

**HP-GPC Characterization of Aging of Recycled CRM Binders Containing Rejuvenating Agents**

Junan Shen\*, Assistant Professor  
Georgia Southern University  
2128 Technology Building, Statesboro, GA, 30460-8045, U.S.A  
E-mail: jshen@georgiasouthern.edu

Serji Amirkhanian, Professor  
Department of Civil Engineering, Clemson University  
110 Lowry Hall, Clemson, SC 29634-0911, U.S.A  
E-mail: kcdoc@clemson.edu

Feipeng Xiao, Ph.D. Graduate student  
Department of Civil Engineering, Clemson University,  
Clemson, SC 29634-0911

**\*Corresponding author**

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**Abstract**

This paper presents a study to characterize aging process of the blends of aged crumb rubber modifier (CRM) binders containing rejuvenating agents by using Gel Permeation Chromatography (GPC). Two SHRP binder specifications proposed aging processes, i.e., RTFO and RTFO+PAV, were used for the aging of the blends. The GPC profiles, namely the molecular size distributions, of the blends of aged binders and rejuvenating agents were measured by GPC and different molecular sizes of these blends were calculated. Three aged CRM binders and two aged control binders of PG76-22 (3% SBS modified binders) were mixed with several percentages of either a rejuvenator or a softer binder to produce the blends. Besides, performance properties of these blends at three different aging states, i.e., no aging, RTFO aging and PAV aging, were tested and correlated with the larger molecular sizes (LMS) of the GPC results. It was concluded that compositional changes of these blends due to the RTFO and RTFO+PAV aging processes were well reflected by GPC results. In addition, correlations between the LMS and the performance properties of the blends are rather good.

**Keywords:** *GPC, RTFO+PAV aging process, CRM binder, larger molecular size*

## INTRODUCTION

### Background

Annually, more than 290 million tires are disposed of in the United States. Currently, approximately 67% of these are utilized for such applications as tire-derived fuel, molded products, crumb rubber, and other applications (Amirkhanian and Corley, 2004). The use of crumb rubber modifier (CRM) in paving asphalt binders has been widely accepted in several states around the country since 1960's. The motivation behind this use was the improvement of the performance properties of the CRM binders (Bahia, and Davies, 1994, Rebala and Estakhri, 1995). Recently the application of the CRM in pavement engineering has received much attention because of the environmental benefits of recycling scrap tires, and the technologies being developed such as stress absorption membrane interlayer, porous asphalt mixtures and low noise asphalt mixtures. The use of CRM binders in pavements would increase even more rapidly if the technology needed in this area can be further developed. On the other hand, those pavements built using CRM binders in the early 90's are more than 10 or 15 years old. As a result, there is a need for recycling of aged CRM binders around the country.

Recycling of an aged asphalt binder is achieved by mixing the aged binder with a rejuvenating agent, which may be either a rejuvenator or a softer binder. Unlike for the recycling of reclaimed asphalt pavements (RAP) using neat binders, the research on the recycling of RAP using CRM binders is not enough for developing a practical guideline. Specifically the properties of the blends of aged CRM binders containing rejuvenating agents are still not clear because of limited studies dealing with the effects of crumb rubber particle on the performance of the mixtures. More importantly, the CRM binders cannot be as precisely and accurately evaluated as neat binders using standard Superpave binder test procedures which were developed for the latter. Several potential problems when using these testing procedures (e.g., DSR) and CRM binders included stiffness-related issues, plate slip, and equipment limits were reported (Stroup-Gardiner and Newcomb, 1995, McGennis, 1995). To address these modifications of test procedures such as increasing the gap of the plates to accommodate a high percentage and the coarse particle sizes of CRM (Bahia and Robert 1994) have been proposed. However, there is no recommended Superpave protocol for CRM binders; therefore, the evaluation of these binders is restricted to using the Superpave binder tests with modifications. A new method to characterize both virgin CRM binders and recycled aged CRM binders is necessary in the near future.

### HP-GPC

High pressure-gel permeation chromatography (HP-GPC) separates an asphalt binder into fractions of various molecular sizes, thus establishing a profile of molecular size distribution (MSD) plotted with detector responses on an ordinate and elution times on an abscissa. The GPC profile of an asphalt binder can be classified into three groups (i.e., LMS, MMS and SMS; large, medium and small molecular size; respectively). The application of this technique to asphalt binders was systematically reviewed by the SHRP research group (SHRP-A/UIR, 1991). So far, research on the use of GPC in pavement asphalt binders has focused on the following aspects: a) the characterization of asphalt binders as a tool; b) the links between the GPC results and both the physical properties of the binders and the field performance of the pavements. The following conclusions were made: 1) GPC can be used to identify differences in binders sources and to detect the presence of modifiers or fillers; 2) the molecular size distribution of asphalt has a definite effect on its physical properties (Glover et al., 1987, Brule et al, 1986, Price and Burati, 1990, Garrick and Biskur, 1990) and 3) conflicting results on whether HP-GPC analysis can help identify the performance of asphalt-aggregate mixture

(Jennings et al., 1985, Bynum and Traxler, 1970). Later, a research on the advanced GPC method was discussed (SHRP-A-630, 1993).

Noureldin and Wood (1989) reported that the variations in the molecular size distribution of virgin and recycled asphalt binders are associated with aging. Kim et al. (1993) investigated the aging properties of asphalt binders. Churchill et al. (1995) discussed the influence of aging on chromatographic profiles and the relationship between selected properties of the binders and the HP-GPC parameters. Wahhab et al. (1999) studied the rheological properties using GPC. A common conclusion among these researchers is that aging of a binder causes an increase in the LMS and a decrease in the MMS and SMS. These changes in molecular size can result in a significant change in the asphalt binder consistency, and therefore its physical properties. Thus, these results on the application of GPC to virgin binders and the RTFO residual of neat and modified binders are helpful to improve the understanding of the asphalt's performance.

## OBJECTIVES

This study proposes the following objectives:

- 1) To investigate whether the aging process produces significant differences in HP-GPC results of the blends of aged CRM binders containing rejuvenating agents.
- 2) To discover, using GPC results, whether significant differences exist among recycled CRM binders containing traditional rejuvenating agents (i.e., a rejuvenator and a softer binder) as measured.
- 3) To determine the correlations between the performance properties and the molecular sizes of the blends at different aging stages.

## MATERIALS AND TEST PROCEDURES

Three CRM binders were produced in the laboratory using 10% (by weight of the base binder) -40 mesh (0.425mm) ambient CRM. This type of CRM was mechanically produced at ambient temperature. In this study, three binder sources (graded as PG64-22, Table 1) were used to make the CRM binders, each of which was produced with a blade mixer at 177C for 30 minutes (Shen et al., 2005 a). The three CRM binders were subsequently graded as PG76-22 after being produced. The artificially accelerated aging processes of RTFO (163C for 85 minutes) and RTFO+PAV (100C for 20 hours) were used to generate aged CRM binders. In addition, two control binders of PG76-22 (3% SBS mixed with two of the three base binders of PG64-22) were aged in the same way. After being produced, all the five aged binders were then mixed completely with 5 and 10% of a rejuvenator, and 100 and 200% of a softer binder (PG52-28); separately, to prepare the blends for GPC tests. Table 2 lists the properties of the rejuvenator used. The combinations of the blends and the percentages of the rejuvenating agents by weight of the aged binders are shown in Table 3.

GPC was then used to measure the molecular size distribution of the prepared blends at three different aging states, i.e., no aging, RTFO residuals and RTFO+PAV residuals. In addition, a DSR test (AASHTO T315-02) was conducted on the blends in the three different aging states. A BBR test (AASHTO T 313-02) was conducted on the blends after RTFO+PAV aging.

The GPC testing equipment consists primarily of a solution injection unit connected to six silica gel porous columns through which the sample solution is pumped. This pore arrangement allows larger molecules of a sample to flow through a differential refractometer detector first, followed by progressively smaller molecules. The detector continuously scales the number of molecules flowing through as a function of time, automatically recording a

continuous tracing of time versus number of flowing molecules.

**TABLES 1 Properties of three base binders (PG 64-22)**

Test properties	Binder sources		
	A	B	C
Rotational Viscosity @ 135 °C (Pa-s)	0.430	0.703	0.472
G*/sin(delta) @ 64 °C (kPa)	1.279	2.413	1.468

**TABLE 2 Properties of the Rejuvenator**

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

**TABLE 3 Combinations of the Blends of Aged Binders and Rejuvenating Agents**

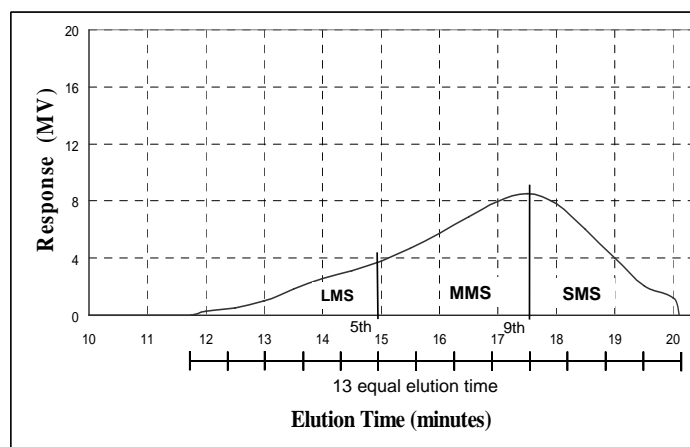
	Aged CRMA	Aged CRM B	Aged CRM C	Aged PG76-22 D	Aged PG76-22 E
<b>Rejuvenator</b> (% by wt. of aged binder)	0	0	0	0	0
	5	5	5	5	5
	10	10	10	10	10
<b>Softer binder (%)</b> (by wt. of aged binder)	100	100	100	100	100
	200	200	200	200	200

The GPC test procedure used in the test is summarized below:

1. An asphalt sample was weighed on a sensitive scale and dissolved in a tetrahydrofuran (THF) solvent. The ratio of asphalt to solution (asphalt and solvent) was adjusted to 1/400 by weight by dissolving 0.0080 g of asphalt binder in a 3.2g solvent.
2. The solution was drawn by an injector and then passed through with a 0.45 µm filter to ensure its purity.
3. A 0.5-ml quantity of the solution was then immediately drawn by a smaller injector and injected into the GPC system.
4. The solution was drawn through the gel permeation columns and allowed to flow at a rate of 1 ml/min.
5. Test temperature was kept at 35C.

The chromatographic profile of each asphalt binder sample was divided into 13 slices based on the equal elution time between the beginning and ending times as shown in Figure 1 (Kim and Burati, 1993). The first 5 slices were defined as Large Molecular Size (LMS), the

next 6-9 slices as Medium Molecular Size (MMS), and the rest of the area under the curve was referred to as Small Molecular Size (SMS). All of the areas were expressed as percentage.



**FIGURE 1 Methodology of calculation of LMS, MMS and SMS**

## RESULTS AND DISCUSSIONS

In general, the curves showing the relationship between the detector response and the elution time moved toward left along the abscissa after RTFO aging, and further toward the left after RTFO+PAV aging. In addition, a more pronounced move of the curves toward the left was observed for PAV aging than for the RTFO aging. Changes in the profile due to aging were similar for the three CRM binders and the two control binders, regardless of the type of the rejuvenating agent used. In the following sections, more detailed information will be covered regarding the molecular size distribution of various binders.

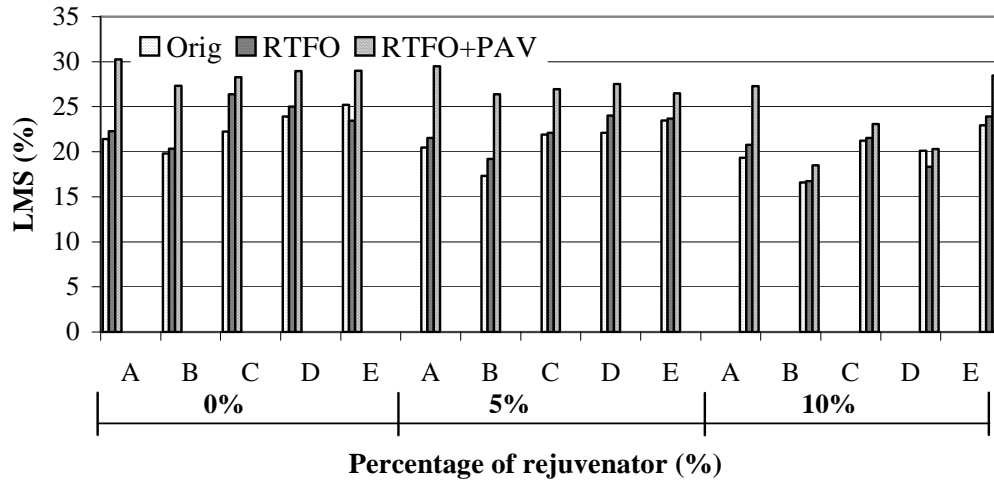
### Variation of LMS, MMS and SMS

Figure 2 shows the average LMS values obtained from the six replicate samples of each blend (i.e.,  $n=6$ ), which included three aging states, i.e., original (no aging), RTFO residuals, and RTFO+PAV residuals. Overall, a higher increase in LMS of the blends was caused by PAV aging, following by RTFO aging. This finding was true for most blends, regardless of the source of the aged binders, the percentage and the type of the rejuvenating agents as seen in 2 a) and b). The increase in the LMS of the blends caused by aging containing aged CRM binders (A, B, C) was similar to those containing aged control binders D and E. These findings are consistent with those reported before for the aging of neat binders (Churchill and Amirkhanian, 1995). In that study, it was indicated that the LMS of an aged binder increased as the aging degree of RTFO increased. It was observed in the present research that the aging caused by either RTFO or RTFO+PAV increased the LMS of all aged CRM binders.

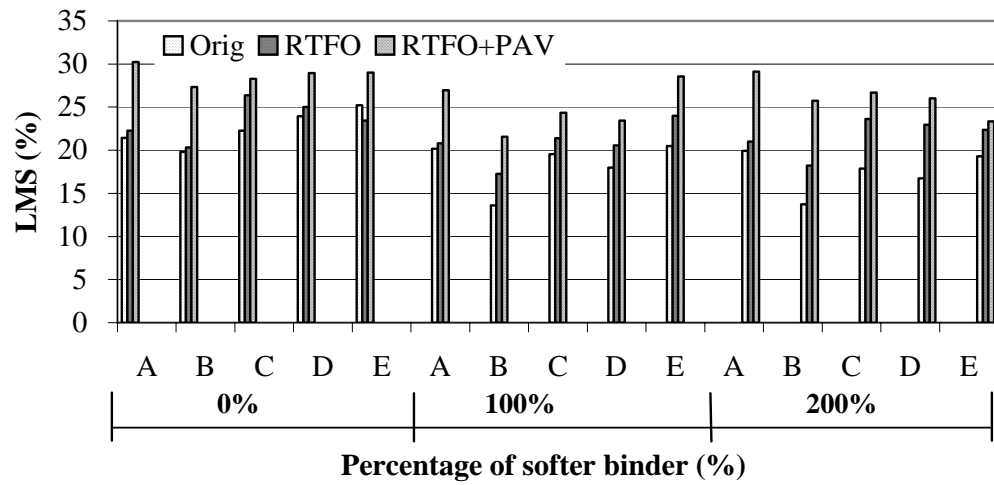
The type of rejuvenating agent influenced, to some extent, changes in the LMS caused by aging. Specifically, blends using the softer binder than using the rejuvenator caused a larger increase in the LMS after RTFO testing.

Figure 3 shows the average MMS values ( $n=6$ ), which also included three aging states. The results indicated that the MMS values of the blends depend on the sources of binder and the type of aging. RTFO aging increased the MMS for some sources and decreased for others, while RTFO+PAV aging generally decreased the MMS for most binders. In addition, the changes in MMS caused by either RTFO or RTFO+PAV aging were not as pronounced as those observed in LMS. The finding was consistent for the two rejuvenating agents at

different percentages and true for both CRM binders and control ones. Therefore, one might conclude that the MMS of a blend did not reflect the aging degree of the binder experience as well as the LMS did.

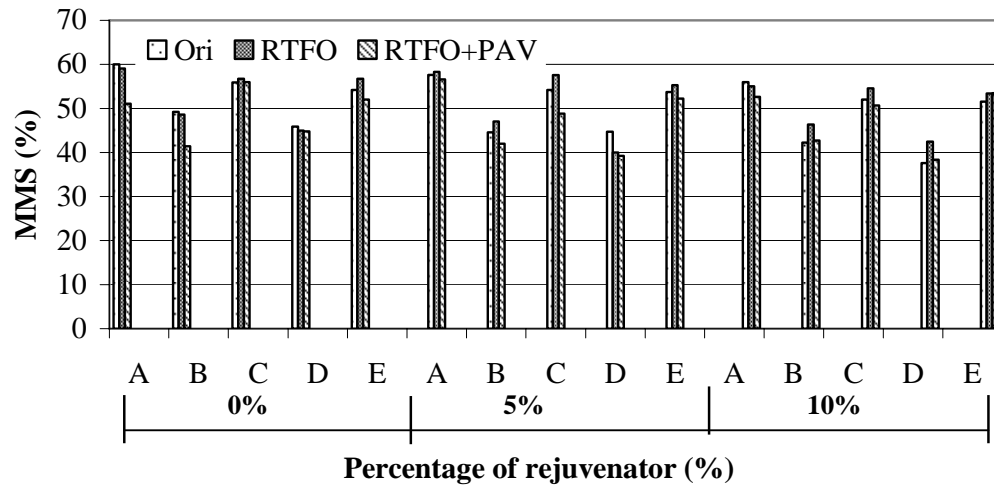


a)

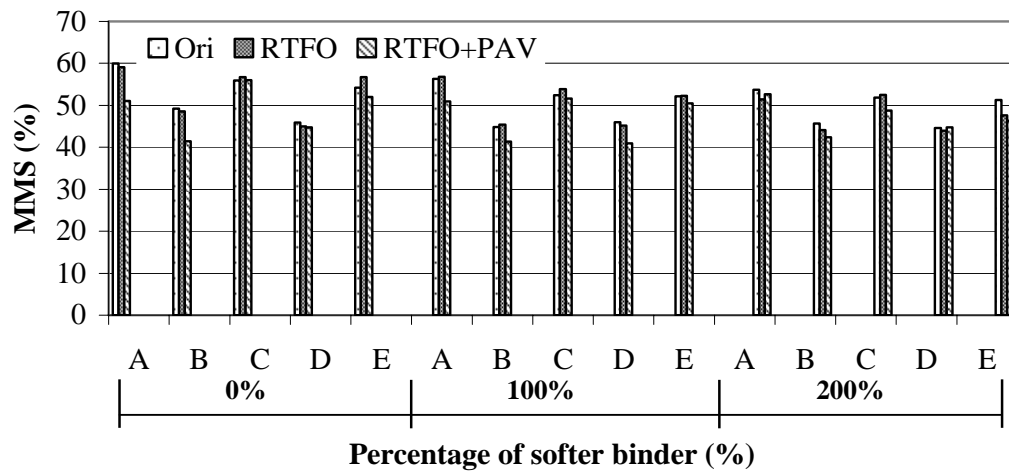


b)

FIGURE 2 LMS of the blends containing: a) rejuvenator; b) softer binder

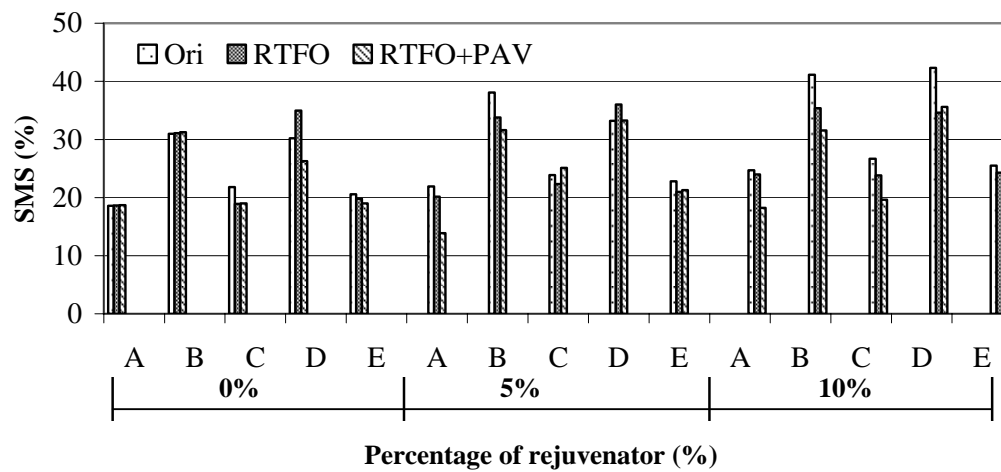


a)

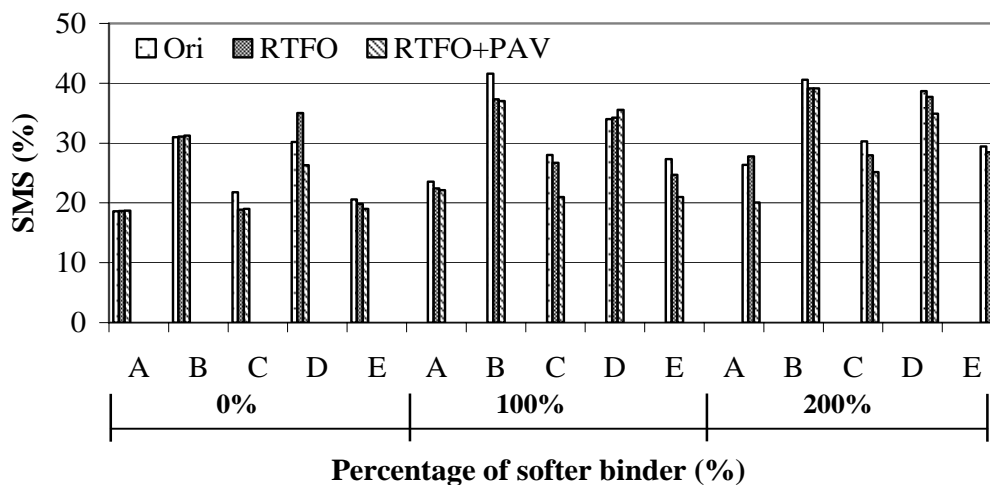


b)

FIGURE 3 MMS of blends containing: a) rejuvenator; b) softer binder



a)



b)

**FIGURE 4 SMS of the blends containing: a) rejuvenator; b) softer binder**

Figure 4 shows the average SMS values (n=6) obtained in the three aging states. In general, RTFO aging caused a decrease in the SMS and RTFO+PAV aging caused a further decrease in

the SMS for most the blends. The changes (decreases) in the SMS caused by either RTFO or RTFO+PAV aging were similar to those (increases) observed in LMS. However, a further PAV aging did not result in a more significant decrease in SMS than RTFO aging, especially for blends containing a low percentage of rejuvenating agents (e.g. 5% rejuvenator and 100% of softer binder). The change in SMS with aging was similar for both the aged CRM binders and the aged control binders. This finding is true for both the rejuvenator and the softer binder.

### Correlations between LMS and performance properties

Table 4 shows the results from DSR on the blends in three aging states.

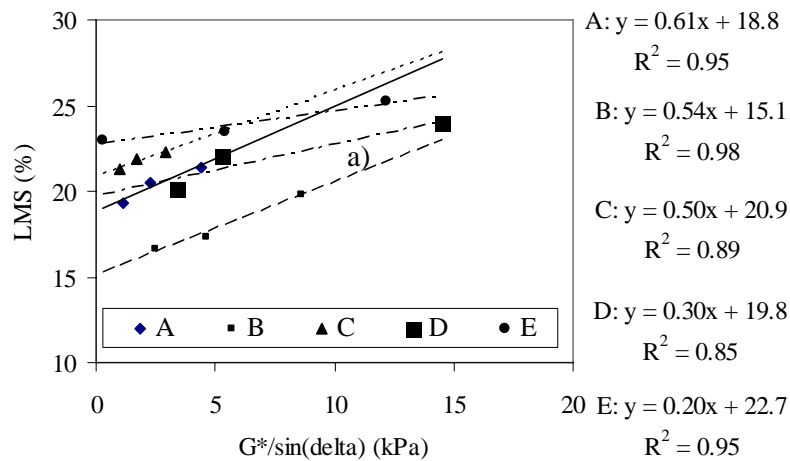
**TABLE 4 Results from DSR on the blends**

	Rej. agents (%)	A	B	C	D	E
G*/sin(delta) at 76C						
No aging	0	4.41	8.58	2.92	14.53	12.16
	5	2.26	4.64	1.69	5.27	5.41
	10	1.15	2.52	1.02	3.40	0.31
	100	0.62	0.72	0.55	0.71	0.83
	200	0.35	0.40	0.33	0.53	0.51
G*/sin(delta) at 76C						
RTFO aging	0	5.80	7.01	12.05	4.45	17.33
	5	3.01	4.37	11.73	2.61	9.46
	10	2.01	2.41	8.30	1.59	4.80
	100	1.01	0.90	3.76	0.96	1.82
	200	0.66	0.47	1.91	0.59	0.32
G*/sin(delta) at 25C						
RTFO+PAV	0	3.55	2.43	6.65	3.44	2.80
	5	3.33	2.57	6.44	2.65	2.81
	10	3.40	1.13	4.66	1.66	2.53
	100	1.39	1.51	3.89	1.57	1.88
	200	0.83	1.61	2.05	1.11	1.31

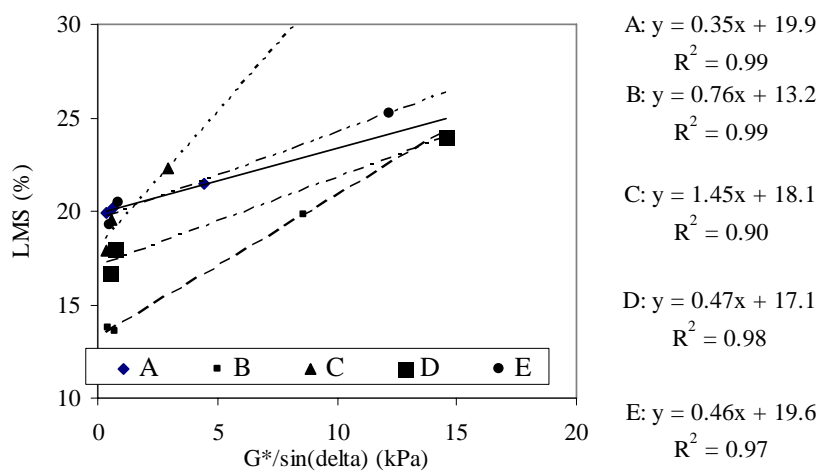
Figure 5 shows the relationship between the LMS and the  $G^*/\sin(\delta)$  of the blends tested at 76C at no aging level. The  $G^*/\sin(\delta)$ , the rutting resistance parameter proposed by SHRP specifications, increased, in general, as the LMS increased. In addition, the LMS values were well correlated with the  $G^*/\sin(\delta)$  of the binders with very high  $R^2$  values for the blends. It was indicated that increasing in the percentage of LMS in the binders caused an increase in the rutting resistance ability of the aged CRM binders and the two control binders. This finding was similar for both of the rejuvenating agents and the binder sources.

Figure 6 shows the relationships between the LMS and the  $G^*/\sin(\delta)$  of the blends tested after RTFO aging at 76C. A similar trend in the relationships to that in the original state was observed in most cases, i.e., the  $G^*/\sin(\delta)$  increased as the LMS increased. There were still fairly good correlations between the  $G^*/\sin(\delta)$  and the LMS for most of the aged binders with two exceptions, source C mixed with rejuvenator and source E with softer binder.

Because increasing the percentage of the rejuvenating agents decreased the percentage of LMS (Figure 2), consequently decreasing the rutting parameters,  $G^*/\sin(\delta)$ . This finding in the study suggests that the right amount of rejuvenating agents should be added so that the proper rutting resistance properties of the blends will be obtained.

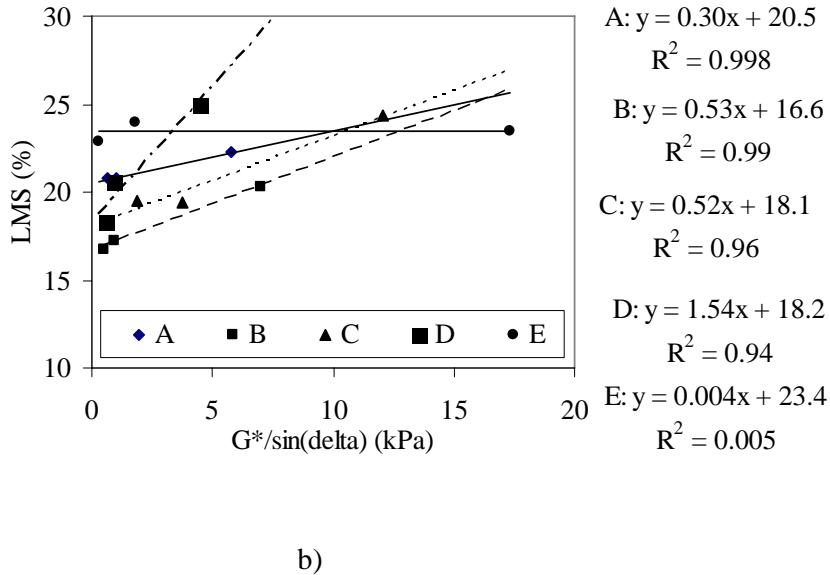
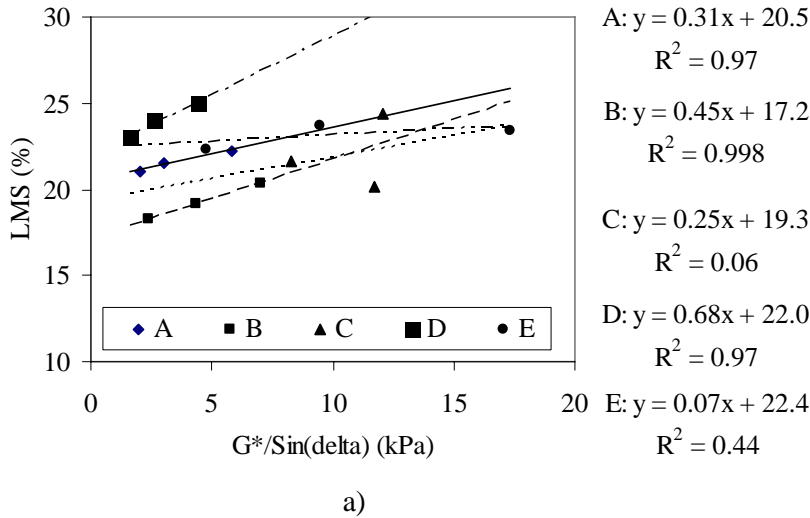


a)



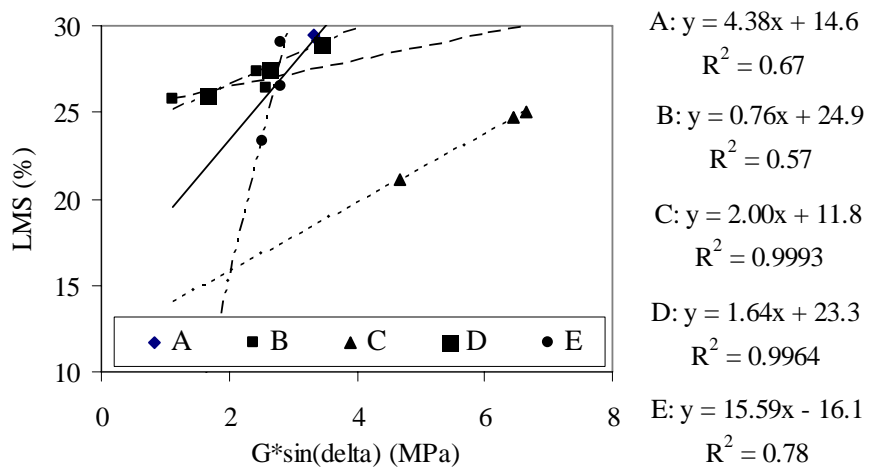
b)

**FIGURE 5 LMS and  $G^*/\sin(\delta)$  at 76C on the blends (no aging) containing: a) rejuvenator; b) softer binder**

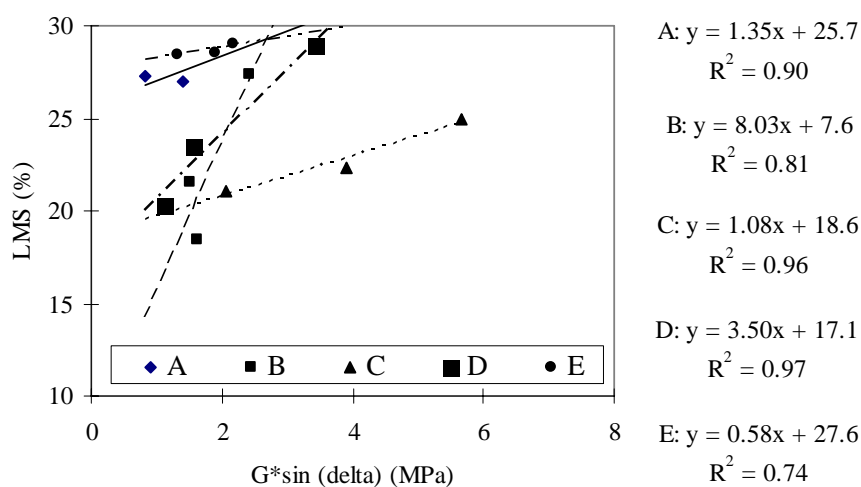


**FIGURE 6 LMS and  $G^*/\sin(\delta)$  at 76C on the blends (RTFO residuals) containing: a) rejuvenator; b) softer binder**

Figure 7 shows the relationship between the LMS and  $G^*\sin(\delta)$ , the fatigue resistance parameter of a binder, after the RTFO+PAV aging at 25C.  $G^*\sin(\delta)$  of the blends increased as % LMS increased, and correlated well. These correlations between these variables were rather high. In other words, the decrease in %LMS of the blends by adding a rejuvenating agent caused decrease in the  $G^*\sin(\delta)$ , improving in the fatigue resistance properties of the binders. The finding is true for all cases regardless of the type of the rejuvenating agent and the source of the binder.



a)



b)

**FIGURE 7 LMS and  $G^*\sin(\delta)$  at 25C on the blends (RTFO+PAV residuals) containing: a) rejuvenator; b) softer binder**

The regression equations denoting the relationship between the LMS (L, %) and the performance properties (S: stiffness and m: m-value) at low temperature are listed in Table 5. These equations showing the relationship between S and L have a positive slope, while those showing the relationship between m and L have a negative slope, indicating that the stiffness increased whereas the m-value decreased as the LMS increased, the  $R^2$  values of the correlations between the LMS and these two parameters were high. This is true for both all binder sources, and for both the softer binder and the rejuvenator.

Increasing the percentage of the rejuvenating agents caused a decrease in the LMS, thus in the stiffness, while decrease in the m-value. In other words, the low temperature properties of the blends were improved by adding the rejuvenating agents from the analysis of molecular size distribution.

**TABLE 5 Regression Equations for Low Temperature Properties  
Stiffness (S) and m-values (m) and LMS (L, %) of the blends**

Recycling agents	Binder sources	Stiffness	R <sup>2</sup>	m-value	R <sup>2</sup>
Rejuvenator	A	S=44.8L-1207.9	0.99	m=-0.067L+2.3	0.98
	B	S=12.2L-221.5	0.98	m=-0.068L+2.2	0.995
	C	S=1.95L+112.1	0.02	m=-0.0047L+0.4	0.06
	D	S=8.2L-35.5	0.66	m=-0.04L+1.4	0.98
	E	S=8.7L-60.2	0.94	m=-0.018L+0.8	0.93
Softer binder	A	S=19.5L-442.4	0.99	m=-0.027L+1.1	0.81
	B	S=4.31L-5.21	0.97	m=-0.015L+0.7	0.996
	C	S=25.2L-445.7	0.97	m=-0.028L+1.0	0.97
	D	S=11.4L-130.3	0.99	m=-0.014L+0.7	0.999
	E	S=173.2L-4831.8	0.99	m=-0.182L+5.6	0.98

## SUMMARY AND CONCLUSIONS

A series of GPC and performance properties tests were conducted on the blends of aged CRM binders containing rejuvenating agents. The following conclusions can be drawn:

1. The compositional changes of different blends of aged binders containing rejuvenating agents caused by aging were reflected well in the GPC results. The chromatographic profiles moved leftward after RTFO aging, and even further left after RTFO+PAV aging.
2. Increases in LMS and decreases in SMS, caused by RTFO and RTFO+PAV aging, were observed for all blends.
3. The rutting resistance parameter,  $G^*/\sin(\delta)$ , on both the original and RTFO residuals of the modifier binders, increased as the LMS increased, and correlated well with the LMS for the blends tested in the research work.
4. The fatigue resistance parameters,  $G^*\sin(\delta)$ , on RTFO+PAV residuals of the modified binders, increased as LMS increased, and correlated well with the LMS for all blends.
5. The shrinkage resistance parameters, stiffness and m-value changed with the LMS. The stiffness increased, whereas the m-value decreased as the LMS increased. These two parameters correlated well with the LMS. These findings were the same for all aged binders and for the two rejuvenating agents.

## ACKNOWLEDGMENT:

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