Relationship Between High-Pressure Gel Permeation Chromatography Data and the Rheological Properties of Asphalts

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Much effort has been expended by researchers in the development of new procedures for characterizing asphalt cements. Such procedures have long been needed to improve the day-to-day monitoring of asphalt composition. Furthermore, the development of these procedures is crucial to the long-term research effort directed at improving the quality of asphalt binders. High-pressure gel permeation chromatography (HPGPC) is one of the procedures currently being evaluated that has produced encouraging results. Some evidence has been presented to indicate that this procedure may be useful for predicting the performance of asphalts. However, some of the results from HPGPC analysis are not fully understood; for example, the relationship between HPGPC data and viscosity is still obscure. Consequently, the main objective of this project was to study the relationship of HPGPC data to viscosity and penetration. In this project, the three products of a residuum oil supercritical extraction refinery unit were blended to produce asphalts of varying composition. Thus, these asphalts are all from the same crude source and refinery process; any variation in their rheology is directly attributable to changes in their chemical composition. It was established that there is a quantitative relationship between HPGPC data and the rheological properties of the blended asphalts. In addition, it was determined that changes in the asphalt composition were accompanied by corresponding changes in the HPGPC profile. Therefore, it was concluded that HPGPC may be useful for monitoring changes in asphalt properties that occur during the construction process and subsequent exposure to the elements.

Many users of asphalt believe that changes in the oil refinery industry since the 1973 oil embargo have adversely affected the properties of asphalt cement. As evidence, they point to such problems as premature cracking and tender mixtures that appear to have proliferated recently. It is believed that current methods of specifying and characterizing asphalts cannot adequately control these problems. Consequently, research has been directed to the development of new characterization procedures.

High-pressure gel permeation chromatography (HPGPC) is one such characterization procedure; it is used to determine the molecular size distribution of polymers and other macromolecular substances. Molecular size separation in GPC occurs when a sample in solution is forced through a bank of columns; each column containing porous, silica-gel packing of a given average pore size. The separation mechanism is designed so that the largest molecules emerge from the system first and are followed by progressively smaller molecules. Thus separation

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is based on molecular size and not molecular weight. This distinction is important for substances, such as asphalt, that consist of molecules of different functional types.

HPGPC has been used sporadically since the mid-1960s for analyzing asphalt [1,2]. Bynum and Traxler conducted a feasibility study in 1970 to evaluate this use of GPC [3]. They concluded that GPC was a useful method for determining differences in the molecular composition of asphalts. In an earlier study, Breen and Stephens found some degree of correlation between GPC profiles and glass transition temperature for 50 Bureau of Public Roads asphalts [4].

More recently, Jennings et al. reported the existence of a relationship between the GPC profile of asphalts and their transverse cracking potential [5]. Asphalts with too great a proportion of large molecules were found to be more prone to cracking. The relationship was affected by factors such as atmospheric temperature fluctuations, temperature extremes, and traffic levels. Jennings et al. suggested that other potential uses of HPGPC may include the following: (a) selecting suitable recycling agents, (b) evaluating asphalt additives, and (c) monitoring asphalts from individual refineries.

There are some problems associated with the use of HPGPC for analyzing asphalt. For example, paraffinic molecules in asphalt are larger than aromatic molecules of the same mass; consequently, during HPGPC analysis, paraffinic molecules emerge before aromatic molecules of the same mass [1]. The comparison of HPGPC profiles for asphalts from aromatic sources with those from paraffinic sources may be complicated by this factor.

Various researchers have demonstrated that some asphalt molecules associate in solution to form larger units [6,7]. In HPGPC analysis, molecules that aggregate in this manner emerge before unassociated molecules of the same size or larger. Thus, HPGPC profiles reflect the apparent molecular size distribution and not the true distribution of sizes in the asphalt. The problem is that the degree of association and hence the apparent molecular size will vary with the following factors: solvent type, solution temperature, asphalt concentration in the solvent, and the original crude source of the asphalt [1].

These factors notwithstanding, many of the studies referred to in the preceding paragraphs demonstrated that changes in the physical properties of a specific asphalt are associated with corresponding changes in its HPGPC profile. These findings suggest the existence of some quantitative relationship between HPGPC data and the physical properties of an asphalt. The purpose of this project was to investigate the nature of such relationships for three rheological properties. The rheological

TABLE 2 ASPHALT BLENDS AND RHEOLOGICAL TEST RESULTS

Asphalt No.	Proportions			Viscosity poises (60° C)	Viscosity cst (135° C)	Penetration 0.1 mm (25° C)
	Asphaltene	Resin	DAO			
13	0.329	0.255	0.416	1257	285	70
14	0.201	0.611	0.188	1510	309	61
15	0.201	0.611	0.188	1366	311	56
16	0.200	0.400	0.400	343	188	161
21	0.223	0.679	0.098	3648	470	31
22	0.290	0.410	0.300	1655	349	52
23	0.200	0.450	0.350	451	196	130
24	0.360	0.140	0.500	870	254	75
25	0.201	0.611	0.188	1360	326	56
26	0.200	0.530	0.270	749	250	89
27	0.300	0.450	0.250	2642	413	38
31	0.100	0.900	0.000	1879	327	49
32	0.380	0.000	0.620	531	189	108
41	0.060	0.905	0.035	975	265	67
42	0.240	0.460	0.300	883	258	71
43	0.200	0.555	0.245	769	250	83
44	0.425	0.000	0.575	1257	285	70
45	0.100	0.810	0.090	840	244	82
46	0.198	0.550	0.252	694	229	87

X_{ia}, X_{ir}, X_{id} = proportions in Section i for the asphaltene, resin, and DAO fractions, respectively.

A comparison of the actual and hypothetical HPGPC data indicates a systematic pattern of variation (see Table 7). In all cases, the proportion of area in Sections 2 and 3 are greater for the actual data than for the hypothetical data. Conversely, in most cases, the proportions of area in the other six sections are less for the actual data than for the hypothetical data. A few asphalts showed a slight variation in this pattern.

It is believed that this systematic difference between the actual and theoretical HPGPC data results from heating the ROSE products during blending. This application of heat appears to cause an increase in the amount of large molecules or of associated molecules in the asphalt. The existence of such a relationship suggests that HPGPC may be useful for monitoring a specific asphalt as it undergoes processing.
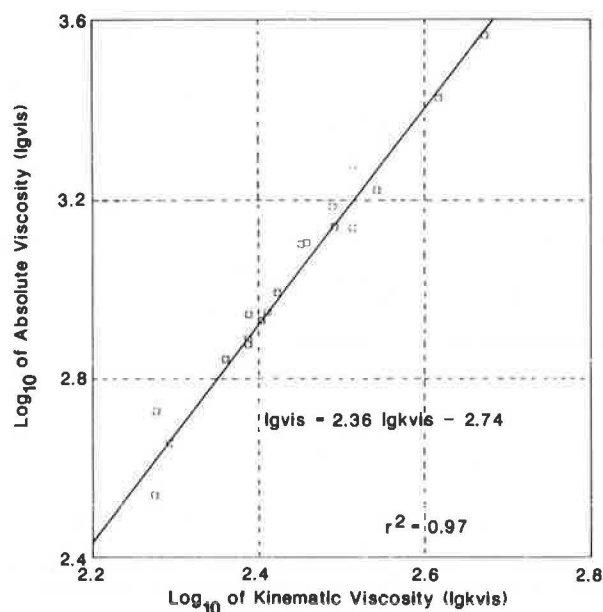

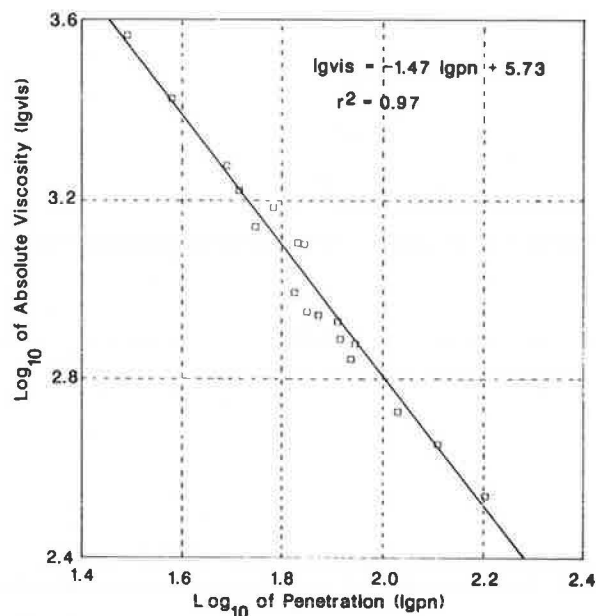FIGURE 2 Absolute viscosity versus kinematic viscosity.

FIGURE 3 Absolute viscosity versus penetration.

TABLE 3 PENETRATION-VISCOSITY NUMBER OF ASPHALTS

Asphalt No.	Proportions			(P-VN)
	Asphaltene	Resin	DAO	
13	0.329	0.255	0.416	−1.10
14	0.201	0.611	0.188	−1.12
15	0.201	0.611	0.188	−1.19
16	0.200	0.400	0.400	−0.88
21	0.223	0.679	0.098	−1.15
22	0.290	0.410	0.300	−1.10
23	0.200	0.450	0.350	−1.05
24	0.360	0.140	0.500	−1.21
25	0.201	0.611	0.188	−1.12
26	0.200	0.530	0.270	−1.06
27	0.300	0.450	0.250	−1.15
31	0.100	0.900	0.000	−1.24
32	0.380	0.000	0.620	−1.30
41	0.060	0.905	0.035	−1.25
42	0.240	0.460	0.300	−1.23
43	0.200	0.555	0.245	−1.13
44	0.425	0.000	0.575	−1.12
45	0.100	0.810	0.090	−1.18
46	0.198	0.550	0.252	−1.22

Note: From Anderson and Dukatz (10);

penetration–viscosity number = $-1.5 (A - \log_{10} N275)/(A - B)$

where

A = $4.258 - 0.79674 \log_{10}$ (pen 25°C)
$N275$ = the kinematic viscosity at 135°C (275°F) (cst), and
B = $3.46289 - 0.61094 \log_{10}$ (pen 25°C).

Regression Analysis of HPGPC Data

Based on the results reported in Table 6, a regression function was developed relating absolute viscosity and HPGPC parameters. The results of this analysis are given in Table 8. The coefficient of determination (r^2-value) for this model is 0.95; thus, there is a significant degree of correlation between vis-
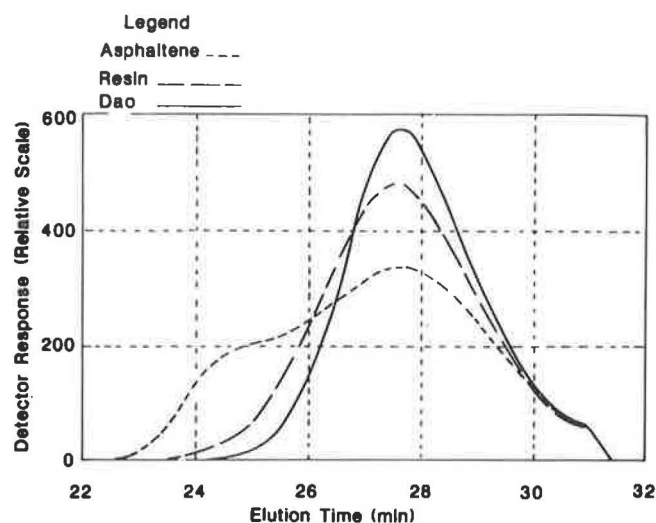

FIGURE 4 HPGPC profiles of ROSE products.

cosity and the HPGPC parameters. Similar results were obtained for regression analyses relating HPGPC data to (a) penetration and (b) kinematic viscosity.

Therefore, the values of all three rheological properties are directly related to the composition of the asphalt. This relationship is not apparent from simply studying the data; there is no obvious correspondence between viscosity and the amount of large or small molecules. Apparently, viscosity is not determined by the preponderance of one molecular size in the asphalt, but is dependent on the overall interaction of molecules of different functional types. This observation correlates with the results reported by Altgelt and Harle in 1975 (7). They found that the viscosity of an asphalt is largely determined by the following factors: (a) the relative proportions of generic fractions, (b) the molecular weight of the asphaltene fraction, (c) the viscosity of the maltene fraction, and (d) the solvent

TABLE 4 ASPHALTS MEETING VISCOSITY SPECIFICATIONS FOR AC-10 AND AC-20 GRADE

Asphalt No.	Proportions			Viscosity poises(60° C)	Grade
	Asphaltene	Resin	DAO		
45	0.10	0.81	0.09	840	AC-10
42	0.24	0.46	0.30	883	AC-10
24	0.36	0.14	0.50	870	AC-10
31	0.10	0.90	0.00	1879	AC-20
22	0.29	0.41	0.30	1655	AC-20

TABLE 5 HPGPC RESULTS FOR ROSE PRODUCTS

ROSE Product	Proportion of Area in Each Section							
	1	2	3	4	5	6	7	8
Asphaltene	15.0	13.2	16.8	9.8	10.1	17.8	11.1	6.2
Resin	2.2	8.6	20.5	14.1	14.3	22.6	12.1	5.6
DAO	0.4	4.0	17.7	16.0	17.1	26.3	13.0	5.5

TABLE 6   HPGPC RESULTS FOR 14 ASPHALTS

Asphalt	Proportion of Area in Each Section								Viscosity
No.	1	2	3	4	5	6	7	8	poises(60° C)
13	5.2	9.9	19.1	13.3	13.6	21.7	11.7	5.5	1257
15	4.4	10.2	20.1	13.5	13.6	21.4	11.4	5.3	1366
16	3.9	9.3	19.8	13.9	14.1	21.9	11.5	5.5	343
22	4.7	9.9	19.5	13.3	13.6	21.6	11.7	5.8	1655
23	3.3	9.0	19.8	14.0	14.3	22.4	11.9	5.4	451
24	4.2	9.0	18.4	13.0	13.9	22.7	12.4	6.4	870
25	3.9	9.6	20.0	13.6	13.9	21.8	11.4	5.8	1360
27	5.7	10.3	19.5	13.0	13.2	21.0	11.4	5.9	2642
31	3.5	10.1	21.0	13.7	13.7	21.4	11.3	5.2	1879
32	5.9	9.1	17.7	13.1	13.9	22.3	12.2	5.8	531
41	2.4	9.0	20.6	13.9	14.2	22.6	11.8	5.4	975
42	4.7	10.0	19.7	13.3	13.5	21.2	11.5	6.1	883
44	6.6	10.1	18.9	13.2	13.5	21.2	11.4	5.2	1257
46	3.0	8.7	19.6	13.8	14.3	22.8	12.2	5.6	694

power of the maltene fraction. Many of these factors are also significant in determining the HPGPC profile of an asphalt.

SUMMARY OF RESULTS

The asphalts used in this study were produced by blending the products of a ROSE plant; thus, these asphalts are identical in terms of their source and method of processing. Consequently, a distinct relationship can be drawn between their physical properties and their chemical composition. In light of this, the following observations can be made concerning the results of this project:

• Temperature susceptibility: In the temperature range of 25°C to 135°C, there is little variation in temperature suscep-

TABLE 7   ACTUAL VERSUS HYPOTHETICAL HPGPC DATA

Asphalt	Difference Between Actual and Hypothetical Results by Section[a]							
No.	1	2	3	4	5	6	7	8
13	-0.5	+1.7	+1.0	-0.3	-0.5	-0.8	-0.5	-0.3
15	+0.0	+1.6	+0.9	-0.1	-0.4	-1.0	-0.7	-0.4
16	-0.1	+1.6	+1.2	-0.1	-0.5	-1.3	-0.8	-0.2
22	-0.7	+1.4	+0.9	-0.2	-0.4	-0.7	-0.4	+0.0
23	-0.8	+1.1	+1.0	+0.1	-0.2	-0.6	-0.3	-0.3
24	-1.6	+1.1	+0.6	-0.5	-0.3	+0.0	+0.2	+0.7
25	-0.5	+1.0	+0.8	0.0	-0.1	-0.6	-0.7	+0.1
27	+0.1	+1.5	+0.8	-0.3	-0.6	-1.1	-0.7	+0.1
31	+0.0	+1.0	+0.9	0.0	-0.2	-0.7	-0.7	-0.5
32	+0.0	+1.6	+0.3	-0.5	-0.5	-0.8	-0.1	+0.0
41	-0.5	+0.4	+0.4	0.0	0.0	-0.1	-0.3	-0.1
42	+0.0	+1.7	+0.9	-0.4	-0.7	-1.4	-0.7	+0.4
44	+0.0	+2.2	+1.6	-0.2	-0.7	-1.5	-0.8	-0.6
46	-1.3	+0.4	+0.5	+0.1	+0.1	+0.2	+0.1	-0.1
Avg	-0.4	+1.3	+0.8	-0.2	-0.4	-0.7	-0.4	-0.1

Note: Numbers in rows do not add to zero because of rounding errors.
[a]A positive difference means that the actual HPGPC parameter is greater than the hypothetical value.

TABLE 8   RESULTS OF REGRESSION ANALYSIS OF HPGPC DATA

Independent Variable	Regression Coefficient
x1	1.01
x2	1.06
x3	1.31
x4	0.21
x5	0.29
x6	1.67
x7	0.53
x8	0.82

Note: Independent variables x1 to x8 are the proportion of area in Sections 1 to 8, respectively. Dependent variable: $\log_{10}$ of absolute viscosity (poises). Coefficient of determination: $r^2 = 0.95$. Constant $= -91.23$.

tibility for the asphalts tested. Thus, temperature susceptibility appears to be relatively insensitive to changes in the chemical composition of the asphalt. However, in this project the range of composition examined was relatively small; consequently, no general conclusion should be drawn from this observation.

• Results of HPGPC analysis: Viscosity (60°C and 135°C) and penetration (25°C) were found to be directly related to the HPGPC parameters of these asphalts. However, the nature of these relationships is complex. Viscosity and penetration are apparently determined by the overall interaction between molecules of different functional types. It is not known whether the relationships developed in this project can be applied to asphalt from other sources.

• Effect of heat on HPGPC profiles: Hypothetical HPGPC parameters were calculated from the HPGPC results of the ROSE products and the proportion of these products in the asphalt. In general, the actual HPGPC parameters for the asphalts contained more large molecules than expected. It is believed that this discrepancy is due to the effect of the heat applied during blending; thus, heating appears to cause an increase in the amount of large molecules in the asphalt.

The scope of this project is limited by the lack of data on asphalts from different sources. Consequently, the study will be expanded to incorporate asphalts of various origins. One goal of the expanded project is to investigate the existence of a general relationship between viscosity and HPGPC data. In addition, the effect of aging on HPGPC profiles will be evaluated by analyzing the thin-film oven test residues of asphalts.

In 1960 Simple et al. showed that the properties of asphalts could be varied in a systematic manner by adjusting their chemical composition (12). They concluded that blending processes could be used to improve the quality of asphalts. The results of the current project indicate that HPGPC is a feasible procedure for characterizing the composition of asphaltic materials. Consequently, it is believed that HPGPC is a suitable analytical tool for use in any such process that is designed to improve the quality of asphalts. Another suggested use of HPGPC is for monitoring the changes in an asphalt that result from the effects of heat and weathering [Jennings et al. (5)]. The trends observed in this project support this view.

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