Rutting Index Prediction of Rubber-Modified Binder Using HP-GPC

Serji N. Amirkhanian, Professor
Department of Civil Engineering
Clemson University
Clemson, SC 29634-0911, USA..
email: kcdoc@clemson.edu

Kwang W. Kim, Professor
Department of Regional Infrastructures Engineering
Kangwon National University
Chun Cheon 200-701, Korea
email: futurepaver@yahoo.com

Abstract:

The rutting resistance index (G*/sin δ) and chemical composition of rubber-modified binders (RMB) were evaluated using a dynamic shear rheometer (DSR) and a gel-permeation chromatography (GPC) system. One source of asphalt binder, PG 64-22, was used to make a total of 18 RMB binders. Superpave binder testing was carried out; RMB as the original binder and then RTFO aged binder as RTFO in DSR test at high temperature. Chromatogram of each binder was measured using a GPC system and relative quantity (%) of large molecular size (LMS) was calculated for each binder. Correlation of LMS with G*/sin δ was evaluated by service temperature, 70 and 76°C. It was found that there was a significant correlation between LMS and rutting resistance index. The size and type of CRM were significant factors affecting the rheology of the binders. Values of G*/sin δ could be estimated using LMS and CRM size by temperature with R^2 of over 0.92 by the developed prediction model.

INTRODUCTION

Various materials are added for modification of an asphalt binder to improve performance of the binder. For example, rubber is one of the materials for modifying performance of binders. Addition of rubber results in improving high-temperature performance grade (PG) of the binder, although rubber type, content, particle size and reaction time are factors affecting the level of improvement. Increasing stiffness brings up an effect of improving high-temperature performance of rubber-modified binder (RMB).

Oxidation changes the structure and composition of binder's molecules, resulting in increased quantity of high-molecular weight molecules, generating the term oxidative hardening. This hardening is reflected, in chromatogram of the asphalt, as change of molecular size distribution. Asphalt binder with large quantities of high-molecular weight molecules tend to exhibit poor low-temperature behavior, but some good high-temperature behavior (1,2).

In general, physical property measurement is the primary means of characterizing a typical binder (1). Gel-permeation chromatogram (GPC) is a relatively easy way for chemical analysis of asphalt by detecting molecular size distribution change of a binder. Recent technology development makes the GPC system affordable for many laboratories. Increased high-molecular weight molecule or large molecular size (LMS) results in increased viscosity and stiffness of a binder. Binder viscosity change due to aging is well reported to be predictable by GPC (3-6).

In this study, various RMBs were prepared using crumb rubbers. The rheology change, caused by addition of rubber, is evaluated based on change of molecular size distribution or chromatogram of the binder. The objective of this study was to evaluate the rut-related rehology properties of RMB and their correlation with GPC characteristics. In addition, the possibility of predicting rutting resistance based on significant factors affecting the performance grade of an asphalt binder was investigated.

MATERIALS AND METHODS

One source of an asphalt binder, PG 64-22 was used in this study. Two different types of crumb rubber production method (ambient: AMB and cryogenic: CRY) were prepared in three different sizes (-14 mesh, -30 mesh and -40 mesh) for this study. The rubber-modified binder (RMB) was made by adding a specified amount of rubber slowly into the binder at 180^{o}C for the specified reaction time while mixing with a stirrer. A total of 18 RMB binders were prepared from 2 rubber types (AMB and CRY), 3 sizes (passing #14, #30 and #40 sieves), 1 content (10% rubber by wt of binder) and 3 reaction times (15, 30 and 45 minutes). Each RMB was used as 1) original binder, 2) the same binders were artificially aged using a rolling thin film oven (RTFO) for simulating a short term aging, and using a pressure aging vessel (PAV) for simulating a long term aging.

Routine PG binder tests were carried out on each binder. Each RMB was tested as the original binder in the dynamic shear rheometer (DSR) at high temperature. The RMB was then RTFO aged and tested as RTFO in DSR at high temperature. The values of $G^*/\sin\delta$, which represents a measure of the high temperature stiffness or rutting resistance of the binder (1), were measured for the original and RTFO binders. Superpave high-temperature performance grades of these binders were determined from DSR data.

Chromatogram is the technique that measures molecular size distribution of a typical asphalt binder. Chromatogram of these binders was measured using a high-performance gel-permeation chromatography (HP-GPC or GPC) system as shown in Figure 1. The GPC system, a Waters Breeze equipment with computerized data acquisition software, consists of a manual injector, a dual head pump, refract index meter (RI detector), a series of two columns (HR 3 and HR 4E) and a column oven. The specification of the columns is shown in Table 1.

Table 1. Pore size and effective molecular weight range

Column	External length (cm)	Pore size (□)	Effective molecular weight range (ps)
Styragel HR 3	30	1,000	500-30,000
Styragel HR 4E	30	Mixed bed	50-100,000

Tetrahydrofuran (THF) was used as a solvent for dissolving binder and buffer (mobile phase) of GPC test. A small amount of binder (eg., 0.1gm) sample was dissolved in THF (eg., 40gm) at the concentration of 0.25% (1/400). The dissolution was filtered by a 0.45μm syringe filter before injection. A $50\mu l$ of dissolved sample was injected into the injection module and constituents of the binder were separated by molecular size after the sample passed through the series of columns. The injected sample was transferred by the THF flow into the columns which were kept constantly at 35^{o}C in the column oven, in which the flow rate of the mobile phase was 1 m*l*/min. The asphalt binder molecules were detected by the time they passed the detector and a chromatogram was obtained for each binder sample. Three samples were tested for each binder and aging conditioning and the average value was reported.

Figure 2 shows typical chromatograms of virgin PG64-22 asphalt and a rubber-modified binder before and after aging. Some of the rubber particles which were not reacted with asphalt binder were filtered out by the syringe filter. Therefore, the chromatogram of rubberized binder does not show any distinct difference compared with that of virgin PG64-22 in its profile.

Researchers have classified asphalt binder constituents into several groups [7-9]. 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). Defining LMS portion as the front 5 slice was verified in the previous study (9). Among quantitative data of the chromatogram, the LMS value was only used for evaluation in this study. Statistical analyses were performed for evaluating correlation of binder rehological properties with GPC results.

RESULTS AND DISCUSSIONS

GPC and DSR properties of PG64-22 base binder used in this study are shown in Table 2 as a reference for the analysis of RMB. Table 2 shows statistical analysis results for variables evaluated in this study. Each variable was statistically evaluated to find out if there is a significant difference in G*/sin δ values, which represent a measure of the high temperature stiffness or rutting resistance (1), within each temperature tested and in large molecular size (LMS) distribution using Duncan's multiple range test at α=0.05. Reaction time was the variable which did not show any statistical significance among three reaction times (15, 30, and 45 minutes). This means that the reaction time does not affect the rutting resistance and the LMS of rubber-modified binder (RMB), and was discarded from test variables. Some variables indicated significant difference, as shown in Table 3. Since the reaction time was not significant variable, all binders in three reaction times were considered as one material.

Table 2. LMS and G*/sin δ of the base binder (PG64-22) for virgin and RTFO conditioned binders.

Binder	Condition	LMS (%)	G*/sin δ (kPa)		
			At 64°C	At 70 °C	At 76 °C
PG64-22	Virgin	12.193	1.628	0.899	-
	RTFO	16.04	-	2.581	1336

Table 3. Duncan's multiple range test results at α=0.05

Variable	G* /sin δ at		LMS (%)
	70°C	76 °C	
Aging	S	S	S
Particle size	NS	S	NS
Reaction time	NS	NS	NS
Rubber type	NS	S	S

Legend: S = significant, NS = not significant.

Table 4 shows measured value of LMS and G* /sin δ by particle size and aging level using DSR for determining PG high temperature grade. All of 10% RMBs were graded as PG70 in high temperature performance grade, and all of 15% RMBs were graded as PG76. None of RMB confirmed to PG82 specification in this study. The rubber content does have significant effect on improving performance of the binder. In 10% CRM case, a couple of RTFO binders passed Superpave specification limit (2.2kPa), but original binders did not meet the limit (1.0kPa). None of 10% CRM binders were confirmed to PG76 grade. Table 5 showed the performance grade of each binder by CRM type, content and particle size determined from high-temperature DSR test.

LMS values show that there was significant increase by aging level. LMS value between CRM contents and type were also found to be statistically significant (Table 3). With an increase in LMS, rutting parameter (G*/sin δ) was observed to increase significantly. It is well known that there is a significant correlation between LMS values and binder's physical properties, and rubberized binder seems to have similar correlation between LMS and rheological properties.

Table 4. LMS and G*/sin δ values for each binder combination.

CMR Type	Content (%)	Size (mesh)	Aging	LMS (%)	G* /sin δ (pa)	
					At 70°C	At 76°C
AMB	10	-14	Original	14.27	1.667*	0.968
			RTFO	17.88	4.434*	2.399*
			PAV	20.34	-	-
		-30	Original	14.24	1.681*	0.911
			RTFO	17.59	3.800*	2.161
			PAV	24.49	-	-
		-40	Original	13.95	1.745*	0.984
			RTFO	16.51	3.065*	1.700
			PAV	22.91	-	-
CRY	10	-14	Original	13.57	1.427*	0.759
			RTFO	16.94	3.863*	2.154
			PAV	18.52	-	-
		-30	Original	14.60	1.544*	0.821
			RTFO	18.82	4.159*	2.278*
			PAV	-	-	-
		-40	Original	13.47	1.408*	0.747
			RTFO	16.54	3.194*	1.687
			PAV	19.15	-	-

Legend: AMB=ambient, CRY=cryogenic, RTFO=rolling thin film oven, PAV=pressure aging vessel,
* pass Superpave specification.

Table 5. Performance grade of each binder.

CRM	Ambient			Cryogenic		
Size (mesh)	-14	-30	-40	-14	-30	-40
High temp. PG	70	70	70	70	70	70

Figures 3 to 5 show relationships of G*/sin δ value versus LMS value with the coefficient of determination (R^2) for 10% RMB. In general, the results indicated that rutting resistance property measured at two service temperatures (70 and 76°C) has a very good linear correlation ($R^2 = 0.86$) with LMS quantity (Figure 3). Increasing LMS results in improving rut resistance within each service temperature. Figure 3 data were divided into two groups by CRM type and used for drawing Figures 4 and 5 to compare correlation level of two CRM binders. The CRM produced by ambient method (AMB) showed higher correlation than the CRM produced by cryogenic method (CRY) in both service temperatures.

Since G* /sin δ had good correlation with LMS and function of CRM content and size, it is possible to estimate this value based on LMS and other variables. Prediction models were developed for G* /sin δ based on regression of these variables by rubber type. The value of G* /sin δ was dependent variable, and LMS, CRM size and content were independent variables. The STEPWISE procedure was performed to select the best model using Statistical Analysis System (SAS). The prediction models for G* /sin δ by CRM type and service temperatures are shown in Table 6.

The average of the above four coefficients of determination (R^2) for these models is 0.9284 and the range is from approximately 0.90to 0.96, as shown in Table 6. Between two types of CRM, R^2 of the ambient was higher than cryogenic. If the rubber type is not considered, R^2 values are slightly lower than the case where the type is taken into account. However, the R^2 values are still over 0.9 and, therefore, it is concluded that there is a good possibility of predicting stiffness index if LMS and rubber size values are known.

Table 6. Prediction models for G*/sin δ by CRM type and test temperatures.

CRM	Temp.	Model	R^2
Ambient	70°C	$Y = 142.02X_1^2 + 0.7387X_2^2 – 3844.2X_1 – 34.625X_2 + 27951$	0.9422
	76°C	$Y= –21.57X_1^3 + 1072X_1^2 + 0.509X_2^2 – 17290X_1 – 29.6X_2 + 92459$	0.9612
Cryogenic	70°C	$Y= 40.58X_1^2 + 3.32X_2^2 – 671.6X_1 – 186.4X_2 + 5252$	0.9105
	76°C	$Y = –17.33X_1^2 + 2.05X_2^2 – 215.8X_1 – 116.9X_2 + 1900$	0.8995
Total	70°C	$Y = –25.9X_1^3 + 1272X_1^2 + 1.025X_2^2 – 20038X_1 – 60.76X_2 + 104669$	0.9134
	76°C	$Y= –18.13X_1^3 + 876.2X_1^2 + 0.6658X_2^2 – 13685X_1 – 29.6X_2 – 70976$	0.9230

Legend: Y=predicted G*/sin δ (kPa), X_1=LMS (%), X_2=CRM size given by mesh, X_3= CRM content (%.).

Figure 6 shows relation of predicted G* /sin δ for ambient (AMB) CRM binder versus cryogenic (CRY) CRM binder at 70°C, as an example. The data was produced based on the equations for Ambient 70°C and Cryogenic 70°C in Table 5, respectively, using LMS value (X_1) in the range of 14 – 18 and mesh size (X_2) of 40. As seen in the figure, AMB values are somewhat higher in lower and higher stiffness index regions. But data points are very well correlated with a $R^2 = 0.98$. Therefore, it is possible to predict the G* /sin δ value of rubber-modified binder, with some degree of accuracy, based on LMS value and rubber size at the specified temperatures.

CONCLUSIONS

This study investigated laboratory evaluation of rubber-modified binder using DSR and GPC. While improving high-temp grade of binder by increasing stiffness using rubber is not a new idea, however, it is not well known whether or not this rheology change is reflected in molecular size distribution or chromatogram of the binder. The results in this study showed that there is a significant correlation between molecular size distribution (i.e., LMS) and the rutting resistance property (i.e., G*/sinδ).

The size and type of CRM were significant factors affecting the rheology of the binders. The value of G*/sin δ could be estimated using LMS and CRM size by the developed prediction model. The coefficient of determination, R^2, was over 0.92 on the average with maximum of 0.96 for the prediction models. Therefore, the rutting property of rubber-modified binder can be well predicted if the LMS of the binder and the size of CRM are known. The ambient CRM binders showed somewhat higher stiffness values than cryogenic CRM. The rheology of the ambient CRM binder could be predicted better (higher R^2 value) by the developed prediction model.

ACKNOWLEDGEMENTS

This study was supported by the Asphalt Rubber Technology Service (ARTS), Civil Engineering Department, Clemson University, Clemson, SC, USA, and by the Kangwon National University, Chun Cheon, Korea.

REFERENCES

1. Yapp, M. T. Durrani, A. Z. and Finn, F. N., “HP-GPC and asphalt characterization literature review,” SHRP-A/ULR-91-503, SHRP, NRC, Washington, D. C. 1991.
2. Jennings, P. W. (1980), “High Pressure liquid chromatography as a method of measuring asphalt composition,” Report No. FHWA-MT-7930, Dept. of Chemistry, Montana St. Univ., Bozeman, Mt.
3. Kim, K. W. and Burati, J. L. (1993). “Use of GPC chromatogram to characterize aged asphalt cements.” Journal of Materials in Civil Engineering, ASCE, Vol. 5 (1), 41-52.
4. Kim, K. W., Doh, Y. S. and Amirkhanian, S. N. (2004). “Effect of polymers on aging of asphalt binder.” Journal of Korean Society of Pavement Engineers, Vol. 6 (2).
5. Price, R. P. A. (1988). “Quantitative method to characterize asphalt using HP- GPC.” Dissertation in partial fulfillment of the requirements for Ph.D. in Civil Eng., Clemson University, Clemson, SC.
6. Asi. I. M., Wahhab, H. I. A. A. Dubabi, I. A. and Ali, M. F. (1997). “Performance modeling of Arabian asphalt using HP-GPC.” Journal of Materials Engineering and Performance, Vol. 6 (4).
7. Nourendin, A. S. and Wood, L. E. (1989). “Variation in molecular size distribution virgin and recycled binders associated with aging.” TRR 1228, Transportation Research Board, Washington, D.C., 191-197.
8. Kim, K. W., Burati, J. L. and J. S. Park. (1995). “Methodology for defining LMS portion in asphalt chromatogram.” Journal of Materials in Civil Engineering, ASCE, Vol. 7 (1), 31-40.
9. Wahhab. H. I. A. A., Asi, I. M., Ali, F. M. and Dubabi, I. A. A. (1999). “Prediction of asphalt rheological properties using HP-GPC.” Journal of Materials in Civil Eng., ASCE, 11(1).
10. “Superpave: Performance graded asphalt binder specification and testing,” (1994). Asphalt Institute, SP-1.

Figure 1. GPC system used in this study.

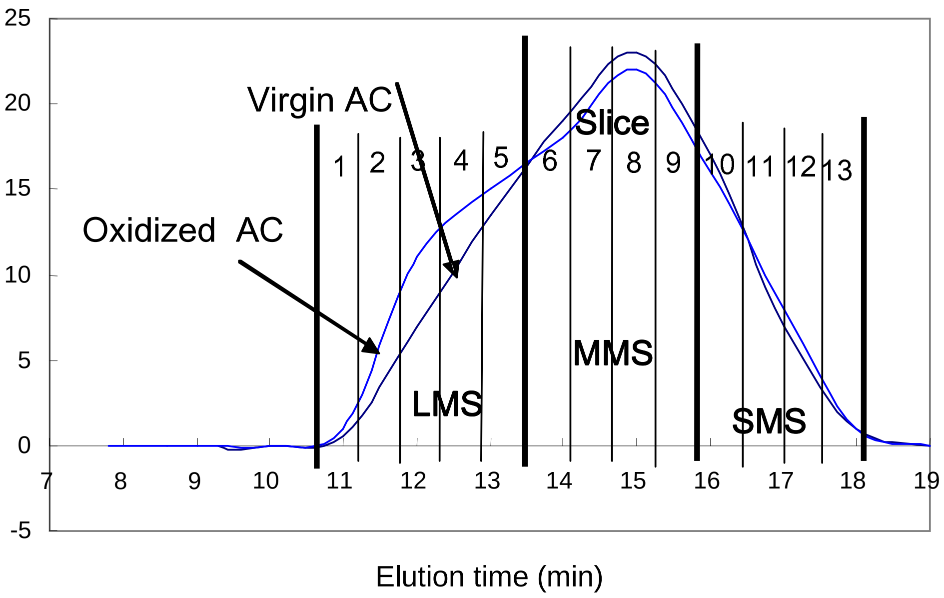

Figure 2. Typical Chromatograms of two binders

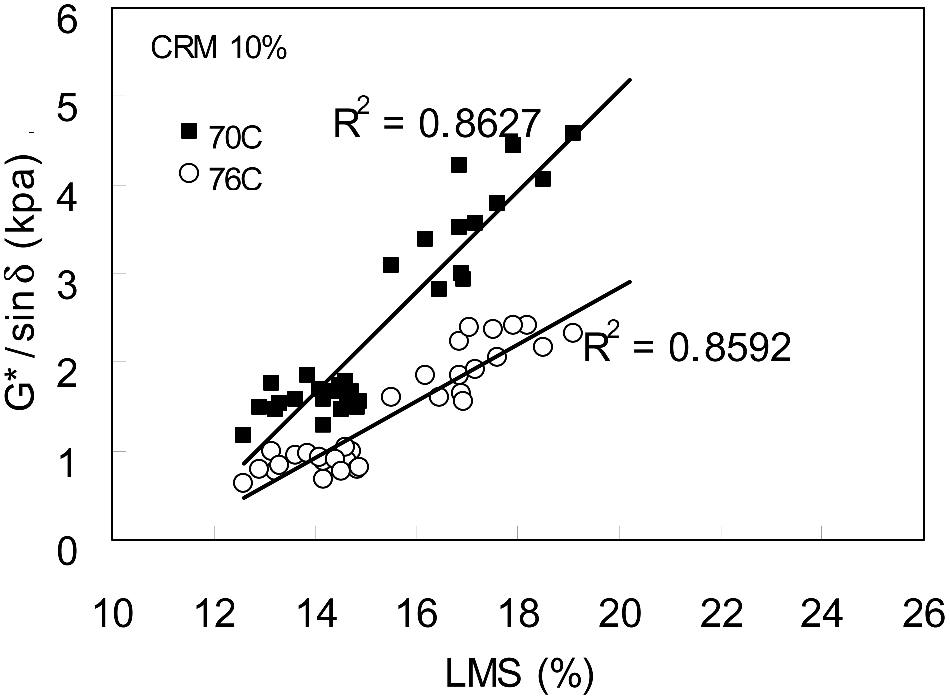

Figure 3. Relationship of G*/sin δ with LMS for CRM (total) modified binder (content: 10% by wt. of binder).

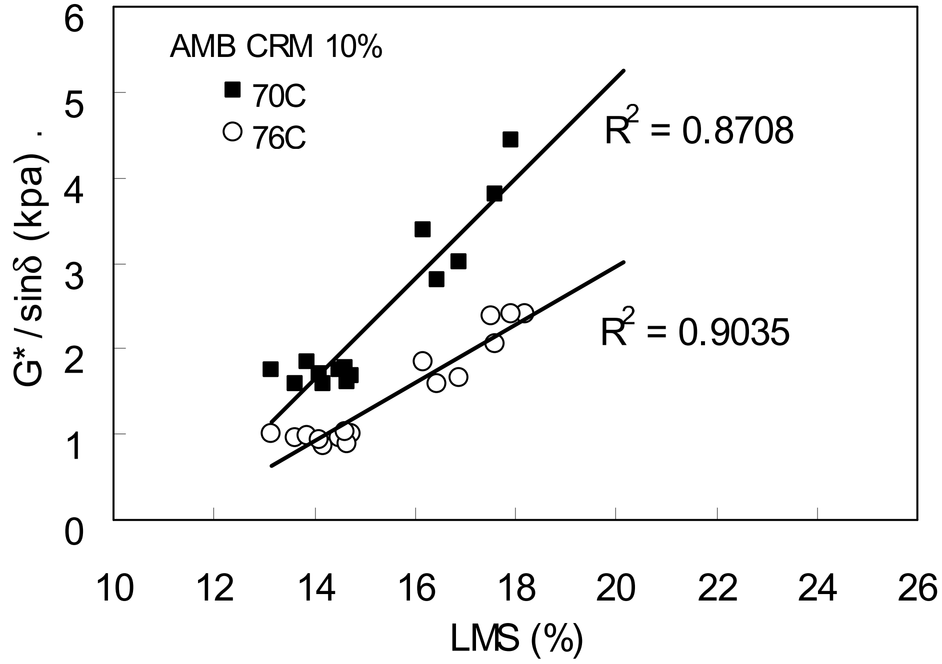

Figure 4. Relationship of G*/sin δ with LMS for CRM (ambient) modified binder (content: 10% by wt of binder).

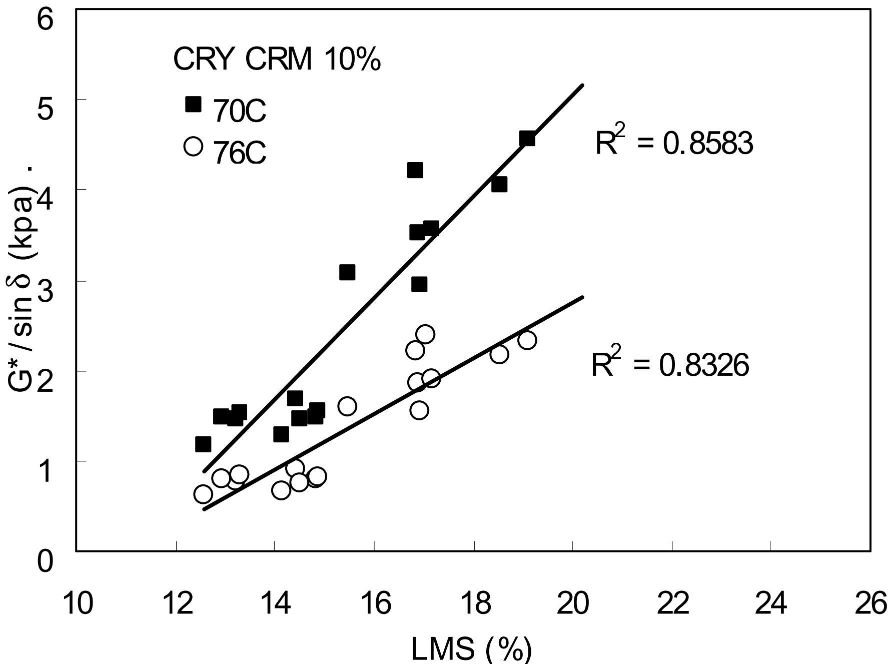

Figure 5. Relationship of G*/sin δ with LMS for CRM (cryogenic) modified binder (content: 10% by wt of binder).

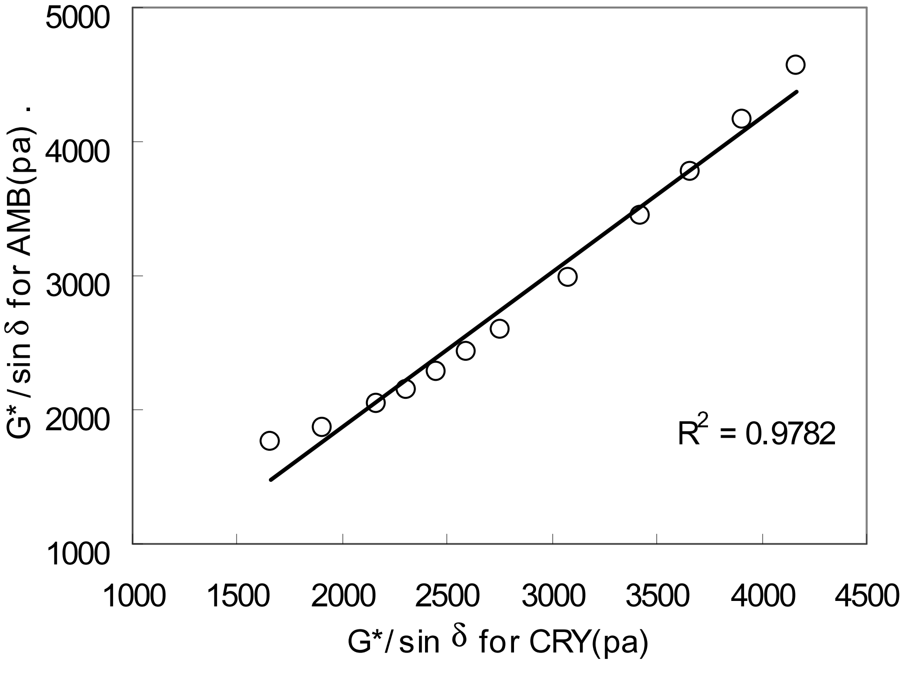

Figure 6. Relation of rutting parameter at 70°C for -40 mesh AMB rubber vs. CRY rubber in the range of LMS 14 – 18%.