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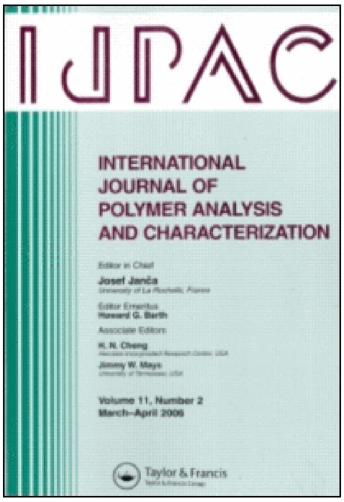

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Characterization of Asphalt Binders Based on Chemical and Physical Properties

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Characterization of Asphalt Binders Based on Chemical and Physical Properties

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The chemical compositions and physical properties of unmodified and polymer-modified asphalts were studied using high-performance gel permeation chromatography (GPC), Fourier transform infrared spectroscopy (FTIR), dynamic mechanical analysis (DMA), thermal mechanical analysis (TMA), and differential scanning calorimetry (DSC). Two viscosity-based asphalt grades (AC-5 and AC-10) and two polymers, namely, styrene-butadiene-styrene (SBS) and styrene-ethylene-butylene-styrene (SEBS) were used to modifiy asphalt in this study. The combination of GPC and FTIR was found to be an excellent approach for fingerprinting and quality control of polymers and asphalt binders. The rheological properties of asphalt binders were determined to be good characteristics for determining the optimum polymer concentrations for effective modification. The DSC results indicated that different asphalt grades have different levels of polar associations as detected from changes in enthalpy. Polymer modification alters these associations. TMA was a fast method for determining the highest possible service temperature of the pavement.

Keywords: Asphalt; polymer modification; GPC; binder; polar association; chromatography

INTRODUCTION

The long-term pavement performance of asphalt concrete (AC) surfaced roads is a function of traffic load and volume, material properties, construction practices, and environmental factors. A typical AC surfaced pavement deteriorates over time and with increasing number of load repetitions. Pavement deterioration manifests itself in several common types of distresses including rutting, fatigue cracking, low temperature cracking, reflective cracking, aging, raveling, and stripping[1–3]. The conventional materials used in the asphalt concrete mixture may perform satisfactorily relative to one distress type but fail prematurely relative to the others. For example, asphalt concrete mixtures made by using hard binders will have low rutting, but high fatigue and temperature cracking potentials. Mixtures made with soft asphalt binders, however, will have low fatigue and temperature cracking, but high rutting potentials. Hence, modification of the asphalt binder to enhance its performance at both high and low temperatures and under traffic loading is desirable for the success of constructing superior pavements. Such modifications include the addition of polymers to enhance the binder properties at both low and high temperatures. It has been shown that polymer modified asphalts can improve pavement performance.[4–6]

Our research program was initiated to study polymer modified asphalt pavements that will address the above considerations. The study is divided into three sections including, the fundamental physical, chemical, and thermodynamic properties of asphalt binders, the basic morphology and microstructure of polymer-fiber-asphalt-aggregate mixtures, and the structural and engineering properties of polymer-fiber-asphalt-aggregate mixtures under extreme low and high temperatures found in Michigan.

This paper focuses on the development of a protocol for fingerprinting, including characterization and identification of asphalts using high-performance gel permeation chromatography (GPC) and other instrumentation. The asphalts studied were unmodified, styrene-butadiene-styrene (SBS) and styrene-ethylene-butylene-styrene (SEBS) modified AC-5 and AC-10 asphalts. The molecular characteristics of the binders were studied using GPC, Fourier transform infrared spectroscopy (FTIR), and differential scanning calorimetry (DSC). The physical properties of the binders were studied using DSC, dynamic mechanical analysis (DMA), and thermal mechanical analysis (TMA).

BACKGROUND

Asphalt is a complex mixture of many different hydrocarbons. The chemical composition of an asphalt is determined by the source of crude oil, refinery process, and the grade of the asphalt. A generic asphalt elemental

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analysis shows that it contains approximately 84 wt% C, 10 wt% H, 1 wt% O, and the remainder consists of several trace elements including N, S, V, Ni, and Fe.[7] The average molecular weight of a generic asphalt molecule ranges from 500 to 5000 g/mol.[7] Table I shows the basic molecular information of three commonly used asphalts, AC-5, AC-10, and AC-20.[7]

In general, asphalt constituents are classified into three categories: oils, resins, and asphaltenes. Oils are the light compounds in asphalt which have the lowest molecular weights (24–800 g/mol) and have a large number of side chains and few rings with carbon/hydrogen atom number ratios less than 0.6, and are soluble in hexane.[8] Resins are intermediate molecular weight compounds (800–2000 g/mol). It is important to note that resins can contain sulfur and nitrogen. Resins are polar, have a carbon/hydrogen ratio between 0.6 and 0.8 and are soluble in light petroleum naphtha.[8] Asphaltenes are the highest molecular weight compounds (1800–8000 g/mol) with aromatic ring structures, few side chains, and carbon/hydrogen ratios greater than 0.8.[8] Asphaltenes contain the trace elements mentioned earlier which may react with potential polymers and are soluble in carbon tetrachloride. An average asphalt sample has an asphaltenes/resin/oil weight ratio of approximately 23/27/50[9] and the asphaltene content is higher for harder asphalts. GPC is usually used to determine the molecular weight, molecular weight distribution, and the fraction of each constituent in the asphalt.

Asphaltenes can exist both in a randomly oriented particle aggregate form or in an ordered micelle form. In the micelle form, the polar groups (water,

TABLE I Asphalt Elemental Analysis

	AC-5	*AC-10*	*AC-20*
C %	85.7	82.3	84.5
H %	10.6	10.6	10.4
O %	—	0.8	1.1
N %	0.54	0.54	0.55
S %	5.4	4.7	3.4
V ppm	163	220	87
Ni ppm	36	56	35
Fe ppm	—	16	100
aromatic C, %	32.5	31.9	32.8
aromatic H, %	7.2	7.1	8.7
mol. wt.*	570–890	810–930	840–1300

*The solvent used in this study was toluene. Different values of molecular weight may be obtained if an other solvent is used.

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silica, or metals such as V, Ni, and Fe) are either oriented toward the center to form an oil-external micelle from hydrogen bonding, charge transfer, or salt formation, or oriented outward to form an oil-internal micelle (Hartley micelle). Asphaltenes are present as discrete or colloidally dispersed particles in the oily phase. Colloidally dispersed asphaltenes are not stable in the oil medium by themselves, but can be stabilized through polar resins. The resins contain aromatic compounds substituted with longer alkyls and a larger number of side chains attached to the rings than asphaltenes. The combination of the saturated and the aromatic characteristics of the resins stabilizes the colloidal nature of the asphaltenes in the oil medium. The growth and ultimate size of the micelles are dependent on temperature, resin content, and the presence of other chemicals such as polymer modifiers. The engineering properties of asphalts are directly related to the quantity of asphaltenes, the size of the micelle structure, and the nature of the dispersion medium, oils and resins. The percentage of the asphaltene present is the defining factor between different grades of asphalt. The higher the asphaltene content, the harder the asphalt becomes. The asphaltene is the main structure component in the asphalt that provides high temperature properties, such as loss and storage moduli as well as rutting resistance.

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According to the functions and behaviors of various modifiers in asphalts, modifiers can be categorized into five types: dispersed thermoplastics, network thermoplastics, reacting polymers, fibers, and crumb rubber (CRM) particles. Dispersed thermoplastics behave like asphaltenes and normally require peptizing agents, like resins, to stabilize the modified systems. Usually, it requires a considerable amount of material before forming a macrostructural network. Network thermoplastics behave like resins and will form a network of themselves inside asphalts. Reacting polymers bond chemically to the asphalt (normally to the asphaltenes) and will form asphalt/polymer networks. Typical functional groups that may react with polymers include: carboxylic acids, ketones, phenols, sulfoxides, acid anhydrides, pyrroles, and quinones.[7] CRM particles behave as aggregates if their sizes are large and behave as dispersed thermoplastics if their sizes are small (<100mm). Fibers increase the available wetting surface area and behave as binder thickeners which reduce asphalt bleeding. In all cases, the goal is to create more structure inside an asphalt without losing its low temperature properties.

Asphalt is a viscoelastic material that displays a variety of different properties depending on the temperature of the sample. Goodrich[10] proposed a physical model of asphalt depicted as a shock absorber and a spring. The shock absorber represents the viscous properties of asphalt and the spring represents the elastic properties. At high temperatures, asphalt shows good viscous flow properties and behaves as a shock absorber with little or no elastic behavior. At low temperatures, asphalt becomes a "brittle elastic solid" with little or no viscous properties. In the spring/shock absorber analogy, the spring becomes over loaded and snaps when low temperature cracking occurs.

In order to reduce the potential of rutting at high temperatures and thermal cracking at low temperatures, various polymers/fibers/rubbers have been added to asphalt. The goal is to increase the temperature range of both the elastic and viscous properties of the asphalt binders and mixtures. Convenient measures of these properties are G', storage modulus (elastic), and G'', loss modulus (viscous). The ideal case will be that at high temperatures both G' and G'' increase upon addition of polymer due to a network structure formation within the asphalt; at low temperatures, G' and G'' decrease upon addition of polymer due to a decrease in the material's effective glass transition temperature. The ideal case leads to the improvement of both viscous and elastic properties over a wide range of temperatures.

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MATERIALS AND EXPERIMENTS

Materials used in this study were (Amoco) AC-2.5, AC-5, AC-10, AC-20, and (Shell Kraton Series) SBS and SEBS. SBS and SEBS were used to modify both AC-5 and AC-10 at 0–10 wt% polymer content. Aged asphalts were also studied. Short-term aging (experienced during processing and the first year of service) was simulated by using the Rolling Thin Film Oven Test (AASFTO T 240; ASTM D 2872). Long-term aging (experienced during approximately 15 yrs of service life) was simulated by using the Pressure Aging Vessel Test (SHRP B-005). All aged samples were undergone both Rolling Thin Film and Pressure Aging Vessel tests.

A Millipore/Waters (Milford, Mass.) high-performance gel permeation chromatography system (pump model 510) was used to analyze the molecular weight distributions of unmodified asphalts, polymer modifiers, and polymer modified asphalt binders. The system was equipped with a differential refractometer (model 410), a photodiode array detector (model 996), a chromatography manager (Millennium software), a dual reciprocating pump, and a manual injection port. A Lab Connection liquid chromatography transform unit (Lab Connections, Marlborough, Mass.) was also installed as an additional detector for the system. The GPC system was equipped with four Waters Styragel columns (7.8 mm I.D. × 300 mm; HR 0.5, HR 1, HR 2, HR 4) that encompassed an effective molecular weight range from 0 to 600,000 g/mol. GPC grade tetrahydrofuran (stabilized) at a flow rate of 1.0 mL/min. was used as the mobile phase for this study. The sample concentration was 10 g/L of solvent, and the injection volume was 250 mL.

The LC-Transform is an off-line unit that collects the effluent from the differential refractometer (separated by molecular weight) on a Ge disc that can be analyzed subsequently using FTIR.

FTIR was used to examine unaged, aged, and polymer modified asphalts. The samples were prepared by evaporating a THF/binder solution on KBr disks. Absorption peaks used in this study were 1375, 1450, 1600, and 1700 cm^{-1} which correspond to CH_3, CH_2, aromatic carbon, and carboxyl groups in the asphalt, respectively. The heights of the absorption peaks were assumed to be proportional to the amount of the functional groups present in the sample. Figure 1 shows the FTIR spectrum of unaged, unmodified AC-5 sample. FTIR was also used to characterize SBS and SEBS polymers. Figure 2 shows the infrared spectrum of SBS in which the trans-1,4 contribution of butadiene in SBS absorbs at 965 cm^{-1}. No unique characteristic peak was identified in the FTIR spectrum of SEBS.

DMA experiments were performed using a Rheometrics RMS-800 apparatus (Piscataway, N.J.). All experiments utilized smooth, 25-mm diameter plates in a parallel arrangement with a gap width between 1.4 and 2.0 mm. Sample handling procedures were consistent with those used for the SHRP (Strategic Highway Research Program) instrument in which the sample is poured hot directly onto the plates and allowed to cool to room temperature. Temperature sweeps were from 25° to 80°C with measurements taken at 5°C intervals with an equilibration period of 2 min. A frequency of 10 rad/s was used (compliance with SHRP specification) and strain levels were controlled to insure that the testing was conducted in the linear viscoelastic range. The strain level was within 0.5 to 9% for all tests. All tests were replicated between three and six times to ensure accurate and reproducible results.

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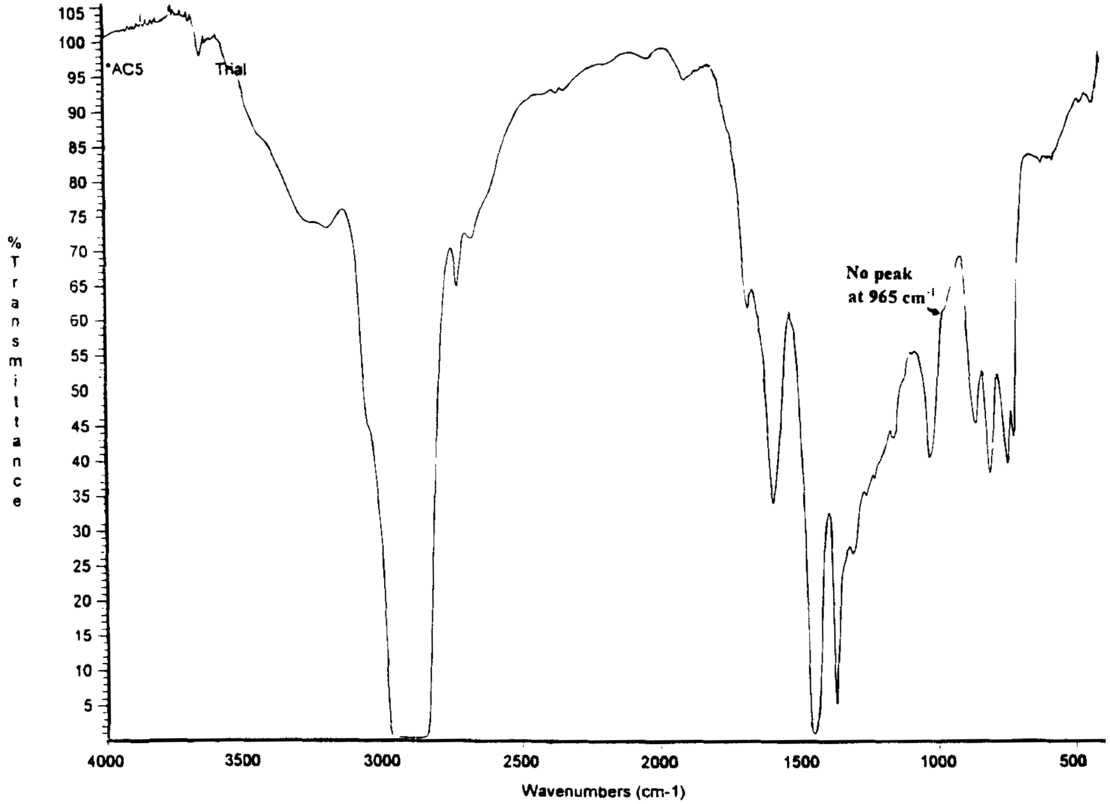

FIGURE 1 FTIR spectrum of unaged, unmodified AC-5.

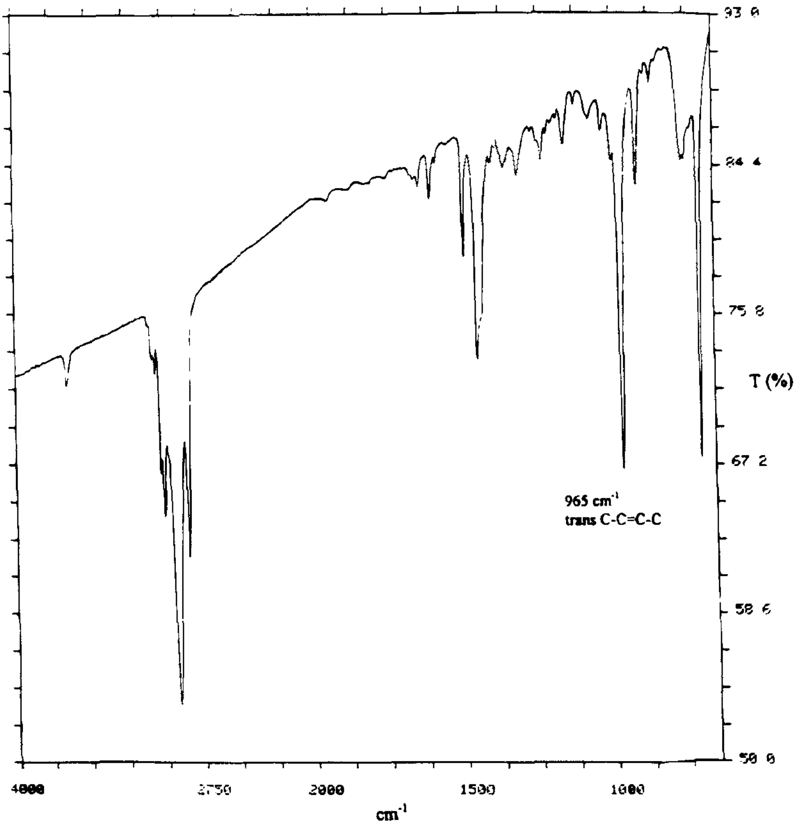

FIGURE 2 FTIR spectrum of SBS.

TMA tests were performed on representative asphalt binder samples. The samples were placed in a 5-mm diameter by 5-mm deep glass boat at room temperature and packed firmly forming a flat top surface. The sample was then covered with a 3-mm diameter by 1.5-mm thick glass plate. The TMA probe was placed directly on the glass plate and a 1 g load was placed on the top of the probe during measurement. The sample was then cooled at approximately 15°C/min to a temperature of −100°C and allowed to equilibrate. The temperature was then raised at a rate of 5°C/min and its height change was measured until a total melt (corresponding to a 1-mm depression of the sample) was achieved. After testing, the boats were retrieved to ensure that the sample did not flow over

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the glass cover/plate. All tests were duplicated to check the reproducibility of the results.

DSC was used to detect glass-transition temperatures and equilibrium temperatures of possible molecular associations. Asphalt samples were equilibrated at different temperatures and then quenched using liquid nitrogen to –100°C. The enthalpy change during heating was then recorded as the sample was heated at a rate of 10°C/min.

CHEMICAL CHARACTERISTICS OF ASPHALT BINDERS

GPC Analysis

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A GPC chromatogram of an unaged, unmodified AC-5 is shown in Figure 3. During GPC analysis, the largest molecules come out first and the smallest molecules come out last. Therefore, large asphaltene molecules will come out first, then medium resin molecules and then small oil molecules. Clearly, those shoulders in the chromatogram represent the beginning and end of each phases. However, the locations of the shoulders are functions of the solvent and the column materials (in this case, the solvent is THF and the column materials are polystyrene) used in the GPC analysis. Three distinct molecular weight ranges (divided by lines A and B) are present, with asphaltenes, resins, and oils in the first, second, and third ranges, respectively. The area-ratios of the three sections separated by lines A and B correspond to the weight percentages of asphaltenes, resins, and oils in the asphalt. For the AC-5 shown in Figure 3, the asphaltene/resin/oil ratio is 7.45/11.85/80.7. The corresponding molecular weight ranges for asphaltenes, resins, and oils are >6600, 2900–6600, and <2900 g/mol, respectively. These values are polystyrene equivalent molecular weights. However, these separations do not necessarily correspond to the molecular weight ranges that classify the oil, resin, and asphaltene constituents given in the literature which were obtained from solubility techniques. The molecular weight ranges for asphaltenes, resins, and oils that were established through the solubility technique are >2300, 950–2300, and 0–950 g/mol, respectively. If these separations are used to calculate the percentages of the constituents in the AC-5 GPC chromatogram, the separation lines will be C and D and the asphaltene/resin/oil ratio will be 23/27/50, which is the same as the ratio reported in the litera-

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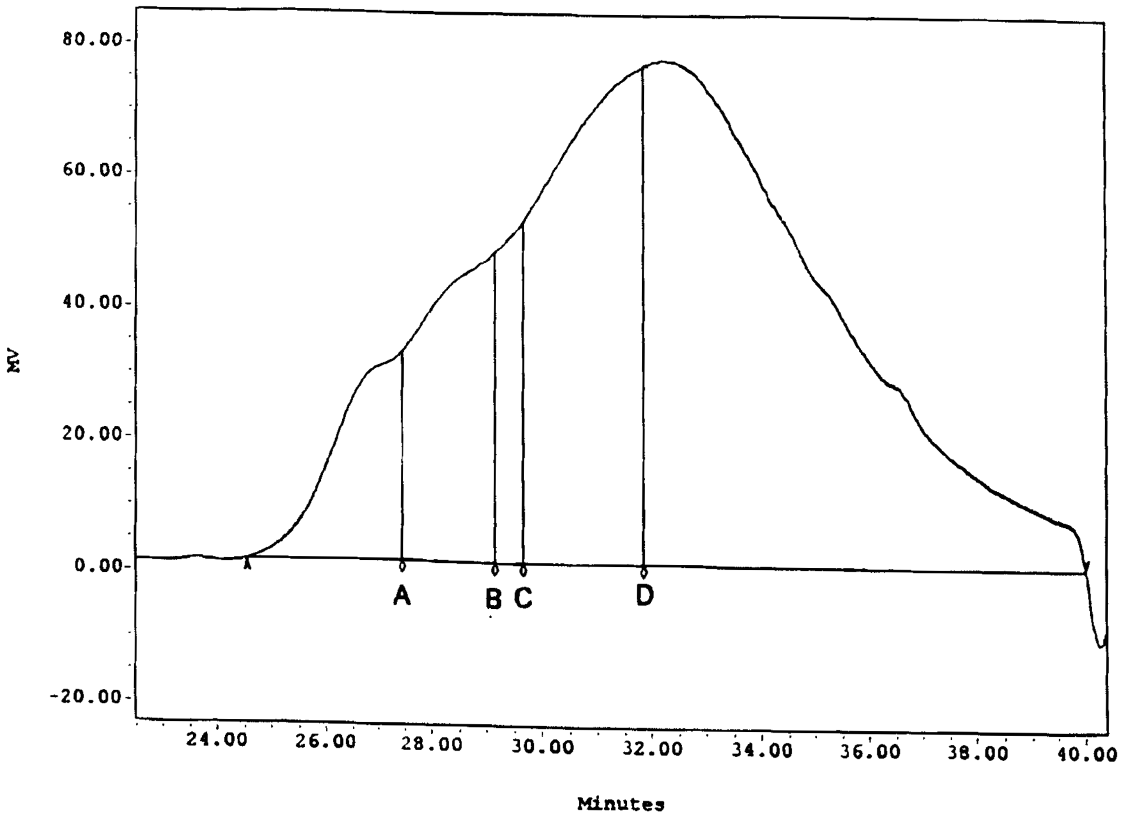

FIGURE 3 GPC chromatogram of unaged, unmodified AC-5.

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ture.[9] Clearly, the molecular weight distribution is a function of analysis method and a standard method needs to be established for a meaningful comparison of research results.

From GPC chromatograms, the molecular weight averages and polydispersities of various asphalt binders were obtained (Table II). A comparison of molecular weight data of unmodified AC-5 and AC-10 shows no significant differences. GPC chromatograms of aged and unaged AC-5 are compared in Figure 4. When AC-5 is aged, there is an increase in the high-molecular-weight material and a decrease in the low-molecular-weight material. Only approximately 0.2% weight loss occurred during aging, suggesting that the low molecular weight material has reacted.

Because SBS and SEBS polymers are higher in molecular weight than asphalt (Table II), GPC was used to determine the polymer content of the asphalt/polymer blends being studied. Figure 5 is an example of this technique for AC-5 modified with 4 wt% SEBS. The entire chromatogram can be divided into three regions: A, B, and C with corresponding areas of 2.5, 1.5, and 96.0%, respectively. Region A is high-molecular-weight SEBS totally separated from the asphalts. Region B is low-molecular-weight SEBS that is eluted with the asphalt. This can be easily seen by comparison of Figure 5 with Figure 4. A total of 4 wt% SEBS can be identified from the GPC data. It is important to note that it appears the SEBS is being degraded, sheared, or reacted during the mixing process. Similar results were obtained for AC-5/SBS, AC-10/SEBS, and AC-10/SBS asphalt/polymer blends.

TABLE II Molecular Weight Averages for Various Materials Determined by GPC*

Sample	*<Mn>*	*<Mp>*	*<Mw>*	*<Mz>*	*Polydispersity*
AC-5	669	862	2099	6725	3.14
AC-10	630	922	1865	5660	2.96
AC-5 (aged)	792	876	3348	11121	4.23
SBS	30002	67865	61900	106729	2.06
SEBS	32730	44092	44445	58327	1.36
AC-5/4% SBS	657	829	4320	51605	6.57
AC-5/4% SEBS	752	871	4322	38754	5.75
AC-5/4% SBS (aged)	803	876	5508	48220	6.86
AC-10/14% SEBS	780	917	4602	42458	5.90
AC-10/14% SBS	791	907	6086	82759	7.69

*Polystyrene equivalent molecular weight

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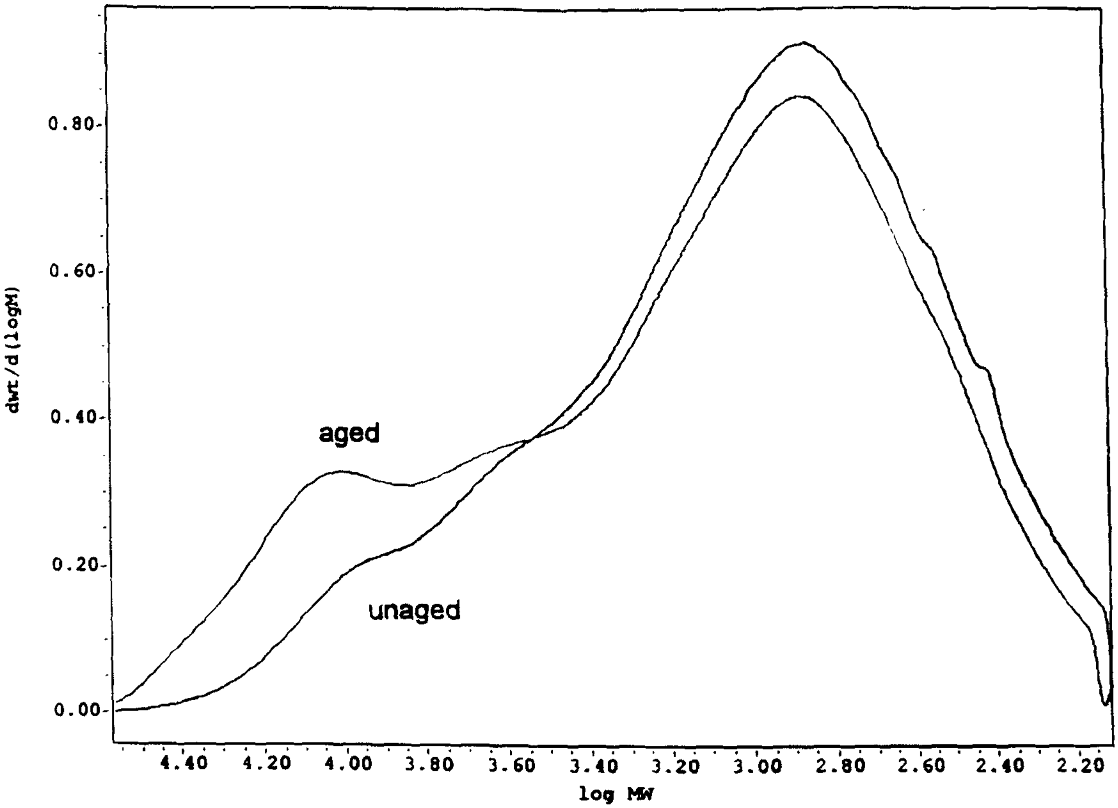

FIGURE 4 Comparison of molecular weight distributions between aged and unaged AC-5 binder.

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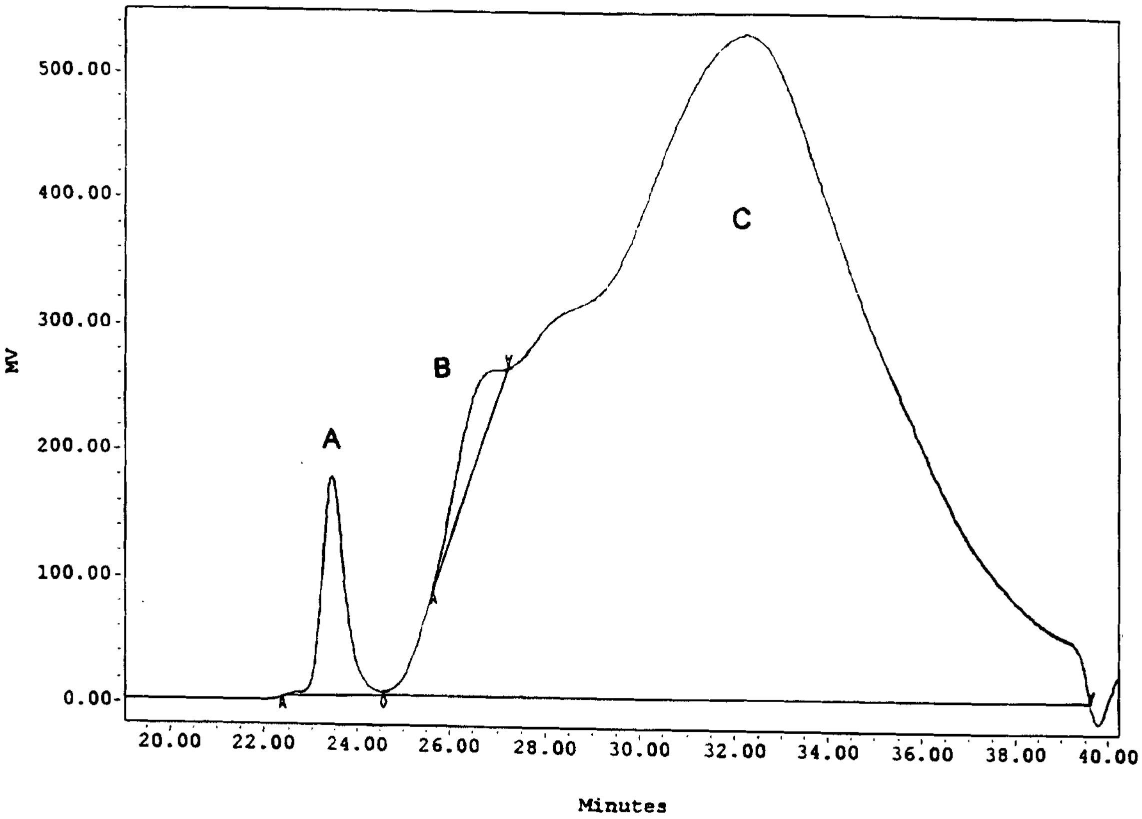

FIGURE 5 GPC chromatogram of unaged AC-5 modified with 4 wt% SEBS polymer.

A comparison of GPC chromatograms of aged, unmodified AC-5 and 4 wt% SBS modified AC-5 is shown in Figure 6. Upon addition of SBS to asphalt, we would expect to see an increase in the amount of the high molecular weight asphaltene component for the aged sample due to both aging and possible SBS degradation. Instead, we see a decrease in this value after aging suggesting that the SBS has reduced the amount of aging that has occurred.

Fourier-Transform Infrared Spectroscopy Analysis

The characteristic absorption peaks for CH_3, CH_2, aromatic carbon, and carboxyl groups in the asphalt are 1375, 1450, 1600, and 1700 cm^{-1}, respectively. Ratios of the absorbance intensities were used for fingerprinting different asphalt grades. AC-10 sample had a greater percentage of aromatic carbon than AC-5 as would be expected, suggesting a larger asphaltene content. However, AC-10 appeared to have less CH_2 functional groups than AC-5 suggesting a lower resin content.

To determine the SBS content using FTIR, the absolute ratio of the 965 cm^{-1} absorption band to the 1375 cm^{-1} band was used as a content indicator. This ratio is linearly proportional to the SBS content in the asphalt. However, a calibration curve must be constructed and it is a function of asphalt, polymer type and source. A calibration curve is constructed by preparing samples that contain known concentrations of SBS polymer in the asphalt sample and plotting this information against the respective absolute absorbance band ratios. Figure 7 is an example of a calibration curve for an unaged AC-5/SBS polymer blend obtained from an average of three separate runs for each polymer content. The ratio at 5 wt% of SBS, the optimum polymer content as listed in Table III, has the highest deviation from the straight line. The defining equation for the unaged calibration curve is:

$$\text{Ratio} = 0.064 \times \text{SBS polymer content} + 0.037$$

It is important to note that the calibration curve is valid only for the given asphalt/polymer blend. The curve must also be corrected for aging discrepancies. A similar calibration curve was constructed for AC-5 aged blends and the defining equation is:

$$\text{Ratio} = 0.051 \times \text{SBS polymer content} + 0.079$$

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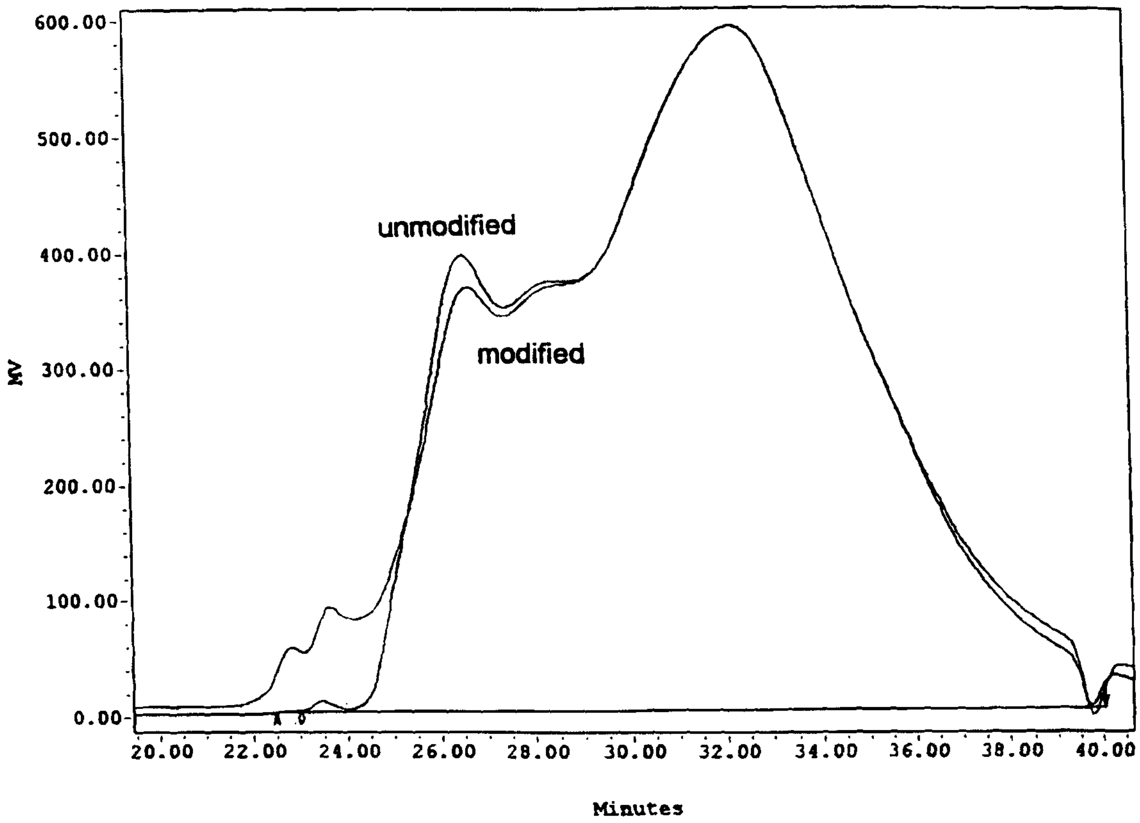

FIGURE 6 GPC chromotograms comparing aged, 4 wt% SBS polymer modified and unmodified AC-5 binders.

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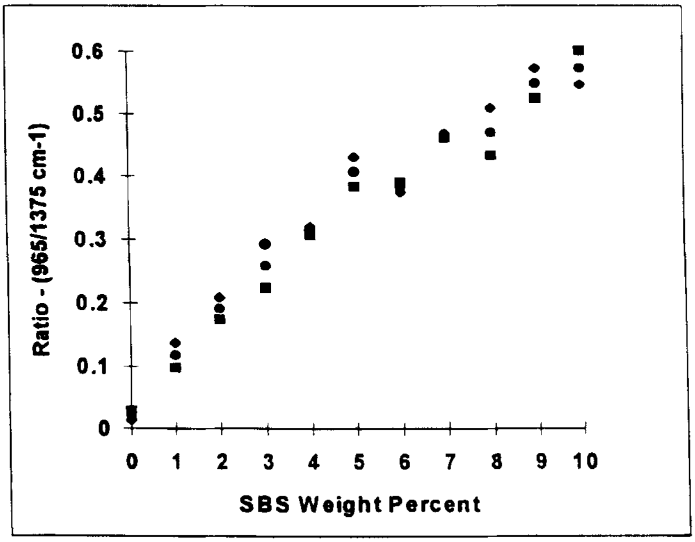

FIGURE 7 FTIR absorbance band ratio calibration curve for unaged AC-5/SBS polymer blends.

TABLE III Optimum and Critical Polymer Content for Asphalt Modification

	Optimum Content	*Critical Content*
	(percent by total weight of the	*asphalt/polymer blend)*
AC-5/SBS	5	4
AC-5/SEBS	5	3–4
AC-10/SBS	2	3
AC-10/SEBS	4	3

With these two defining equations, FTIR can be used as an effective QA tool to determine the SBS content in any unknown SBS modified AC-5 sample, before or after paving. However, when either the asphalt or SBS source is changed, a new calibration curve must be constructed for accurate QA.

Since not all polymer modifiers have a characteristic absorption peak that is unique from that of the asphalt spectrum, FTIR was taken of separated samples using the LC-Transform unit. By attaching an LC-transform unit to the end of the GPC system, the polymer portion of the blend was collected on a Ge disc. The Ge disc was then adapted to the FTIR for polymer identification. Figure 8 shows the FTIR spectrum of SBS collected using this technique. The spectrum in this figure shows the same characteristics as those found in the spectrum presented in Figure 2 (original SBS).

PHYSICAL CHARACTERISTICS OF ASPHALTS

Rheometrics Analysis

Figure 9 shows the sensitivity of tan delta with respect to SBS polymer content and temperature for modified AC-5 asphalt binders. Clearly, SBS polymers enhance the rheological properties of AC-5, especially at high temperatures. Similar results were found for all blend combinations studied including AC-5/SEBS, AC-10/SBS, and AC-10/SEBS. It is important to note that an extensive mixing study was first conducted to ensure that optimum blend properties were being measured. The mixing procedure was preheating the raw materials to 135°C for 1h and then mixing with a low shear mixer (approximately 1600 rpm) equipped with a four-blade, 5-cm diameter impeller for two additional hours at 180°C.

It is also important to determine the optimum and/or critical polymer content for best modification. After an extensive study, the optimum was defined as the point at which there was no longer a significant increase in the rheological properties of the blend with increasing polymer content. The critical content, however, was defined as polymer concentrations where a deviation from the normal trend in the rheological properties was detected. The Strategic Highway Research Program (SHRP) uses the inverse loss compliance, $1/J''$, at 60°C as a rheological property indicator for its original binder specification. Figure 10 shows the inverse loss compliance as a function of SBS polymer content at 60°C for modified AC-5 asphalt binders. Clearly, the optimum and critical polymer contents are 5 and 4 wt% for this system. The same experiments were conducted for AC-5/SEBS, AC-10/SBS, and AC-10/SEBS systems. The optimum and critical polymer contents are listed in Table III.

The decrease in properties at the critical polymer content was also observed in TMA analysis, described below. A possible explanation of the observed behavior is that as synthetic polymer is added to the asphalt, the thermo-physical properties of the unmodified material are altered due to

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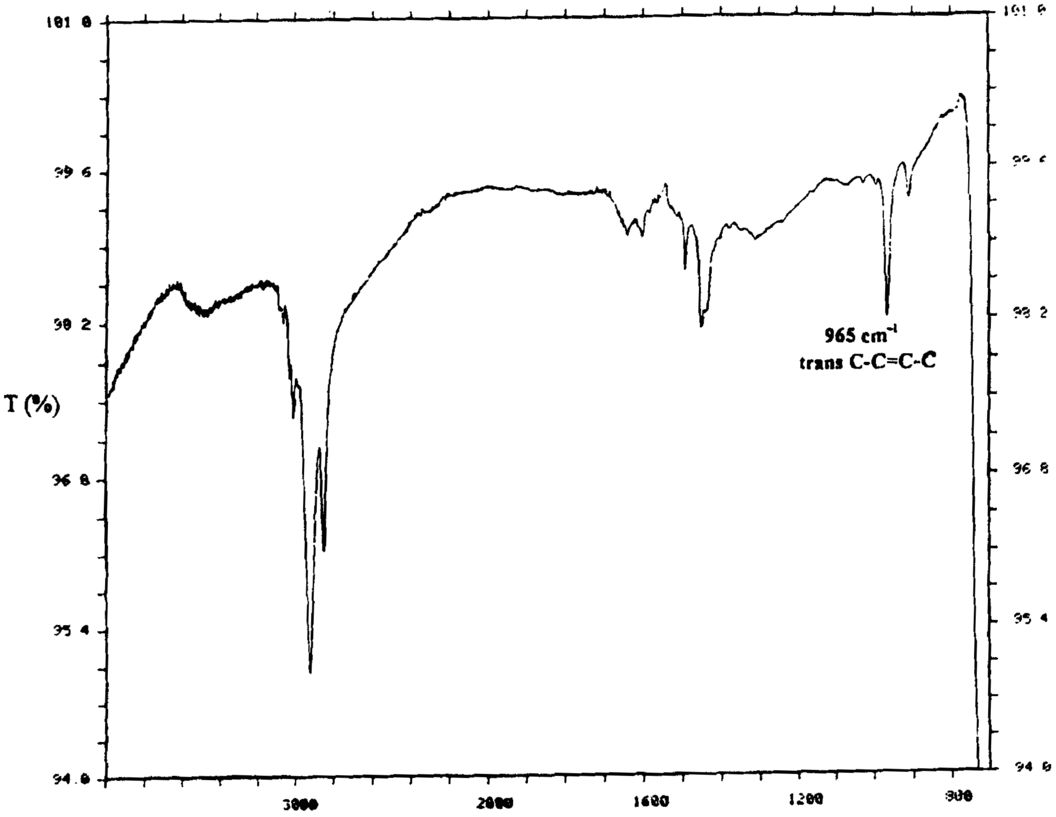

FIGURE 8 FTIR spectrum of SBS polymer from LC-transform separation.

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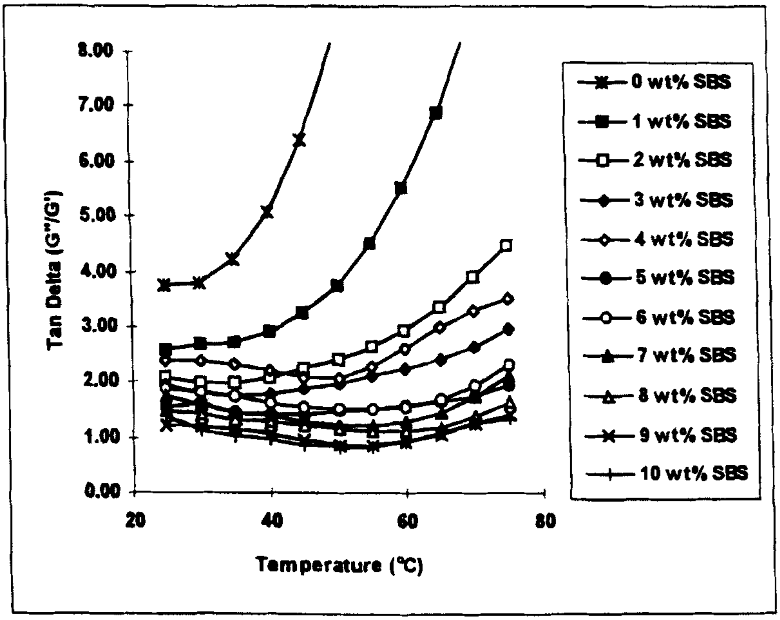

FIGURE 9 Sensitivity of tan delta with respect to SBS polymer content.

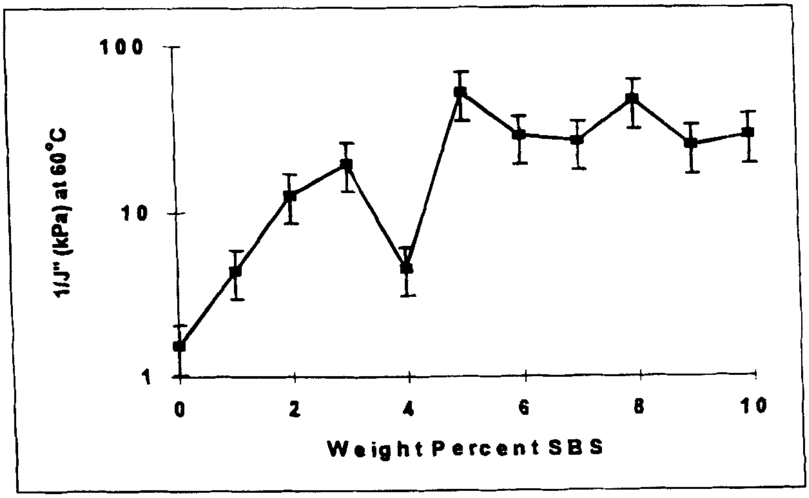

FIGURE 10 Inverse loss compliance as a function of SBS polymer content at 60°C.

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solubility of the oils in the polymer, or some other structural phenomenon. At the same time, the synthetic polymer is enhancing the overall rheological properties of the entire blend. It could be envisioned that when two rheological property profiles are added together they yield a resultant property profile similar to that observed in this study.

The aging effects on the rheological properties of AC-5/SBS blends (SBS contents from 0–10 wt%) were also studied. The samples were aged using the Thin Film Oven and Pressure Aging Vessel tests. The rheological properties of aged samples were then measured and the results were compared with those of the unaged samples. In general, aging increases the storage modulus of the binder and the increase of the storage modulus at 60°C after aging is usually used as an aging index. Figure 11 depicts the percent increase in G′ at 60°C of the aged versus unaged SBS modified binder for several SBS contents. Increasing the SBS content appears to decrease the magnitude of increase in the storage modulus. This suggests that asphalt aging is retarded through the addition of a polymer modifier which agrees with the conclusion drawn from the GPC analysis.

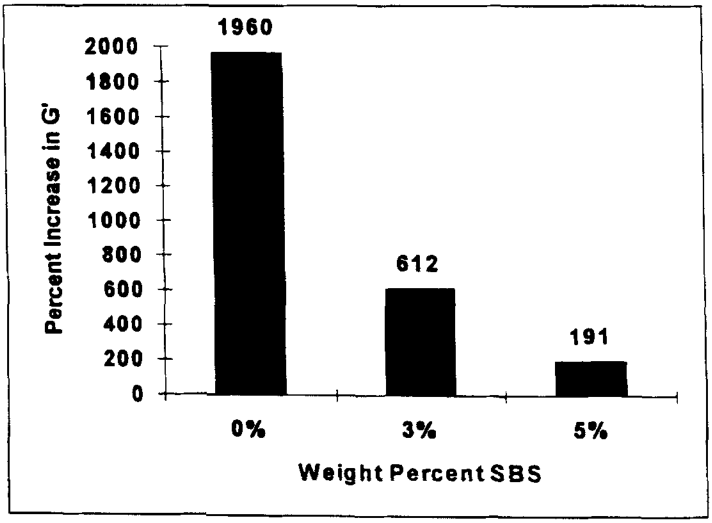

FIGURE 11 Percent increase in the storage modulus at 60°C of aged versus unaged SBS polymer modified AC-5 binders.

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Thermal Mechanical Analysis

TMA results show that the glass-transition temperatures T_g of both SBS and SEBS polymers are in the range of –60° to –90°C. Upon addition of synthetic polymer to asphalt, the T_g of asphalt/polymer blends was lowered because the T_g values of unmodified asphalts are much higher than –60°C. TMA tests were used also to determine the final melt temperatures of four asphalt/polymer systems: AC-5/SBS, AC-5/SEBS, AC-10/SBS, and AC-10/SEBS (Figure 12). TMA results indicate that: 1. all of the TMA data support the conclusions drawn for the critical and optimum polymer contents based on rheological properties (see Table III); 2. the final melt temperature of AC-10 is greater than that of AC-5, as expected; and 3. at their respective optimum polymer contents, there is an increase of approximately 25°C in the final melt temperature for the asphalt/polymer blends with respect to the unmodified binder.

The aged AC-5/SBS polymer blends were also tested using TMA to determine the final melt temperatures of the samples as shown in Figure 13, which indicates that increasing the polymer content beyond the optimum percentage has no significant effect on the final melt temperature of the aged AC-5/SBS blends. The difference in the final melt temperatures of the aged versus unaged samples for increasing polymer content decreases. At

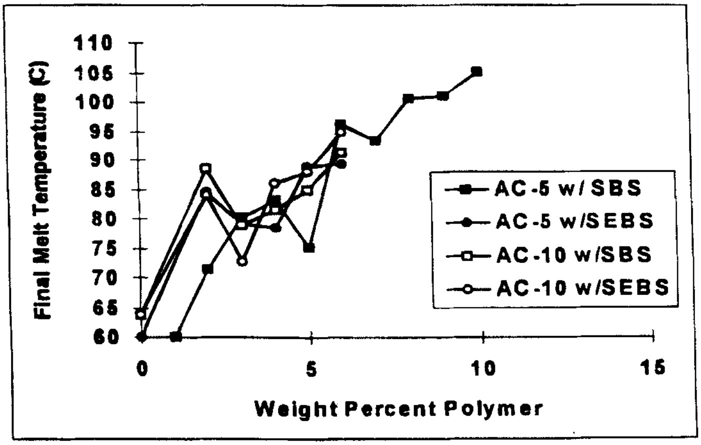

FIGURE 12 Melt temperatures of asphalt/polymer blends as a function of polymer content determined by TMA.

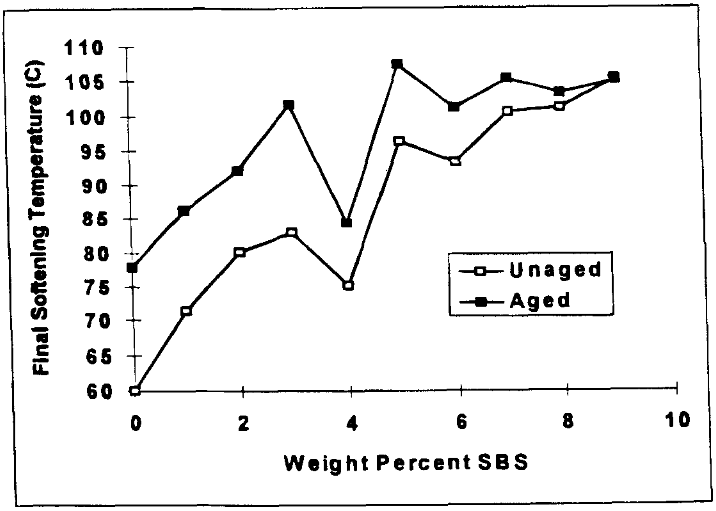

FIGURE 13 Melt temperatures of aged and unaged AC-5/SBS polymer blends as a function of polymer content determined by TMA.

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approximately 9 wt% SBS, there is no difference in the final melt temperatures between the aged and unaged samples. This polymer content roughly corresponds with the level of modification thought to cause a matrix inversion of the AC-5/SBS blend. The TMA data support the GPC results in that the addition of SBS retards age hardening. Also, TMA data show that no age hardening occurs beyond the matrix inversion (about 9 wt%).

Differential Scanning Calorimetry

DSC was used to measure the glass-transition temperature and to examine any temperature dependent structure that may exist in asphalt. Unmodified AC-2.5, AC-5, AC-10, and AC-20 asphalt samples were quenched from room temperature to −100°C using liquid nitrogen. The samples were then heated at a rate of 10°C/min. Figure 14 shows an example of the DSC thermograph for an AC-5 asphalt. Three distinct thermal transitions occurred in the unmodified asphalt at approximately −14, 14, and 35°C. The first transition is the glass transition of the asphalt. The second and third transitions may be due to polar associations among asphalt molecules. The two transition temperatures correspond to the breakdown temperatures of two associations.

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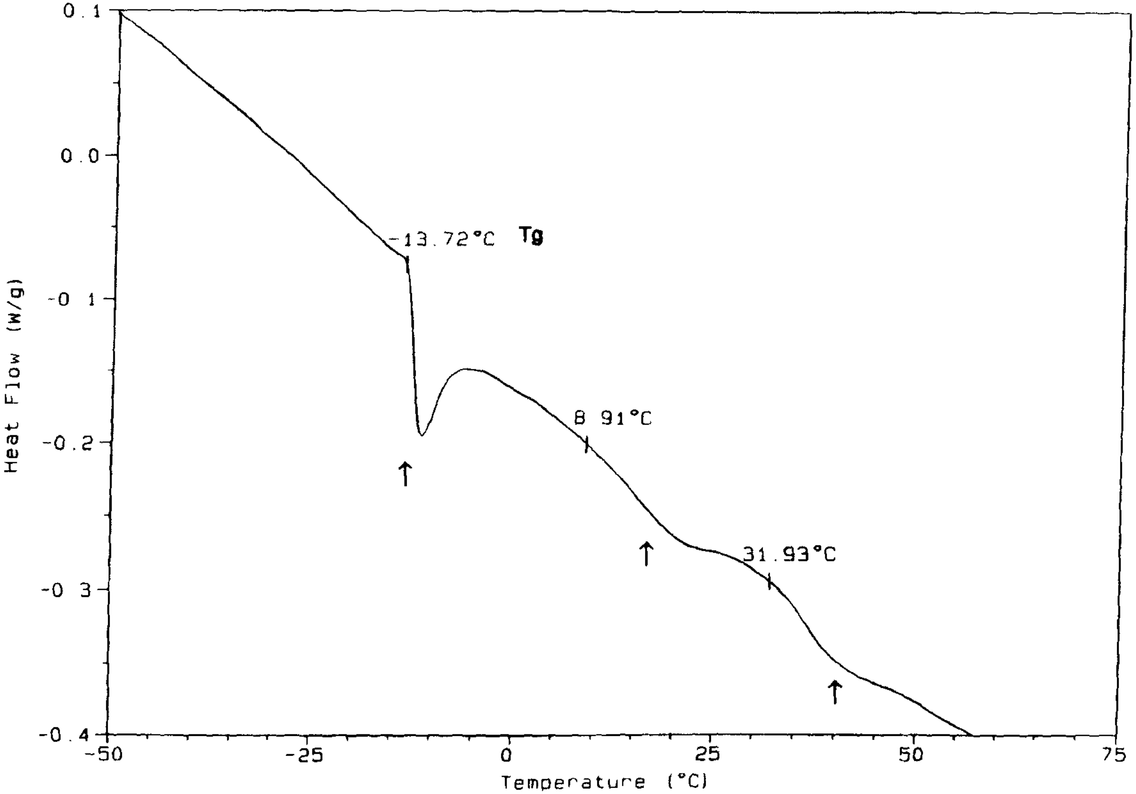

FIGURE 14 DSC data for determination of the glass-transition temperature of AC-5.

The glass-transition temperatures of both AC-5 and AC-10 were found to be within the range from –10° to –20°C. The speculation on the molecular association was qualitatively verified by the fact that if an asphalt sample was equilibrated at an elevated temperature higher than the transition temperature for a period of 1 h before quenching, the transitions at 14° and 35°C could be eliminated. Figure 15 shows the DSC thermographs of two unmodified AC-5 asphalts that have undergone the following conditions before quenching: curve #1, sample equilibrated at 180°C; curve #2, sample re-equilibrated at room temperature; curve #3, sample re-equilibrated at 180°C. The glass-transition temperature maintains between –10° to –20°C for all the curves. For the curve #1, the sample has been equilibrated at 180°C before quenching, the two transitions corresponding to the molecular associations disappeared. However, these transitions reappeared when the sample was allowed to re-equilibrate at room temperature as shown in the curve #2. The two transitions corresponding to the molecular associations disappeared again when the sample was re-equilibrated at 180°C as shown in the curve #3. The reversible phenomenon verifies the speculation that these transitions are structural changes due to polar associations and not chemical transitions. More research is needed in this area to determine the nature of these transitions and how they are affected by the addition of polymer.

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CONCLUSIONS

Chemical and physical properties of unmodified, and SBS and SEBS polymer modified AC-5 and AC-10 asphalt binders were studied by using GPC, LC-transform, FTIR, TMA, DSC, and DMA. This study showed that 1. rheological properties were enhanced upon addition of polymers to asphalt binders, especially at high temperatures; 2. the melt temperature of a binder increased with polymer content and asphalt grade; 3. polymers tended to retard asphalt age hardening; and 4. there was an optimum level of polymer modification for an effective enhancement of rheological properties of an asphalt binder. A combination of GPC and LC-transform/FTIR could be used for effective fingerprinting the nature of asphalts and polymers as well as quality control of asphalts and polymer modified asphalt binders. DSC results suggested that different extents of structure existed for different asphalt grades.

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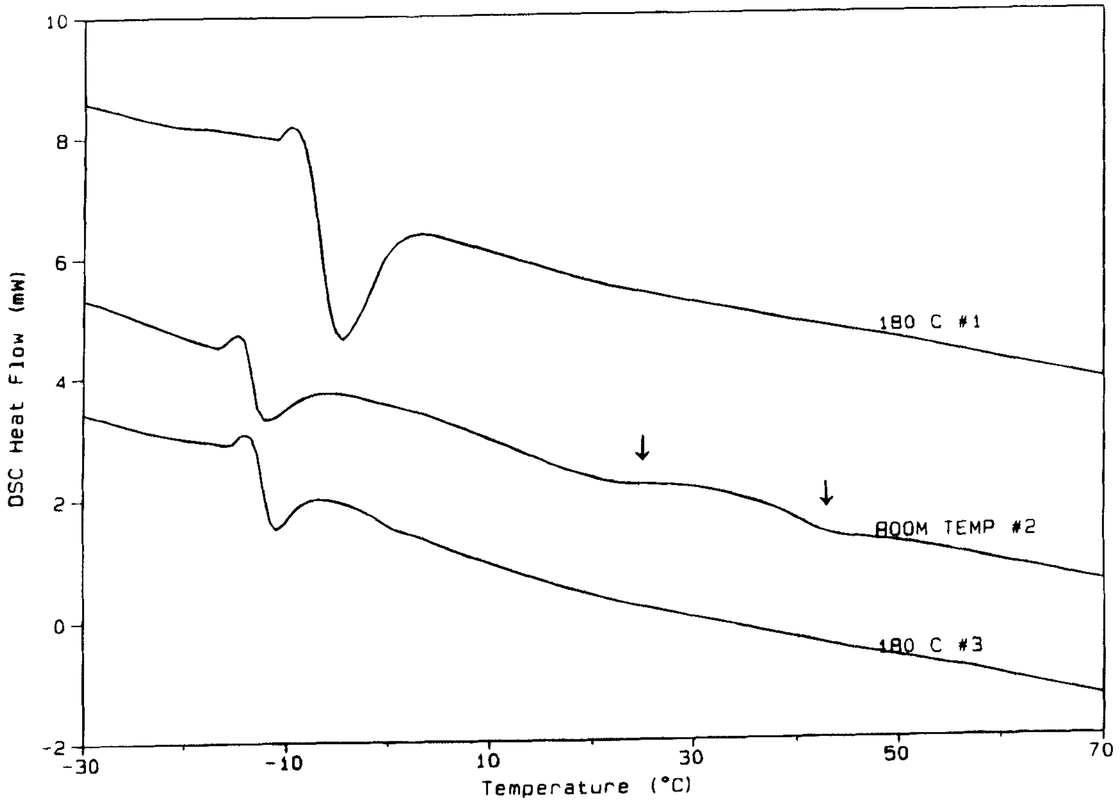

FIGURE 15 DSC thermographs indicating the existence of reversible polar associations.

Acknowledgments

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