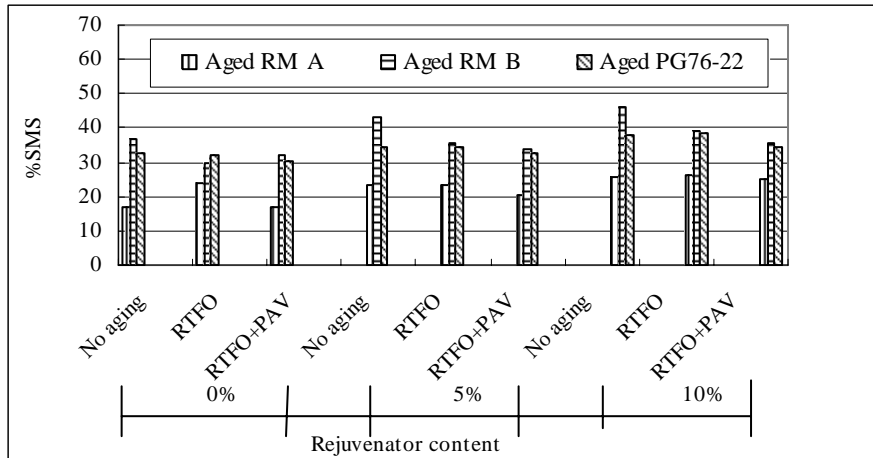
A further PAV aging caused further reduction in MMS. Decreases in SMS of the blends by the RTFO aging were observed also, as shown in Figures 7 c) and 8 c) as well. Similarly, this finding was true for all the blends discussed in the study.



a)

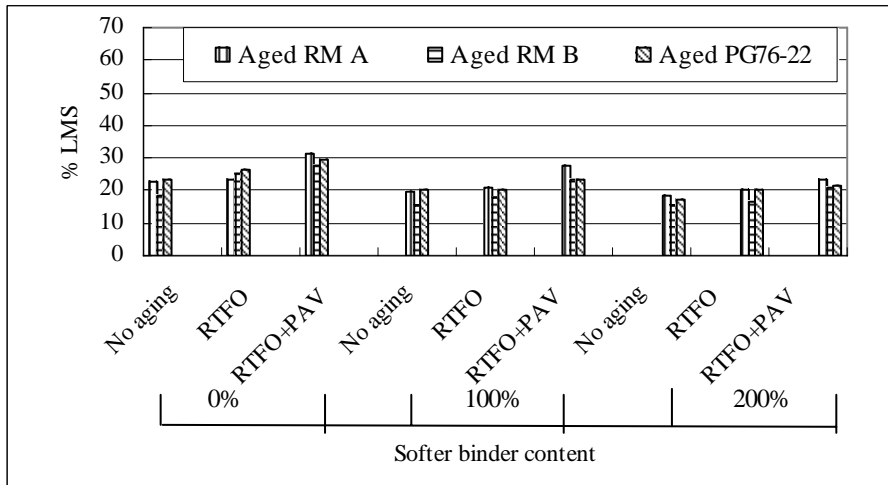


b)

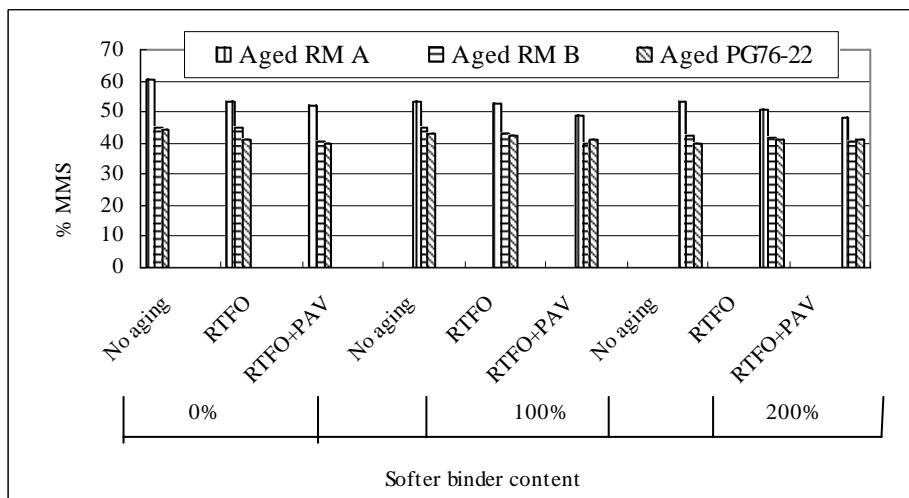


c)

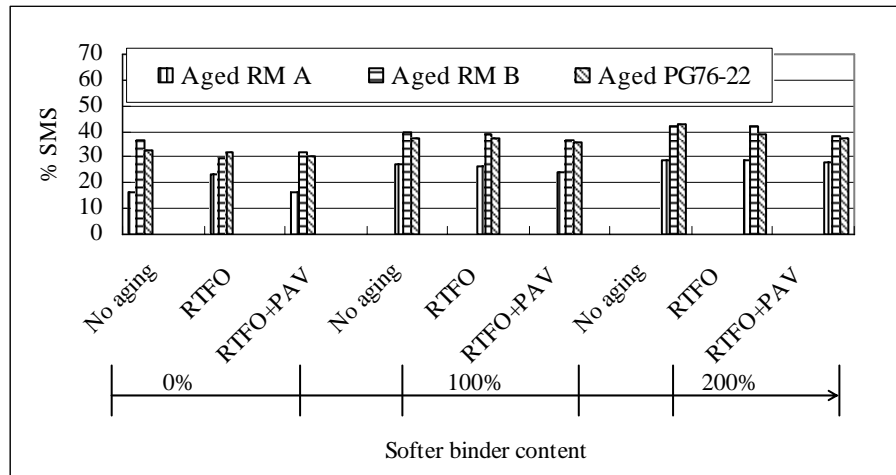
Figure 7 Aging influence on the molecular sizes of the blends using rejuvenator
a) LMS; b) MMS; c) SMS



a)



b)



c)

**Figure 8 Aging influence on the molecular sizes of the blends using rejuvenator
a) LMS; b) MMS; c) SMS**

SUMMARY AND CONCLUSIONS

A series of GPC tests was carried out for recycled aged rubber modified asphalt binders and a control PG 76-22. The influence of RTFO and PAV aging on the chromatographic profile change was investigated. In addition, the influence of the aging on the three molecular size distributions was discussed. Conclusions are drawn as follows:

- 1) Compositional changes of different blends of aged binders, which were caused by aging are reflected well by the GPC. The chromatographic profiles moved forward after RTFO aging, and moved further after PAV aging.
- 2) Increases in LMS and decreases in MMS and SMS, which were caused by RTFO and PAV testes, were observed for all blends, regardless of the types of the aged binder, the types of the rejuvenating agent and the contents of the rejuvenating agents added.

REFERENCES

- 1) Norman W. Garrick and Leonard E. Wood (1988), Relationship between High-pressure Gel Permeation Chromatography Data and the Rheological Properties of Asphalts, TRB, 1096, pp35-41.
- 2) Kim, Kwang W., Burati, J. L. and Park, Je-Seon (1995), Methodology for defining LMA portion in asphalt chromatogram, Journal of Materials in Civil Engineering, ASCE, Vol. 7. No.1, pp31-40.
- 3) Kim, Kwang W., Burati, J. L. Jr. (1993), Use of GPC chromatograms to characterize aged asphalt cements. Journal of Materials in Civil Engineering, Vol.5, No.1 pp 41-52.
- 4) C.J. Glover, R.R. Davison, J.A. Bullin, J.W. Button, and G.R. Donalson (1988), Chemical Characterization of asphalt cement and performance-related properties. TRB No.1171, pp71-81.
- 5) H.I. Al-Abdul Wahhab, I.M. Asi, F.M. Ali, and I.A. Al-Dubabi (1999) Prediction of asphalt rheological properties using HP-GPC, Journal of Materials in Civil Engineering, ASCE, Vol.11, No.1, pp6-14.
- 6) Ahmed Samy Noureldin and Leonard E. Wood (1989), Variations in molecular size distribution of virgin and recycled asphalt binders associated with aging, TRB 1228, pp191-197.
- 7) Eleni Vassiliadou Churchill, Serji N. Amirkhani, and James L. Burati Jr. (1995), HP-GPC Characterization of Asphalt Aging and Selected Properties, Journal of Materials in Civil Engineering, ASCE, Vol. &. No.1, February, 1995.
- 8) Junan Shen, Serji Amirkhani and Soon-Jae Lee (2005 a), GPC Characterization of Recycled Aged

Rubber Modified Binders, International Conference on Pavement Technologies, Seoul, South Korean.

9) Junan Shen, Serji Amirkhanian and Soon Jae Lee (2005 b), "Effects of Rejuvenating Agents on Recycled Aged Rubber Modified Binders", TRB, 84th Annual Meeting, Compendium of papers CD-ROM.