Chemical Characterization of Asphalt Cement and Performance-Related Properties

C. J. GLOVER, R. R. DAVISON, J. A. BULLIN, J. W. BUTTON, AND G. R. DONALDSON

Gel permeation chromatography (GPC), the Corbett analysis procedure (ASTM D 4124-82), and the Heithaus test for component compatibility have been used to characterize asphalts and to investigate relationships among these chemical properties and physical properties and performance. The asphalts used in the present study were periodic samples of virgin asphalt from various suppliers in Texas, test pavement asphalts from three locations in Texas, and a group of 12 asphalts that had been rated according to pavement tenderness. GPC chromatograms, using toluene or tetrahydrofuran (THF) as the carrier solvent, show significant differences from one supplier to the next. Differences in chromatograms for a single supplier over a period of time may be quite significant. Furthermore, the differences between toluene and THF chromatograms are considerable and can likely be used as supplementary analyses. Finally, differences in viscosity grades (for a given refiner at a given time) frequently may be detected as differences in the shapes of the GPC chromatograms. For virgin asphalts from the Texas test sections, viscosity temperature susceptibility was found to correlate quite well with the molecular size fractions of the GPC chromatograms using either toluene or THF as a carrier solvent. Studies of pavement tenderness showed a relationship between component compatibility and tenderness and between the GPC large molecular size fractions and tenderness. In addition, asphaltene content was found to relate to component compatibility and to tenderness. Finally, as a cross correlation, the large molecular size region of the GPC chromatograms is directly related to the asphaltene content of asphalts with the exception of the Texas Diamond Shamrock asphalt.

Ultimately, the physical performance and durability of any material are determined at the molecular level. For pure component materials, molecular packing, structure, and interactions determine physical properties. In multicomponent materials these features are important, and interactions between differing molecular species play a significant role as well. These interactions can cause not just crystallinity or packing differences but also cohesive energy and compatibility effects manifested in phase behavior. Consequently, if the chemical nature and composition of a material can be adequately described, it ought to be possible to predict its physical properties, at least in principle.

One technique that has been used in numerous asphalt studies, and with some significant success, is gel permeation chromatography (GPC), also referred to as high-pressure GPC and size exclusion chromatography. This technique is used to separate the constituents of an asphalt, for the most part, on the basis of molecular size. Superimposed on the size exclusion separation, however, are solvent and gel interaction effects, so molecular functionality can play a significant role as well.

One of the earliest efforts at relating asphalt performance to GPC analyses was that by Bynum and Traxler (1). They determined GPC chromatograms on virgin asphalts and pavement cores from nine test sections in Texas. Rheological properties and vanadium concentrations were also determined. Considerable differences were noted among asphalts from different sources. Also the chromatograms obtained from asphalts from a given source often showed change with time. After 2 or 3 years, no consistent relation between molecular size and performance was evident, although the chromatograms of the poorer asphalts appeared to change more with time, and it was found that all of the inadequate asphalts contained a high percentage of vanadium.

More recently, Hattingh (2) used GPC and high-pressure liquid chromatography (HPLC) to study four South African road asphalts and reached conclusions on the large molecular size (LMS) fraction and its effect on tender mixes. Two roads were in good condition after 9 and 3 years, respectively, and two exhibited serious setting properties. The two "good" asphalts showed a much higher LMS fraction than the tender asphalts. Hattingh also used HPLC and a series of solvents to separate both whole asphalt and the maltenes into nine fractions following hexane precipitation of asphaltenes following extended thin-film oven tests (TFOT) on the asphalts used in the roads. He observed that the tender asphalts did not gain in large molecules with aging. This is the reverse of the situation with asphalts that tend to crack, and he thus concluded that too high an asphaltene or LMS percentage causes cracking and too low a percentage causes setting problems.

The most extensive studies of the use of GPC in predicting asphalt pavement performance have been those of Jennings and coworkers (3–7) in which they concluded that LMS can play a significant role in cracking. A study of 39 Montana roads of different ages built with asphalts of five penetration grades from all four of Montana's refiners led Jennings to conclude that cracking was related to the relative size of the LMS region of the GPC chromatograms (3). Conversely, he determined that low LMS is desirable to reduce cracking. He also concluded that asphaltene content as determined by heptane solubility was related in the same way to cracking.

Jennings and Pribanic (6) expanded the road study to include samples in 15 other states that have a wide range of climatic

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conditions. The nation was divided into zones of similar climate, and the condition of roads within each zone was compared on the basis of molecular size distribution. In general, in each zone there was an LMS level above which all of the roads were bad (again, with respect to cracking), and most of the good and excellent roads in each zone were those with a lower LMS. There was, however, a large difference between the LMS percentage that could be tolerated in warm zones and in very cold zones. Interestingly, several roads in Georgia with low LMS were exhibiting rutting.

Variation of GPC chromatograms with viscosity grades for the asphalts of Jennings's study of Montana highways was inconsistent. Some refineries showed identical GPC for the different viscosity grades; some showed consistent variation with grade; some showed random variation. Some old pavement exhibited GPC chromatograms that could not be derived from any of the asphalts now supplied in the state.

Adams and Holmgreen report GPC results for test pavements at three locations in Texas (8). There were ten asphalts and six or seven were used at each location. GPC chromatograms showed similarity in the common asphalts used at the different locations, and essentially no variation with viscosity grades, either AC-10 or 20, is reported. There was also no correlation found between the chromatograms of the virgin asphalts and tensile strength of the paving mixture.

In another study, Plummer and Zimmerman (9) evaluated asphalt cracking and its relation to molecular size distributions. Their study was based on 11 pavement samples in Michigan and 8 in Indiana. The Indiana results were more consistent than those of Michigan, but both showed more cracking with an increase in molecular size. Results from the Michigan roads showed that asphalts extracted immediately after construction were harder for the roads that eventually cracked (a mean penetration of 48 versus 62).

Still more recently, Zenewitz and Tran (10) reported a statistical evaluation of the pooled study of Jennings et al. that supports the earlier conclusion that cracking, LMS fraction, and climate are related. Although they observed no statistical correlation between LMS and cracking when all of the data were analyzed together, there was correlation within climatic zones. There was also correlation between LMS and climate. Colder climates tended to have asphalts that were lower in LMS than did warmer climates. This suggests that highway engineers and refiners have found that some asphalts work better than others in their region. In essence, it appears that a natural selection process has led highway districts to use the asphalts that have approximately the proper LMS range for the climate.

Although these studies highlight the efforts and successes at relating chemical properties of asphalt to physical properties and performance, they also point out that quantitative correlations of GPC chromatograms (as one example) with viscosity, cracking, or propensity for producing tender mixes have not been reported. Because of the complexity of asphalts and their variety of composition, such correlations will certainly be limited. Ultimately, it will take a number of chemical characterizations to accurately predict physical properties and performance.

Despite this inherent limitation, the objective of this work was to pursue quantitative relations among certain chemical characterizations of asphalts and their physical properties and performance. Specifically, this paper is a report on recent results on a number of aspects of GPC chromatograms and their relation to physical properties and performance of asphalt cement. GPC techniques involve using both toluene and tetrahydrofuran (THF) as carrier solvents. Reported are results on the variation of GPC chromatograms with supplier, with time, and with viscosity grade. Also included are results on the relation of chromatogram molecular size fractions to viscosity temperature susceptibility and to asphalt tenderness.

EXPERIMENTAL METHODS

The GPC technique has been reported previously (11, 12). The Heithaus peptization test was used for determining flocculation ratio (13). The Corbett analysis (ASTM D 4124-82) was used to obtain Corbett fractions; asphaltenes are reported in this paper (14, 15). Further details of these procedures are given as appropriate.

GPC Analysis

To prepare the asphalt samples for injection, the asphalt was weighed to 0.001-g accuracy and dissolved in distilled solvent measured to 0.1 mL to give a concentration of 7 percent by weight. The sample concentration was closely controlled because sample size has a definite impact on the results. After dissolution, the sample was filtered through a 0.45-micron filter to remove particles that might damage the column. Injecting a reference asphalt as a standard and known compounds, as described previously (12), was essential for monitoring column performance and obtaining reproducible data. Typical reproducibility that was obtained when proper procedures were followed is shown in Figure 1 for THF carrier solvent. Comparable reproducibility was obtained for toluene.

Two column configurations were used in this work according to the carrier solvent employed. When THF was used as a carrier, a 500-Å column followed by a 50-Å column was used. When toluene was used as the carrier solvent, only a 500-Å column was employed. The 50-Å column was omitted because of excessive fouling in the toluene system. The sample size injected in each case was 100 μL of the 7 percent by weight solution.

Heithaus Compatibility Test

The Heithaus peptization test (13) gives a measure of how well the asphaltenes are solubilized, or held in solution, by the resins and oils in the asphalts. The technique has been reported previously in the literature as a routine test procedure. In this work, an abbreviated version was used for determining the flocculation ratio. The flocculation ratio is determined from the amount of heptane required to initiate precipitation of asphaltenes in a toluene-asphalt solution. Starting with 1 g of asphalt and 1 mL of toluene, the flocculation ratio (FR) is calculated as

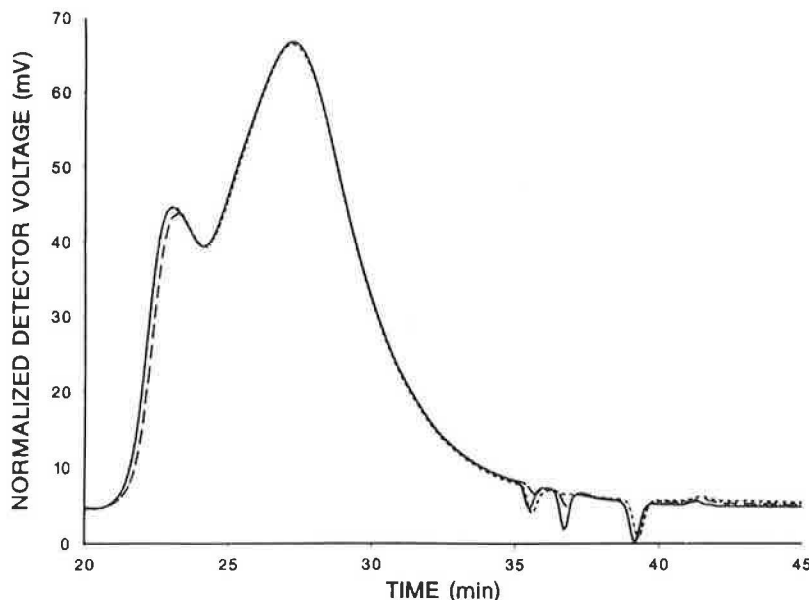$$\text{FR} = \text{Volume of toluene}/(\text{Volume of toluene} + \text{Volume of heptane})$$

FIGURE 1 Reproducibility of three asphalt standard chromatograms in THF (500-Å and 50-Å columns; THF: 100μL, 7 percent by weight).

Hence, the more heptane required to initiate precipitation (i.e., the better solubilized the asphaltenes are by the asphalt-toluene solution), the smaller the flocculation ratio, and a large flocculation ratio indicates poor compatibility.

RESULTS AND DISCUSSION

Chromatograms of Several Asphalt Suppliers

As has been the case in other studies, significant differences in the GPC chromatogram of asphalts provided by several suppliers were observed. Figure 2 shows chromatograms of virgin asphalts from six suppliers; five are AC-20 viscosity grades, and the other is an AC-10. These chromatograms are all taken using THF as the carrier solvent. In some respects, all of the chromatograms except that of the Diamond Shamrock asphalt

are quite similar. First, all have an early peak or shoulder (an LMS fraction) eluting at about the same time. This is followed by a large, broad peak that again elutes at about the same time in each of these asphalts. The differences in the GPC chromatograms of these five asphalts are primarily differences in the relative sizes of these two features. The Cosden AC-20 has the smallest LMS region; it appears only as a shoulder on the broad major peak. For the other four similar asphalts, this region is better defined and somewhat better separated from the major peak. In terms of these features, these five asphalt chromatograms qualitatively are quite similar even though quantitatively they are readily distinguishable.

In contrast, the sixth asphalt, the Diamond Shamrock, is considerably different both qualitatively and quantitatively. Although it still exhibits an LMS peak and a broader later eluting peak, both of these differ from those of the other five
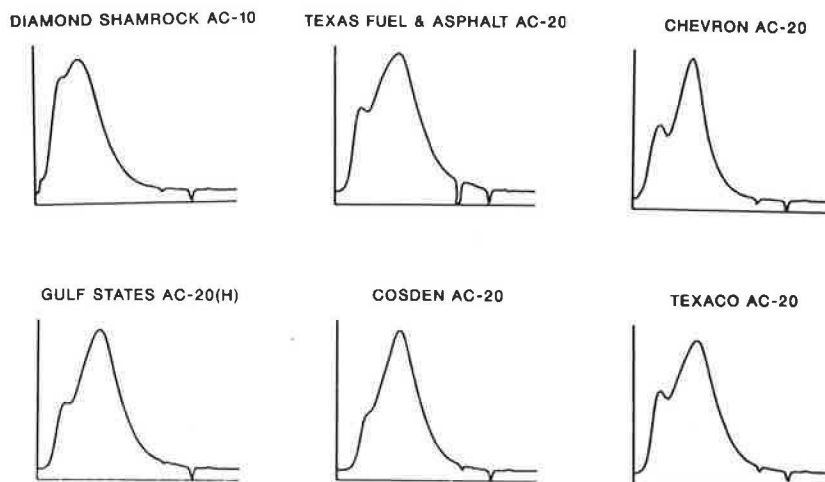

FIGURE 2 Representative chromatograms for several refiners in THF (500-Å and 50-Å columns; THF: 100μL, 7 percent by weight).

asphalts in that each one elutes much earlier and, therefore, consists of, on average, larger molecular size material. Furthermore, the first peak is nearly as high as the second peak, and the overall spread of the Diamond Shamrock chromatogram is considerably narrower than that of the others. The Diamond Shamrock asphalt is different in other characteristics as well, and this makes it a unique and interesting asphalt for further study.

A comparison of several asphalts using toluene as the carrier solvent is shown in Figure 3. Again, striking differences among the different asphalts are seen to exist. As with THF, the average elution time for the Diamond Shamrock asphalt is less than it is for the others indicating, on average, a higher molecular size material. In toluene, however, it is not unusual to see a larger number of waves or peaks in the chromatogram than in THF. The Diamond Shamrock asphalt has three distinct peaks, and the MacMillan has four peaks or waves. The Cosden and the Exxon have fewer peaks (two and one, respectively). It may be that the toluene carrier solvent offers a better discriminating capability among various asphalts and, therefore, may have special value in asphalt analyses in spite of some problems that have been observed such as excessive fouling of the column or with desorption rates of the asphalt materials from the column (12).

Variability of Asphalt Supply with Time

Analyses of asphalts by GPC over a period of time have shown some significant differences in the chromatograms of single suppliers. Figures 4 and 5 show the variability of asphalts from
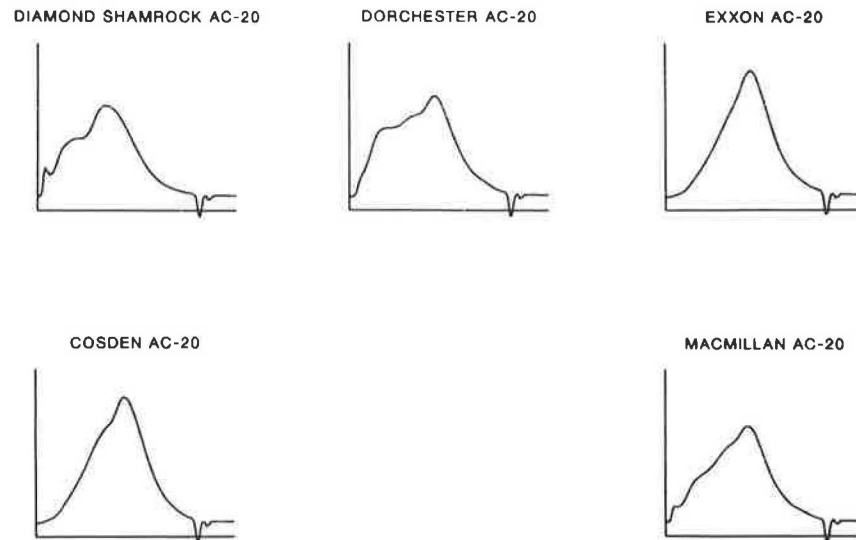

FIGURE 3 Representative chromatograms for several refiners in toluene (500-Å column; toluene: 100μL, 7 percent by weight).
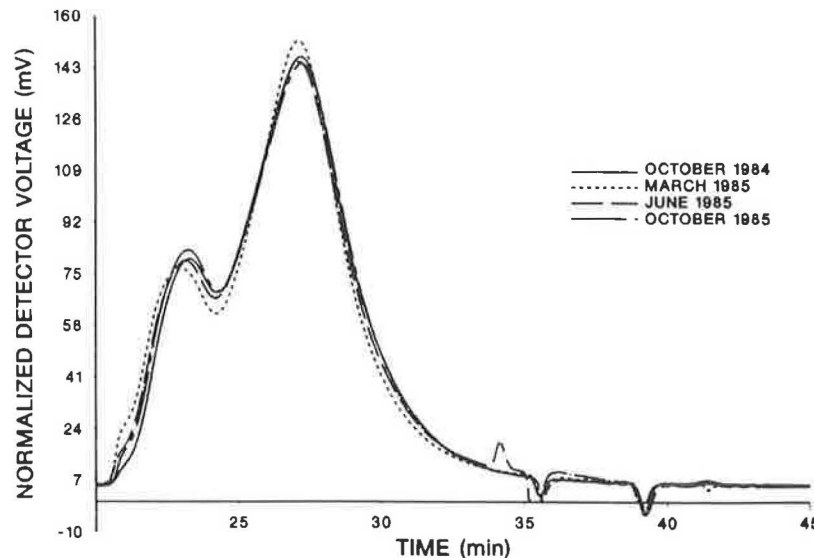

FIGURE 4 Variability of Chevron AC-20 over time (500-Å and 50-Å columns; THF: 100μL, 7 percent by weight).
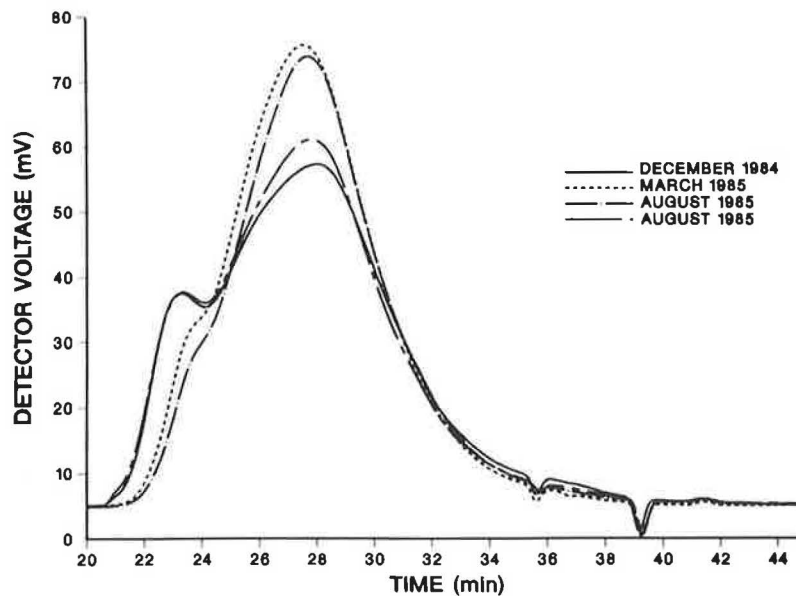
FIGURE 5   Variability of Gulf States AC-20, Houston over time (500-Å and 50-Å columns; THF: 100μL, 7 percent by weight).

two suppliers over a 1-year period. These are all AC-20 asphalts, and the chromatogram variability should be compared with the reproducibility shown in Figure 1. The Chevron asphalts, over this period of time, showed minimal variability whereas, in comparison, the Gulf States Houston exhibited some significant changes. It should be noted that the Gulf States Houston facility does not refine asphalts but is an intermediate supplier. Evidently, they had two different sources of asphalt during this time. Again, it should be pointed out that, in spite of these extreme differences shown by GPC, all four of these asphalts supplied by Gulf States in this figure, as well as those of Chevron in the preceding figure, are the same viscosity grade. Obviously, and not unexpectedly, asphalt viscosity is a highly nonunique function of composition. This provides considerable complication in relating different asphalt compositions to their physical properties and ultimately to their field performance.

GPC and Viscosity

As has been the case in previous research, inconsistent relations between GPC chromatograms and asphalt cement viscosity grade have been observed. In some cases, there are quite obvious and rational differences in the chromatograms for different grades; in others, the differences are minimal. In most cases, differences are fairly evident. Figure 6 shows chromatograms for virgin Witco AR 1000, 2000, and 4000 cements. The addition of a small molecular size cut to lower the viscosity is apparent. Figure 7 shows differences at the other (LMS) extreme for a Dorchester asphalt. A third asphalt (Texaco, Figure 8) shows minimal significant difference between AC-10 and 20 grades, whereas the AC-5 asphalt shows differences that exceed reproducibility. This last set of chromatograms emphasizes that, in spite of the obvious trends of the previous two examples, factors other than those detected by GPC, such as molecular interactions, play a significant role in establishing

asphalt viscosity. This prevents a clean correlation between GPC chromatograms and viscosity.

GPC and Viscosity Temperature Susceptibility

In a previously reported study, ten asphalts from five suppliers were used at three different locations in Texas test pavements (8). For each test pavement, samples of virgin asphalts delivered to the construction site, hot mixes used in the test pavements, and 2- and 3-year cores from the test pavements were obtained. Standard viscosity tests were performed on the virgin asphalts as well as on asphalt extracted from the hot mixes and from the cores. The hot-mix samples were laboratory prepared and compacted. In addition, penetration was determined at 39.2°F and 77°F on the virgin asphalts, laboratory mixes, and cores. Data on the laboratory mixes and cores were obtained on asphalt extracted using trichloroethylene. The viscosities were determined at 77°F, 140°F, and 275°F. These data are reported by Adams and Holmgreen (8).

From these data, viscosity temperature susceptibility (VTS) using viscosities at 140°F and 275°F (16) and penetration index (PI) were calculated according to the equations.

$$VTS = [\log\log(100\eta_1) - \log\log(100\eta_2)]/(\log T_2 - \log T_1)$$

where η_1 and η_2 are the viscosities (poises) at temperatures T_1 and T_2 (kelvin), respectively, and

$$PI = (20 - 500A)/(1 + 50A)$$

where $A = [\log(\text{pen}_{T_1}) - \log(\text{pen}_{T_2})]/(T_1 - T_2)$ and pen_{T_1} and pen_{T_2} are the penetrations at the two temperatures.
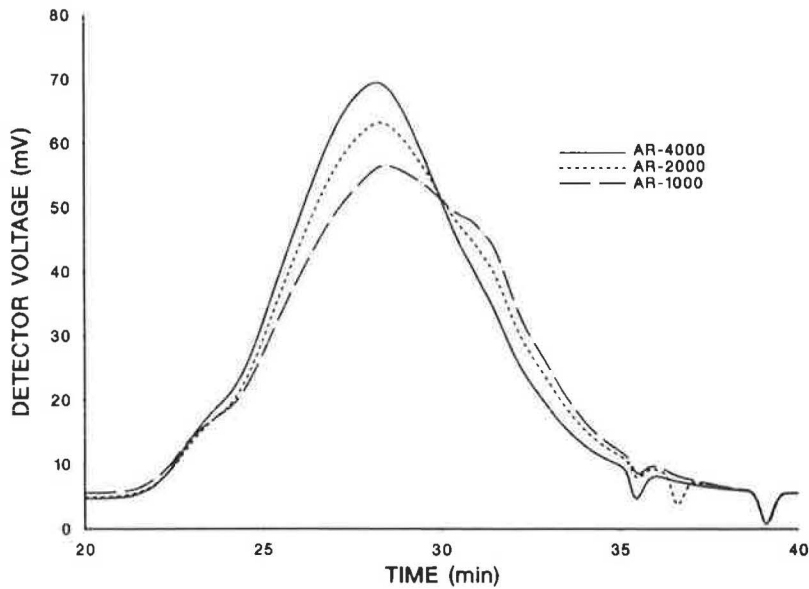
FIGURE 6 GPC comparison of three viscosity grades of a Witco asphalt (500-Å and 50-Å columns; THF: 100μL, 7 percent by weight).
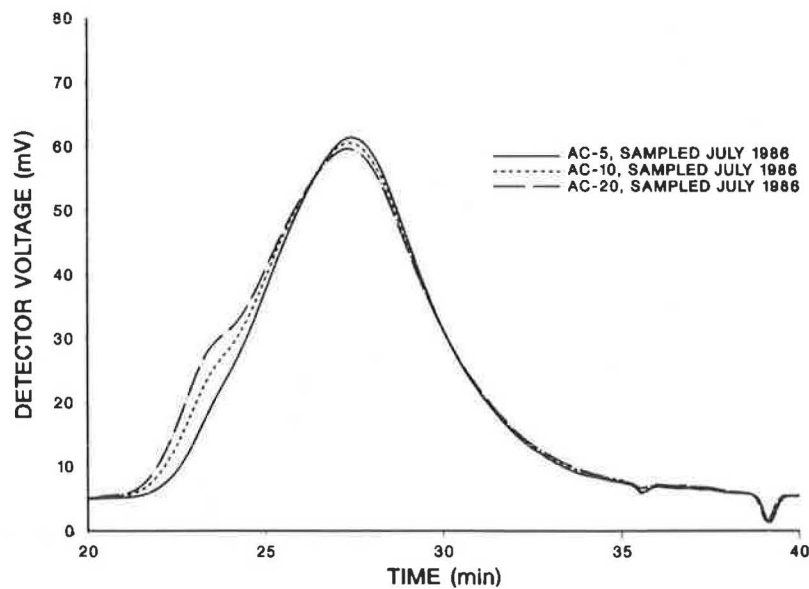

FIGURE 7 GPC comparison of viscosity grades of a Dorchester asphalt (500-Å and 50-Å columns; THF: 100μL, 7 percent by weight).

For the purposes of correlating GPC chromatograms with these VTS and PI properties, the chromatograms have been divided into three equal time sections according to the procedures of Jennings and coworkers (4, 5, 17). For the THF analyses that used two columns in series, the chromatograms were divided into three 5-min sections between 20 and 35 min. For the toluene analyses, which used only a 500-Å column, the chromatograms were broken into three 4-min sections ranging from 10 to 22 min in retention time. Following Jennings, the terms large molecular size (LMS), medium molecular size (MMS), and small molecular size (SMS) are used for the three regions even though this interpretation is not exactly correct.

Using these calculated values, correlations of the viscosity temperature susceptibility and of the penetration index to the chromatogram molecular size distribution characteristics were checked. In each case, a multiple linear regression of the VTS or PI using two of the chromatogram areas as independent variables was attempted. Summaries of the fit parameters and correlation coefficients are given in Table 1. When all of the virgin, or tank, asphalt samples are lumped together, the THF GPC analyses correlate with viscosity temperature susceptibility with a correlation coefficient (r^2) of 0.88. This includes 18 asphalt samples. For the toluene analyses, using the 20 samples available in this data set, the correlation coefficient is
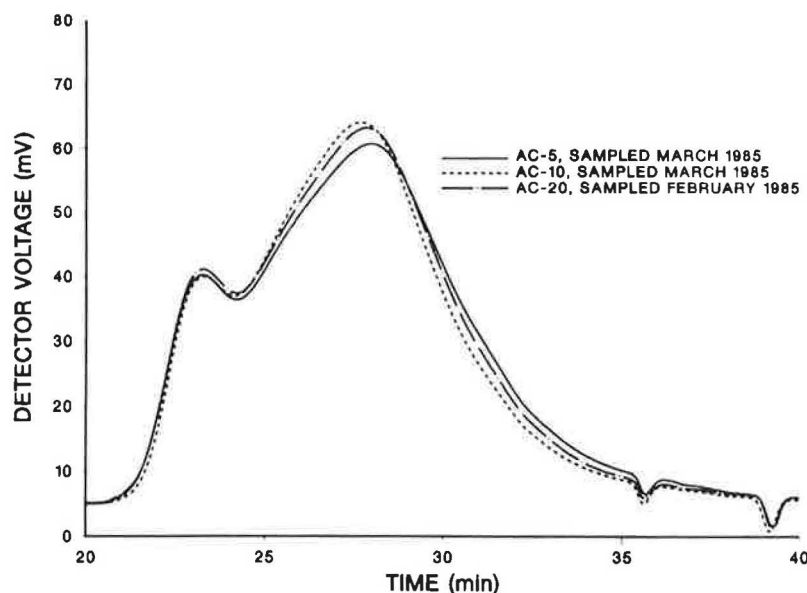
FIGURE 8 GPC comparison of three viscosity grades of a Texaco asphalt
(500-Å and 50-Å columns; THF: 100μL, 7 percent by weight).

TABLE 1 VTS CORRELATIONS OF DICKENS, DUMAS, AND
LUFKIN TEST SITE ASPHALTS

Carrier Solvent	Data Set	a	b	c	r^2
THF	Tank—all grades (18 data points)	3.27	−0.00889	0.0275	0.88
	Tank—all AC-10 (8 data points)	2.48	0.00580	0.0543	0.95
	Tank—all AC-20 (10 data points)	3.73	−0.0174	0.0129	0.93
	Cores—all grades (25 data points)	0.854	0.0350	0.134	0.49
Toluene	Tank—all grades (20 data points)	2.97	−0.00763	0.0714	0.87
	Cores—all grades (17 data points)	2.56	0.00600	0.0930	0.49

NOTE: $VTS = a + b(LMS) + c(SMS)$.

essentially the same at 0.87. If all eight of the AC-10 asphalts are considered as a group, an r^2 of 0.95 is obtained, and if all of the AC-20 are grouped together (10 samples), the correlation coefficient is 0.93. Smaller subsets of the data probably are not warranted. Calculated VTS-values are shown versus experimental VTS-values for the THF analyses in Figure 9. A comparable plot was obtained for toluene analyses. Grouping the AC-10 and AC-20 asphalts is supported by the notion that VTS reflects changes in viscosity with temperature rather than the actual absolute values of viscosity for a given asphalt refiner or supplier. It may be reasonable to expect that both AC-10 and AC-20 grades will behave similarly with respect to these changes even though their viscosities may differ by a factor of 2. However, some improvement is observed when the AC-10 and the AC-20 asphalts are grouped separately.

Correlations of PI with LMS and SMS are not nearly as good as for VTS. For THF analyses a correlation coefficient of only 0.05 was obtained. For toluene the value was 0.59.
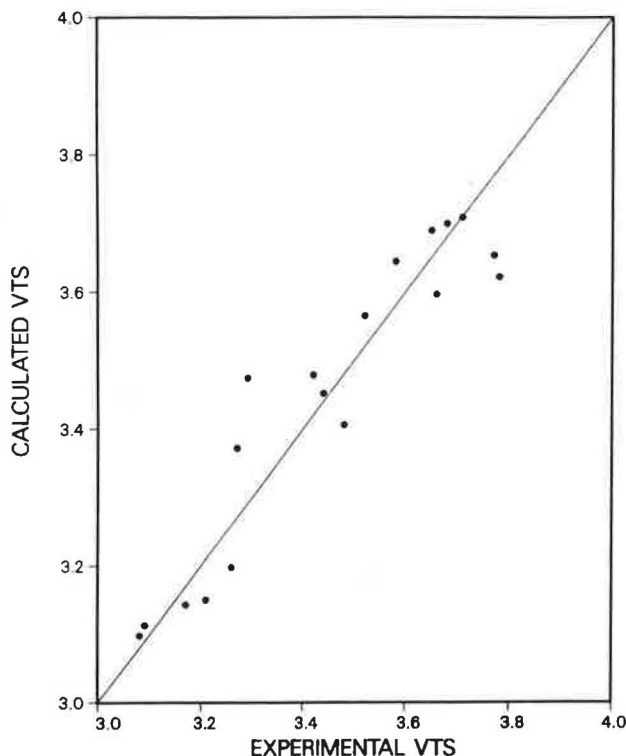

FIGURE 9 Comparison of calculated and experimental VTS for the Texas test section tank asphalts in THF.

No correlation of either VTS or PI with molecular size distribution was observed for the asphalts extracted from core samples. Using both THF and toluene analyses, the correlation coefficient for VTS for 25 cores was only 0.49. The correlation coefficients for PI, including all cores in the data set, were 0.12 for THF and 0.11 for toluene.

Asphalt Cement Tenderness and Component Compatibility

The word "peptize" means to cause to disperse in a medium or to bring into a colloidal solution. According to Heithaus (*13*), "Asphalts consist of a highly aromatic material (asphaltenes) of moderate molecular weight (ca. 2,000-1,000) dispersed or dissolved in a lower molecular weight medium (maltenes)." Considerable evidence indicates that the "apparent" high molecular weight often reported for asphaltenes is due to association of lower molecular weight molecules (*18*). Heithaus discussed the importance of the peptizability of the asphaltenes and of the peptizing power of the maltenes in determining the mutual solubility of these asphalt fractions. The state of peptization of the asphaltenes plays a major role in determining the rheological properties of an asphalt and the susceptibility of these properties to changes in asphalt composition and environmental factors. Heithaus suggests that in a neat asphalt there is probably no physical basis for a distinction between dissolved and dispersed phases. Altgelt and Harle (*19*) showed that the polarity of the so-called asphaltenes in petroleum asphalt greatly influenced their self-association and that the dispersibility of these asphaltenes in the asphalt was a dominant factor influencing asphalt viscosity.

The term "compatibility," as used herein, relates to mutual solubility of the molecular components in asphalt to produce homogeneity in the asphalt system and is thus a function of the state of peptization of the asphalt. By definition then, as highly associated molecular agglomerates in the asphalt become separated from their dispersing or solubilizing components, the system will have reduced component compatibility. An extreme example of poor compatibility might be a highly polar (heteroatom content or highly condensed aromatic ring systems) asphalt containing an excess of a low–molecular weight, nonpolar, paraffinic blending stock (*18*).

Heithaus (*13*) investigated asphaltene peptizability or degree of dispersion, the dispersion power of maltenes, and the state of peptization of asphalts. Little application of the state of peptization parameters applied by Heithaus appears in the literature. The California Highway Department, in extensive pavement performance studies (*20, 21*), indicates that the parameters used by Heithaus for the state of peptization of asphalt may be useful in predicting pavement durability. Researchers at the University of New Mexico (*22, 23*) have related Heithaus' results to compatibility of asphalt with modifiers. Good component compatibility is probably a necessary requirement for good pavement durability. Akzo Chemie America uses the test to measure emulsibility of asphalts (J. Dybalski, unpublished data).
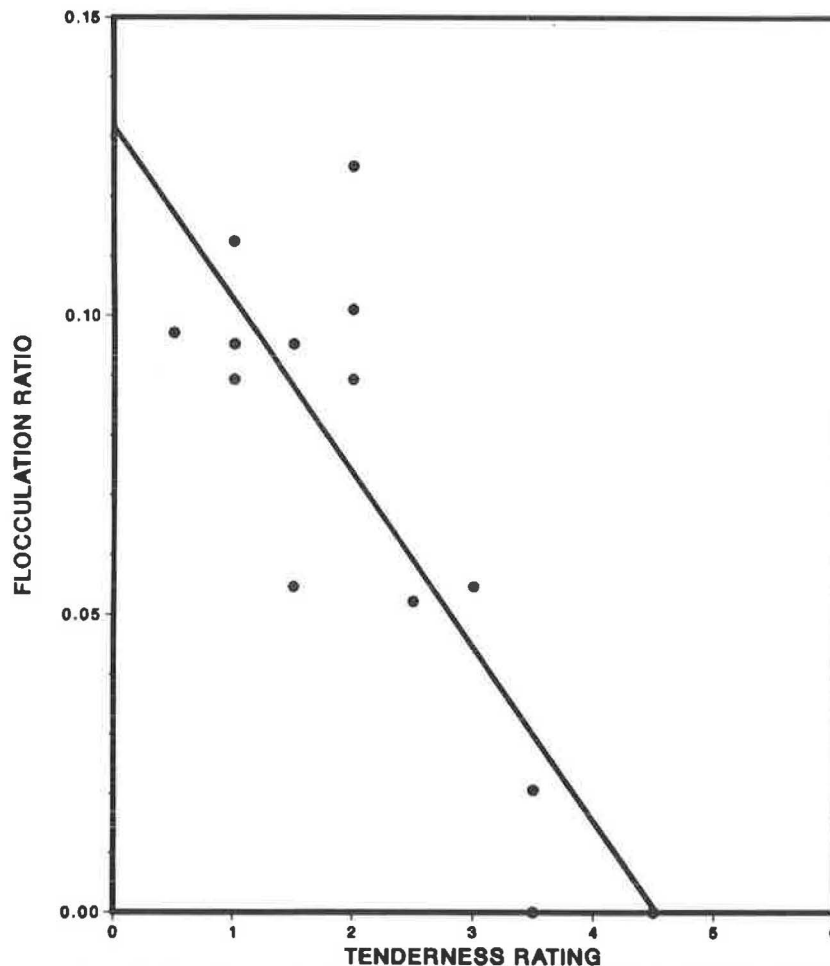

FIGURE 10   Virgin asphalt flocculation ratios and tenderness ratings.

A number of asphalts of various paving grades and from different sources were studied with respect to tenderness and possible correlation with chemical properties. In this study, pavement tenderness is based on user comments about the asphalt's general performance history with particular emphasis on construction and early pavement performance (*24*). The tenderness rating ranges from 0 to 5 with 0 indicating that tenderness or slow-setting problems are never associated with the asphalt and 5 indicating that these problems are always associated with the asphalt.

Figure 10 shows a reasonable correlation between the Heithaus peptization flocculation ratio and the subjective tenderness ratings. This correlation was expected because highly peptized asphalts had been previously associated with slow-setting mixtures (*25*).

GPC and Tenderness

It has been suggested previously that low values of the LMS fraction as determined by GPC are an indicator of tenderness (*2, 6*). The asphalts in Figure 10 have also been correlated using LMS, and the results are similar to those shown in Figure 10, except for one asphalt, a Diamond Shamrock AC-10, which is off the graph in LMS even though it sometimes produces tender mixtures.

Asphalt tenderness is compared with asphaltene content in Figure 11. In this plot, Diamond Shamrock (denoted by DS) fits quite well. With the exception of this one asphalt, all of the techniques plot about equally well with much of the scatter undoubtedly due to the subjectivity of the tenderness rating.

Basically, asphalts can be broken into two families with relation to tenderness. The tender asphalts are those with tenderness ratings above 2. These asphalts have low flocculation ratios, low LMS (with the exception of Diamond Shamrock asphalt), and low asphaltene content. The nontender asphalts have tenderness ratings of 2 or lower. Accordingly, they have high flocculation ratios, high LMS, and high asphaltene content. This implies that there are strong cross correlations between flocculation ratios, LMS, and asphaltene content. A plot showing the variation of LMS with asphaltene content is shown in Figure 12. With the exception of Diamond Shamrock, which is again off the graph, the correlation is very nearly within the accuracy of the data, so that, in most cases, when high LMS is found, it means high asphaltenes. Figure 13 shows the complete chromatograms of several asphalts spanning the range of tenderness rating. The presence of a significant amount of LMS materials in nontender asphalts and, conversely, the absence of a significant LMS peak for tender asphalts are evident.
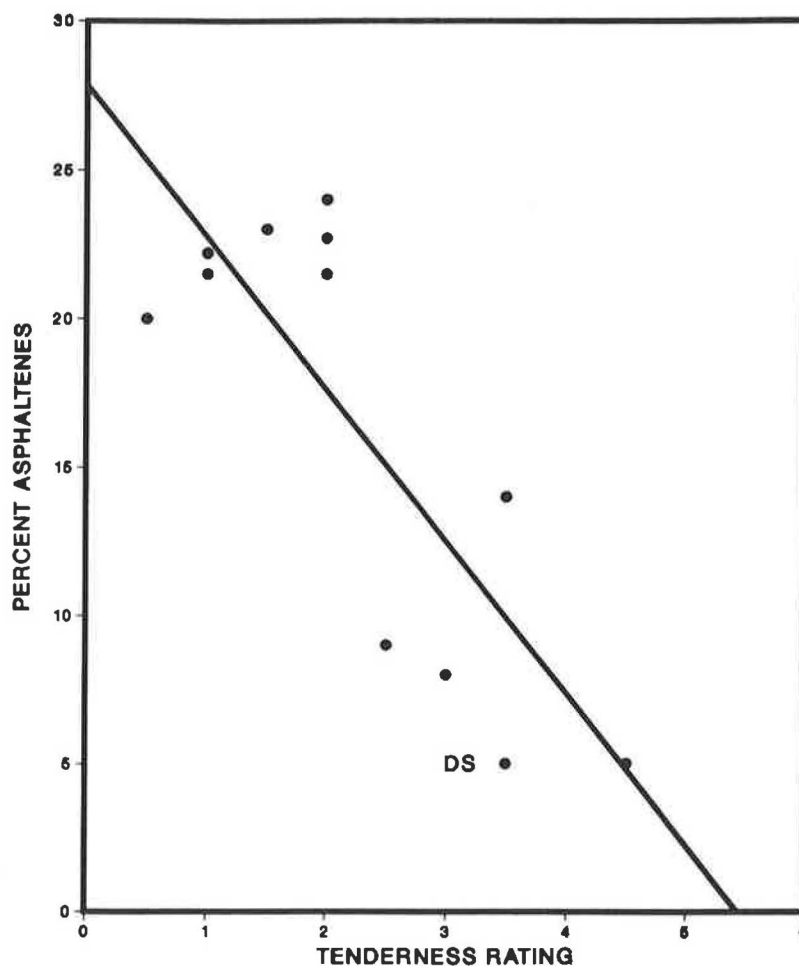

FIGURE 11 Corbett analysis of asphaltene fractions and pavement tenderness ratings.
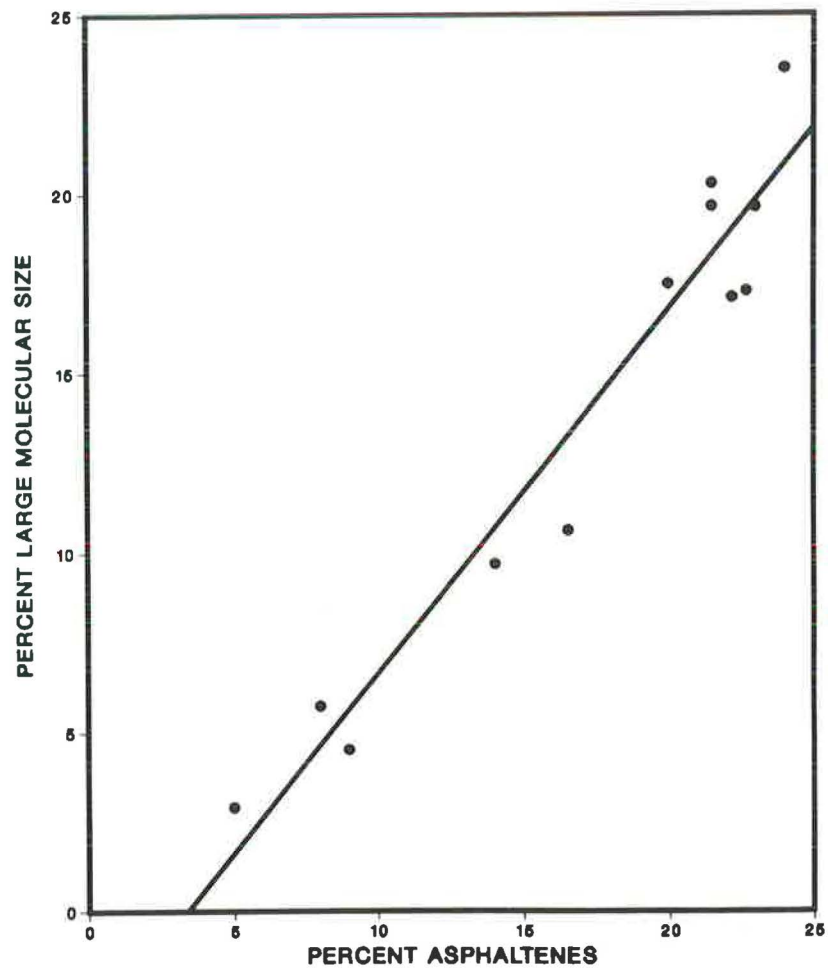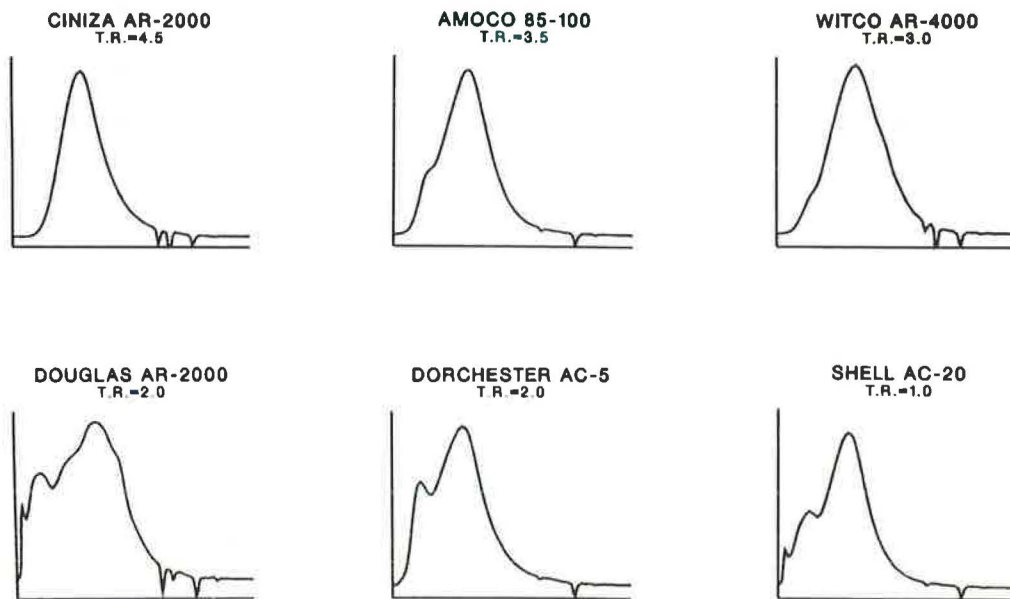
FIGURE 12 LMS fractions and asphaltene fractions.

FIGURE 13 Comparison of GPC profiles and pavement tenderness ratings (500-Å and 50-Å columns; THF: 100µL, 7 percent by weight).

CONCLUSIONS

In this work, a number of asphalt properties and characteristics have been studied in light of gel permeation chromatography chromatograms. Results using both THF and toluene as carrier solvents, which give distinctively different chromatograms, were obtained. The chromatograms are quite distinctive with respect to asphalt supplier and there are readily observed differences over time in the chromatograms for selected suppliers. Usually, differences in viscosity grades for a given refiner at a given time are evident from the shapes of the GPC chromatograms.

Viscosity temperature susceptibility has been found to correlate quite well with the large and small molecular size fractions of the GPC chromatograms for virgin asphalts. Correlations of VTS for asphalts extracted from cores, however, were not found, and neither did the penetration index for either virgin or extracted asphalts correlate with the GPC areas.

Finally, the Heithaus flocculation ratio was found to relate to asphalt tenderness. Asphalts that often produce tender mixtures were also observed to have a smaller fraction of the GPC chromatogram area in the LMS region.

ACKNOWLEDGMENTS

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