HP-GPC Characterization of Recycled Aged Rubber Modified Binders

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Abstract

The chemical compositions of asphaltens, resins, aromatics and saturates of asphalt binders change greatly by aging. As a result, the aged binders become harder and brittle. Recycling of aged asphalt binders is essentially a reverse process of aging that is typically achieved by adding rejuvenating agents into the aged mixes. The properties of the aged binders are thus recovered due to the rebalance of the characteristics. This paper presents a study to characterize the recycled aged rubber modified binders by Gel Permeation Chromatography (GPC). 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 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; respectively. Totally, 15 blends were tested using GPC. It was concluded that compositional changes of the blends with various contents of either rejuvenator or softer binder are well reflected by GPC. Larger molecular size (LMS) of the blends decreased and small molecular size (SMS) increased with the increased concentration regardless of the type of aged binders and the rejuvenating agents.

Key words: GPC, Rubberized asphalt, Recycling

INTRODUCTION

The chemical compositions of asphaltens, resins, aromatics and saturates of asphalt binders change greatly by aging. As a result, the aged binders become harder and brittle. Recycling of aged asphalt binders is essentially a reverse process of the aging that is typically achieved by adding rejuvenating agents into the aged binders. The properties of the aged binders are thus recovered due to the rebalance of the characteristics. Asphalt is a complex compound with different fractions in molecular size. The fractions have an important attribute of the asphalt's durability and its ability to perform properly paving mixture. Aging of asphalt binders caused by thermal, oxygen, light and environmental factors changes their characteristics towards producing more asphaltens and less aromatics. When recycling, rejuvenating agents are added into the aged binders and thus adjust the unbalanced chemical compositions to a consistency level appropriate to the mix. In another word, recycled aged binders have to have proper molecular size distribution.

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). It 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 researches is that aging of an asphalt binder causes an increase in the LMS and decreases in the MMS and SMS. These molecular size changes could result an drastic change in asphalt binder's consistency.

Recycling is traditionally evaluated by the physical and performance-based properties of the blends of aged binders mixed with rejuvenating agents, regarding to the selection of the type of the rejuvenating agents and the determination of the content of the agents, such as viscosity, penetration and more recently by rheological properties (DSR, BBR). Some reports suggested a chemical composition analysis be carried out for the blends of aged binders with a rejuvenating agent so that the blends can have a uniform composition.

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 base asphalts. 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 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 objectives of the study were to study compositional changes of recycled aged modified binders with rejuvenating agents, as measured by HP-GPC techniques, and to investigate the possibility of using GPC results to evaluate the rubber modified binders and aged rubber modified binders. Specific objectives of this study included

1) To study the feasibility of using GPC results to evaluate the recycled aged rubber modified binders.
2) To investigate whether recycled aged rubber modified binder and the control PG76-22 produced significant differences among HP-GPC profile of aged asphalt binders.
3) To determine whether significant differences existed among traditional rejuvenating agents, a rejuvenator and softer binder, when mixed with binders as measured by GPC results.

MATERIALS AND TEST PROCEDURES

Two crumb rubber modified binders are produced in laboratory using -40 mesh (maximum size 0.425mm) (ambient crumb rubber modifier and two binder sources (graded as PG 64-22) mixed at 177C for 30 minutes (Shen et al, 2005). 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. The tested sample 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 GPC test combinations

Rejuvenating agents	Aged RM A	Aged RM B	Aged PG76-22
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

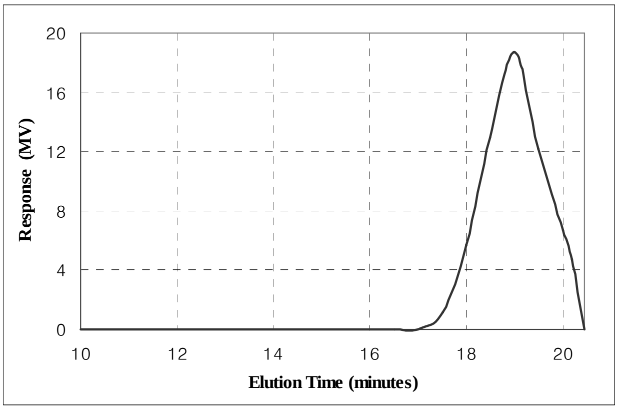


Figure 1 Profile of the rejuvenator

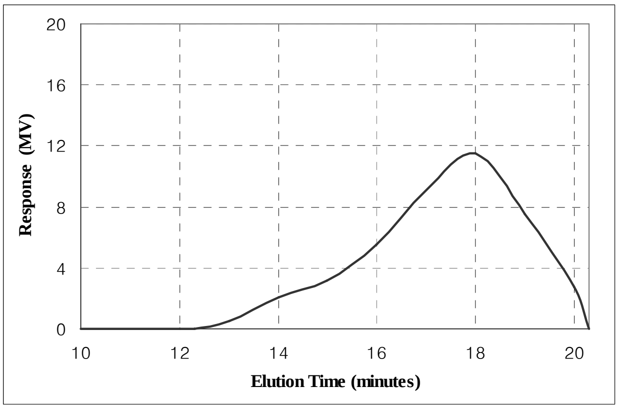


Figure 2 Profile of the softer binder PG 52-28

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 photo1.

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.
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 staring 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 is 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.

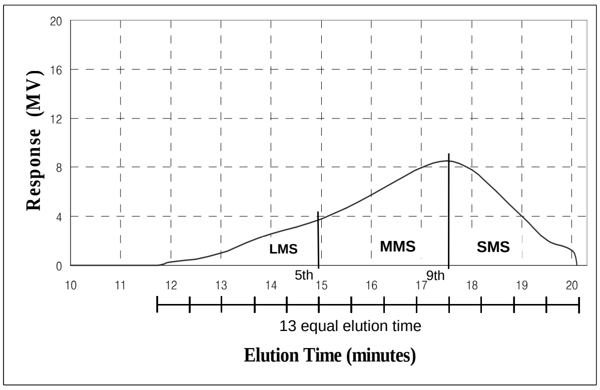


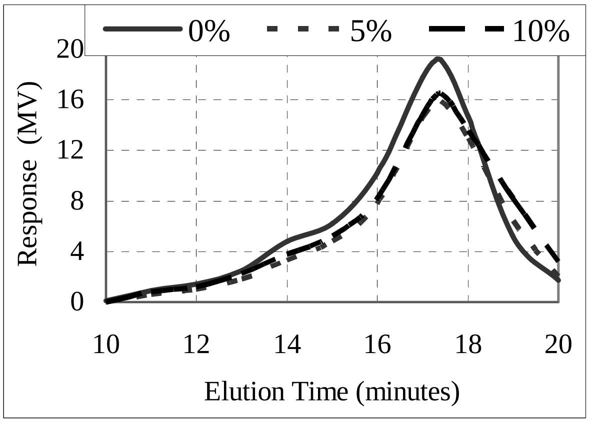
Figure 3 Methodology of Calculation of LMS, MMS and SMS

RESULTS AND DISCUSSIONS

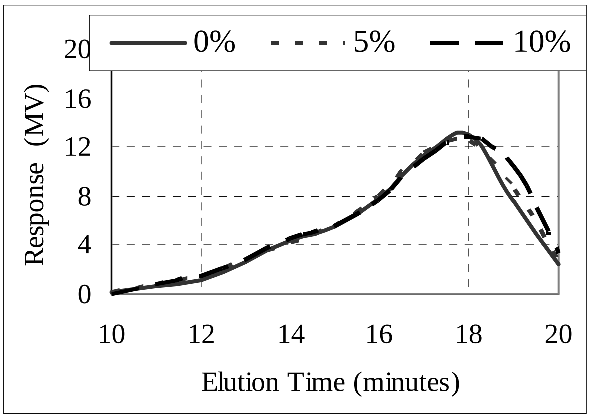
GPC profiles of the blends

Figure 4 illustrates the profile changes of all the three aged binders by adding rejuvenator. The profiles of all the recycled aged binders changed with the content of the rejuvenator. Generally, the profiles of recycled aged binders moved backward with increased rejuvenating content. With the increased content of the rejuvenator, LMS of the blends increased and SMS decreased. These results indicated that recycling of aged rubber modified binders using rejuvenator is apparently a reverse process of aging of asphalt binders as observed by most researchers using GPC.

The profiles of the blends of aged PG76-22 with rejuvenator contents of 5 and 10% have higher peak values than the aged PG 76-22 binder compared with the other two pictures of aged rubberized binders, see Figure 4 c). However, this difference did not change the fact that the LMS of the blends of aged PG76-22 decreased, whereas SMS increased with the increased content of the rejuvenator.
Figure 5 illustrates the profile changes of all the three aged binders by adding softer binder. Similarly, the profiles of all the recycled aged binders changed with the content of the softer binder. The profiles of the recycled aged binders moved backward with an increase in the softer binder content. The profiles of recycled aged PG76-22 have higher peak values than the aged PG 76-22 binder, see Figure 5 c), however, with the increased content of the rejuvenator, the LMS increased and SMS decreased. There is no different between the chromatographic profile trends of the blends using either a rejuvenator or a softer binder.



a)



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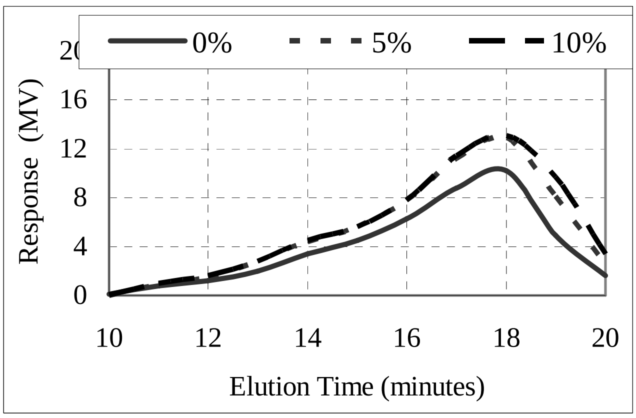
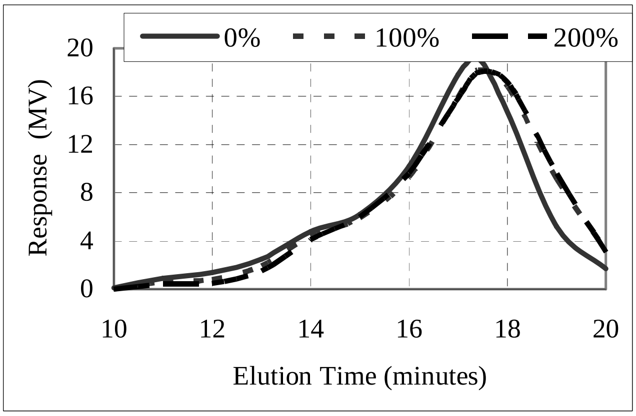


c)

Figure 4 Profiles of blends of the aged binders with rejuvenator;
a) aged rubber modified binder A;
b) aged rubber modified binder B;
c) aged control PG76-22



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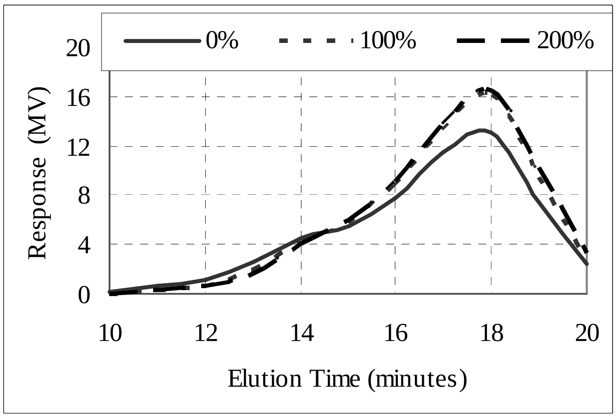

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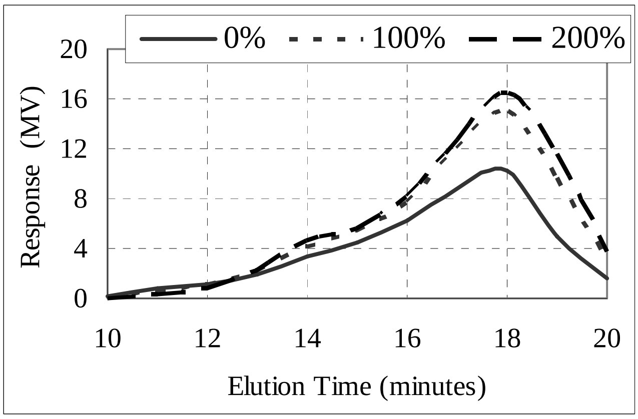


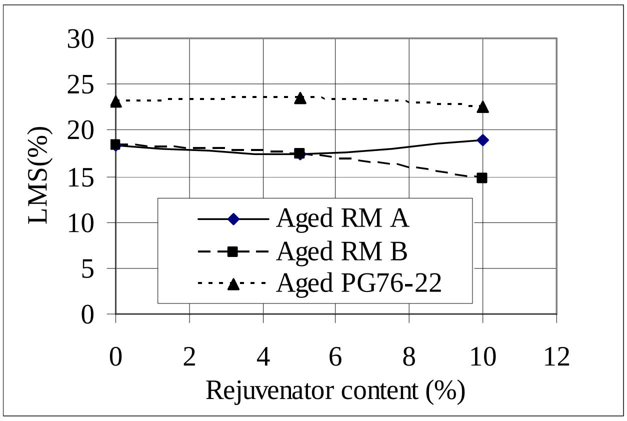
c)

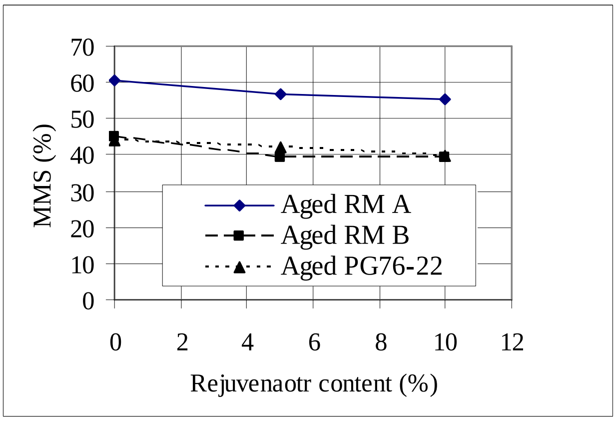
Figure 5 Profiles of blends of the aged binders with softer binder;
a) aged rubber modified binder A;
b) aged rubber modified binder B;
c) aged control PG76-22

LMS, MMS and SMS of the blends

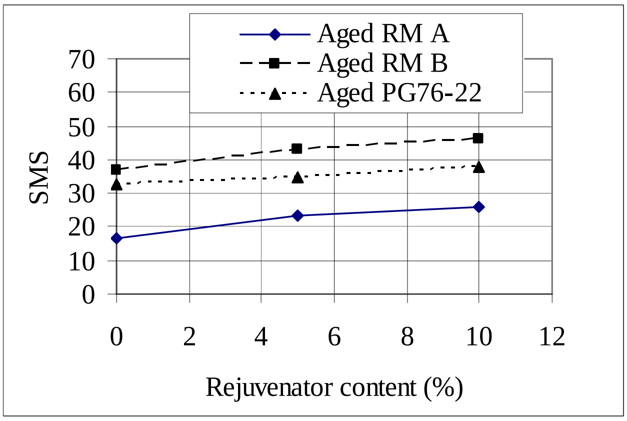
Figure 6 illustrates the changes of the three portions of the chromatographic profiles of the recycled aged binders with the increased content of rejuvenator. The LMS of the blends decreased with the content of the rejuvenator with the exception of rubber modified binder A at 10% of rejuvenator (Figure 6 a). The MMS of the blends also decreased as the rejuvenator content increased (Figure 6 b). The SMS increased (Figure 6 c) as the rejuvenator content increased. These data are average values from three replicate samples.

Figure 7 illustrates the changes of the three portions of the chromatographic profiles of the recycled aged binders with the increased content of softer binder. The LMS of the blends decreased with an increase in the softer binder content (Figure 7 a). The same trend was true for MMS (Figure 7 b). The SMS increased with an increase in the softer binder content (Figure 7 c). These data are average values from three replica samples.



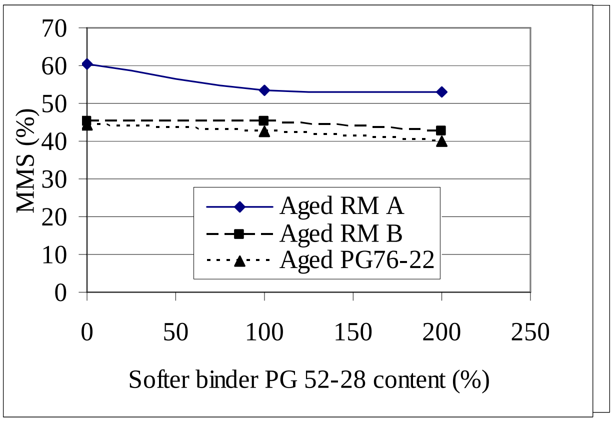


a) b)



c)

Figure 6 LMS, MMS and SMS of the blends verses the rejuvenator content; a) LMS; b) MMS; c) SMS



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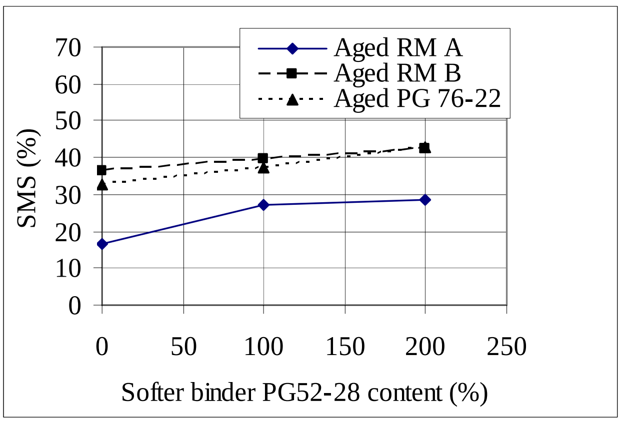

c)

Figure 7 Fractions of the Profiles; a) LMS; b) MMS; c) SMS

SUMMARIES 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 rejuvenating agents on the chromatographic profile was investigated, and the influence of the rejuvenating agents on the three molecular size distributions was discussed. Conclusions are drawn as follows:

1. Compositional changes of different blends of aged binders at various contents of both the rejuvenator and the softer binder are reflected well by the GPC. The chromatographic profiles moved backward as the rejuvenator content increased. This phenomenon is a reverse process of a typical aging process of asphalt binders. In general, the profiles of aged binders move forward with aging time increase.
2. Both the rejuvenator and the softer binder used in recycling of the aged binders in the study can change the chromatographic profiles in the same way; based on the limited data, regardless of the type of aged binders.
3. By adding both the rejuvenator and the softer binder, the LMS and MMS of the blends of the aged rubber modified binders decreased, whereas the SMS increased. These changes may be important to the improvement of the durability of the recycled aged binders.

REFERENCES

1) Norman W. Garrick and Leonardn 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, 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. Amirkhanian, 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 Amirkhanian and Soon Jae Lee (2005), "Effects of Rejuvenating Agents on Recycled Aged Rubber Modified Binders", TRB, 84th Annual Meeting, Compendium of papers CD-ROM.