Artificial Aging of Polymer Modified Bitumens

XIAOHU LU, ULF ISACSSON

Royal Institute of Technology, Division of Highway Engineering, SE-100 44, Stockholm, Sweden

Received 5 October 1999; accepted 8 December 1999

ABSTRACT: This paper presents an investigation of artificial aging of polymer modified binders, prepared from three base bitumens and six polymers. Aging of the binders was performed using the Thin Film Oven Test (TFOT), the Rolling Thin Film Oven Test (RTFOT), and modified RTFOT (MRTFOT). The binders were characterized by means of infrared spectroscopy, different types of chromatography, and dynamic mechanical analysis. It was found that the effect of aging on the chemistry and rheology of the modified binders was influenced by the nature of the base bitumens and was strongly dependent on the characteristics of the polymers. For styrene–butadiene–styrene (SBS) and styrene–ethylene–butylene–styrene (SEBS) modified binders, aging decreased the complex modulus and increased the phase angle. Aging also increased the temperature susceptibility of these modified binders. The rheological changes of SBS modified bitumens were attributed to polymer degradation and bitumen oxidation. However, for SEBS modified bitumens, the mechanisms of aging are unclear. In the case of ethylene vinyl acetate (EVA) and ethylene butyl acrylate (EBA) modified binders, the process of aging increased the complex modulus and elastic response (decreased phase angle), and reduced temperature susceptibility. These changes were mainly due to the oxidative hardening of the base bitumens. The study also showed statistically significant correlation between TFOT, RTFOT, and MRTFOT. However, no definite conclusions could be drawn regarding the difference in severity of aging between these methods. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 76: 1811–1824, 2000

Key words: polymer modified bitumens; artificial aging; infrared spectroscopy; chromatography; dynamic mechanical analysis

INTRODUCTION

Aging of bituminous binders is induced by chemical and/or physical changes during the production of the pavement and throughout its service life. The process is usually accompanied by hardening of the binders, which in general influences the deterioration of asphalt pavements. The most important aging related modes of failure are traffic and thermally induced cracking, and raveling.

Bitumen aging takes place in two stages: short-term and long-term. Short-term aging occurs during the production, storage, laying, and compaction of asphalt mixtures. Long-term aging (in-service aging) is mainly caused by exposure of binders to oxygen in a pavement. Bitumen aging may be influenced simultaneously by several factors, such as characteristics and content of the binder, nature and particle size distribution of the aggregate, void content of the mixture, production related factors, and external conditions (e.g., temperature and time). To simulate aging, a number of laboratory methods have been proposed, some of which have been standardized.[1] In those tests, bitumen aging is accelerated by increasing temperature, decreasing bitumen film thickness, increasing oxygen pressure, or applying various combinations of

Correspondence to: X. Lu (xiaohu@infra.kth.se).

Journal of Applied Polymer Science, Vol. 76, 1811–1824 (2000)

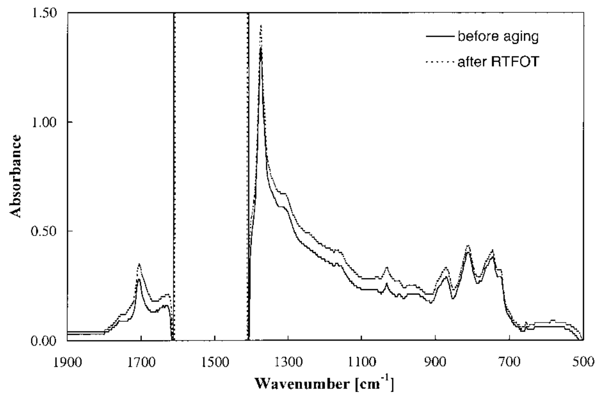

Figure 1 FTIR spectra of bitumen B before and after artificial aging.

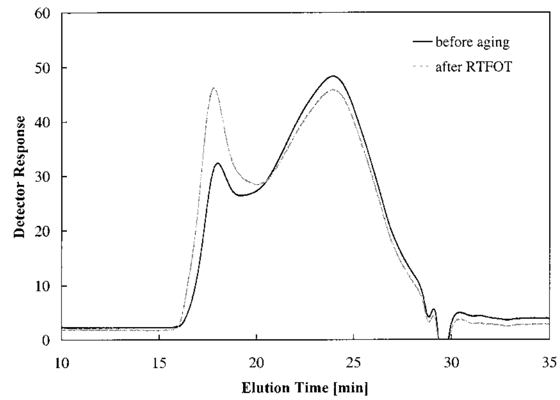

Figure 3 GPC profiles of bitumen B before and after aging.

these factors. However, due to the difficulties of simulating environmental conditions during production and service life of asphalt pavements, a general relationship between laboratory and field aging is difficult to obtain.

From the chemical point of view, aging is a very complex process, to which various irreversible mechanisms (e.g., oxidation, volatilization, exudation) and reversible mechanisms (physical hardening) are related. For polymer modified bitumens (PMBs), the mechanisms of aging are influenced by the characteristics of bitumen and polymer, as well as the molecular interaction between the two components. In the past, numerous studies on different aspects of bitumen aging have been carried out.[2,3] The chemical and rheological changes associated with aging are well understood for plain bitumens. However, for PMBs, many topics in this research area remain to be studied.

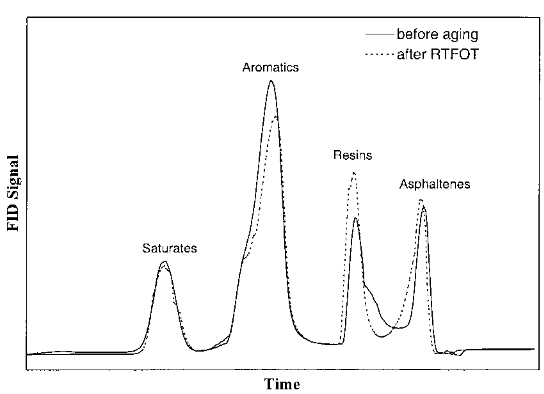

Figure 2 Effect of aging on the generic fractions of bitumen B.

In this paper, a characterization of the aging behavior of different types of PMBs is presented. Three artificial methods, the Thin Film Oven Test (TFOT), the Rolling Thin Film Oven Test (RTFOT), and modified RTFOT (MRTFOT), are used. The effect of aging on the chemical and rheological properties of PMBs is investigated using infrared spectroscopy, different types of chromatography, and dynamic mechanical analysis. In addition, correlation between different aging procedures is examined.

EXPERIMENTAL

Materials

Three penetration-grade bitumens (coded A, B, and C) from two sources were used in this study. They are Venezuela B85 and B180, and Mexico B180. Typical properties of the base bitumens have been reported previously.[4]

The polymers investigated were styrene–butadiene–styrene (SBS), styrene–ethylene–butylene–styrene (SEBS), ethylene vinyl acetate (EVA), and ethylene butyl acrylate (EBA) copolymers. The SBS polymers used were Kraton D-1101 (SBS1) and Kraton D-1184 (SBS2), supplied by the Shell Chemical Company. Kraton D-1101 is a linear SBS polymer, and Kraton D-1184 a radial polymer, both with a 70/30 butadiene/styrene ratio. The SEBS polymer is Kraton G 1650 (Shell), which contains 29% styrene. The two EVA copolymers used were Elvax 260 (EVA1) and Elvax 420 (EVA2), supplied by DuPont. The

Table I Effect of Aging on Infrared Absorbance (Peak Area) of Bitumens

	Before Aging		TFOT		RTFOT		MRTFOT	
Bitumens	C═O	S═O	C═O	S═O	C═O	S═O	C═O	S═O
A	3.55	0.73	4.91	0.90	4.60	0.91	3.60	0.86
B	3.86	0.68	5.53	0.90	5.45	0.92	5.00	0.95
C	0.49	0.65	1.40	1.21	1.49	1.00	0.85	0.94

melt indices (MI) of Elvax 260 and Elvax 420 are 6 and 158, and their vinyl acetate contents are 28 and 18%, respectively. The EBA polymer was produced by Neste and supplied by Nynas. These polymers are representative of elastomers (SBS and SEBS) and plastomers (EVA and EBA).

The modified bitumens were prepared by mixing polymers with the base bitumens using a low shear mixer at 180°C and a speed of 125 rpm. In preparation, 600 g of the bitumen was heated to fluid condition and poured into a 2000 mL spherical flask. Upon reaching 175°C, the polymers were added to the bitumen at a content level of 3, 6, or 9% by weight. After reaching 180°C, mixing was continued at that temperature for two hours. The modified bitumens have been characterized using conventional methods.[4,5]

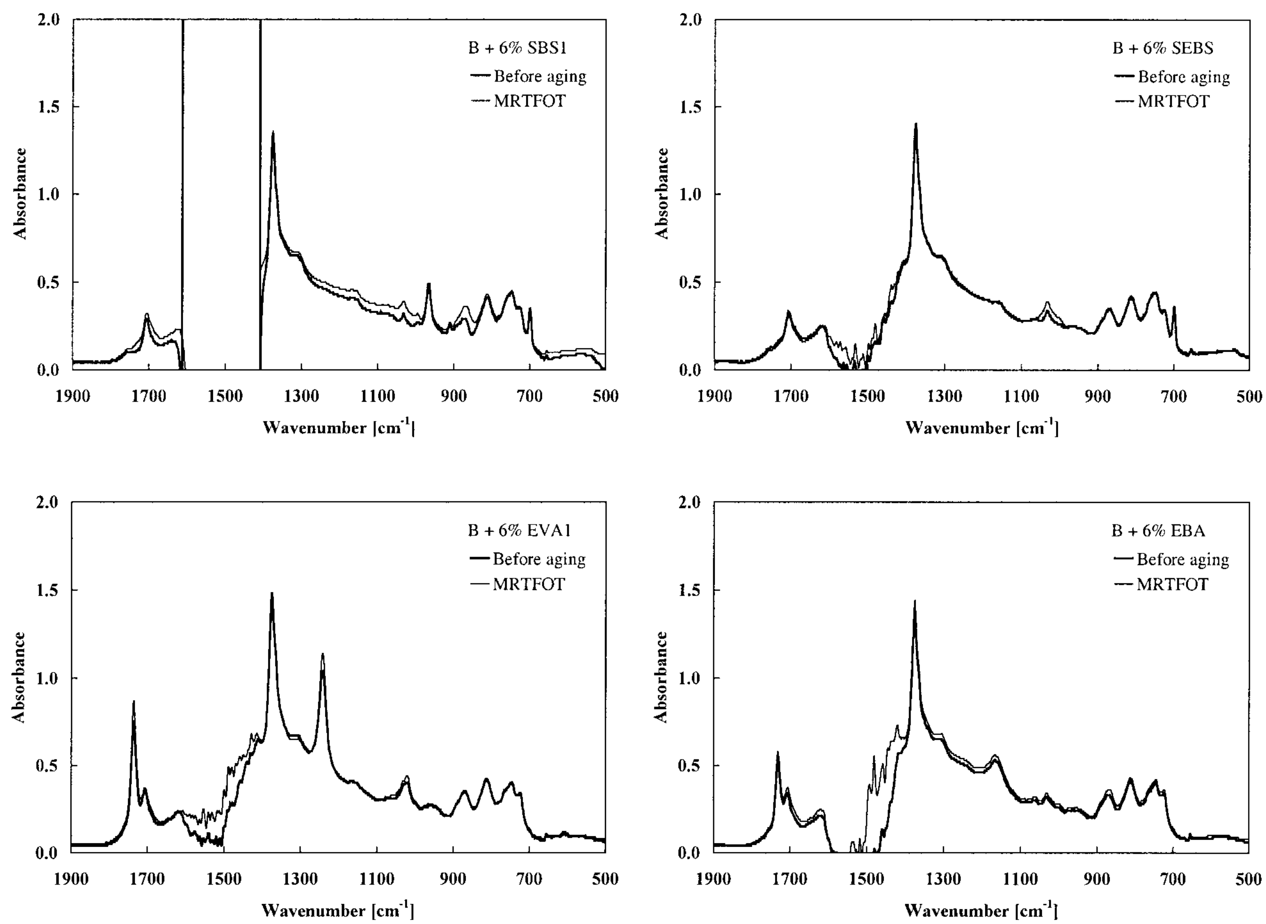

Figure 4 FTIR spectra of modified bitumen B with different polymers before and after artificial aging.

Table II Sulfoxide Index[a] of Base and Polymer Modified Bitumens

Binders	TFOT	RTFOT	MRTFOT
Bitumen A	1.23	1.25	1.18
A + 6% SBS1	1.09	1.03	1.04
A + 6% SBS2	1.06	1.13	1.13
A + 6% SEBS	1.21	1.12	1.09
A + 6% EVA1	1.51	1.17	1.25
A + 6% EVA2	1.38	1.23	1.32
A + 6% EBA	1.16	1.07	1.06
Bitumen B	1.32	1.35	1.40
B + 3% SBS1	1.16	1.19	1.19
B + 6% SBS1	1.12	1.04	1.32
B + 9% SBS1	1.19	1.22	1.26
B + 6% SBS2	1.05	1.27	1.39
B + 6% SEBS	0.72	0.74	0.72
B + 3% EVA1	1.23	1.24	1.09
B + 6% EVA1	1.33	1.16	1.21
B + 9% EVA1	1.22	0.99	1.18
B + 6% EVA2	1.16	1.15	1.07
B + 6% EBA	1.06	1.09	1.03
Bitumen C	1.86	1.54	1.45
C + 6% SBS1	1.45	1.38	1.34
C + 6% SBS2	1.53	1.49	1.35
C + 6% SEBS	0.98	1.21	1.08
C + 6% EVA1	1.23	1.09	1.09
C + 6% EVA2	1.03	1.36	1.22
C + 6% EBA	0.95	1.15	1.07

[a] Sulfoxide index is defined as the ratio of IR absorbance at 1030 cm^{-1} after and before aging.

Aging Procedures

Aging of the binders was performed using the TFOT (ASTM D 1754), the RTFOT (ASTM D 2872), and the MRTFOT, respectively. In TFOT and RTFOT, aluminum pans and glass bottles were heated to 160°C before loading the sample. In MRTFOT, a stainless steel rod, 6 mm in diameter and 127 mm long, was used in the glass bottle. This type of modification was proposed to reduce the effect of high consistency of PMBs on the rolling process.[6,7] Other aging conditions were the same as those standardized, i.e., 163°C and 5 h for TFOT and, 163°C and 75 min for RTFOT and MRTFOT.

Test Methods

Fourier Transform Infrared Spectroscopy

Fourier transform infrared (FTIR) spectroscopy was applied to determine the functional characteristics of the bitumens before and after aging. Sample solutions (5% by weight) were prepared in carbon disulfide. Blank (solvent) and sample scans were performed using circular sealed cells (ZnSe windows and 1 mm thickness). IR spectra were obtained by 32 scans with 5% iris and 4 cm^{-1} resolution in wave numbers ranging from 1900 to 500 cm^{-1}.

Thin-Layer Chromatography with Flame Ionization Detection

In thin-layer chromatography with flame ionization detection (TLC-FID, Iatroscan analyzer), 2% (w/v) solutions of binders were prepared in dichloromethane, and 1 μL sample solution spotted on chromarods using a spotter. The separation of bitumen into four generic fractions (saturates, aromatics, resins, and asphaltenes) was performed with a three-stage process using n-heptane, toluene, and dichloromethane/methanol (95/5 by volume), respectively.

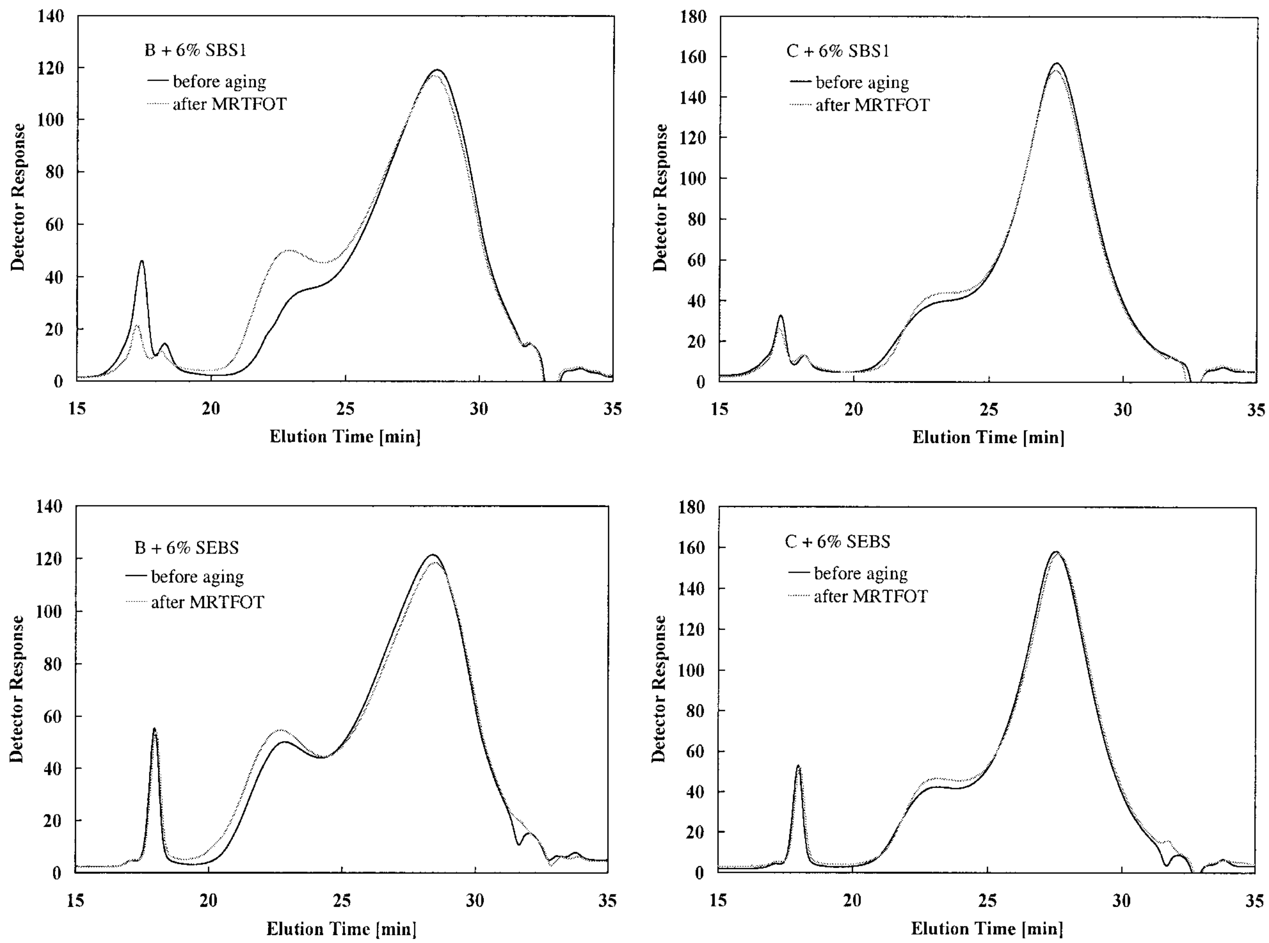

Figure 5 GPC profiles of the modified binders containing elastomers before and after aging.

High Performance Gel Permeation Chromatography

The high performance gel permeation chromatography (HP-GPC) system used was a Waters 515 HPLC pump equipped with a Waters 410 differential refractometer. Three ultra-styragel columns were arranged in the order of pore size (500, 10^3, and 10^4Å). The system was kept at 35°C. In the analysis, 5% by weight solutions of bitumens were prepared in tetrahydrofuran (THF) and 50 μL of the sample solution was injected into the column. The flow rate of the THF mobile phase was 1 mL/min.

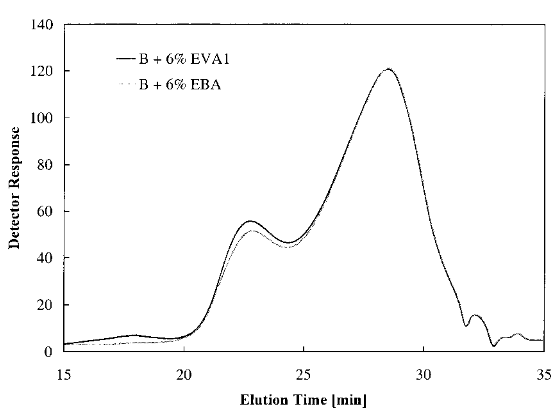

Figure 6 GPC profiles of modified bitumen B with 6% EVA1 and EBA, respectively.

Dynamic Mechanical Analysis

In dynamic mechanical analysis (DMA), frequency and temperature sweeps were carried out using a rheometer (RDA II, Rheometrics). Frequency sweeps (0.1–100 rad/s) were applied at fixed strain amplitude and 60°C, and temperature sweeps (−30–135°C) with 2°C increments were conducted at 1 rad/s and variable strains. Parallel plates, diameter 8 (gap 1.5 mm) and 25 mm (gap 1 mm), were used in temperature ranges

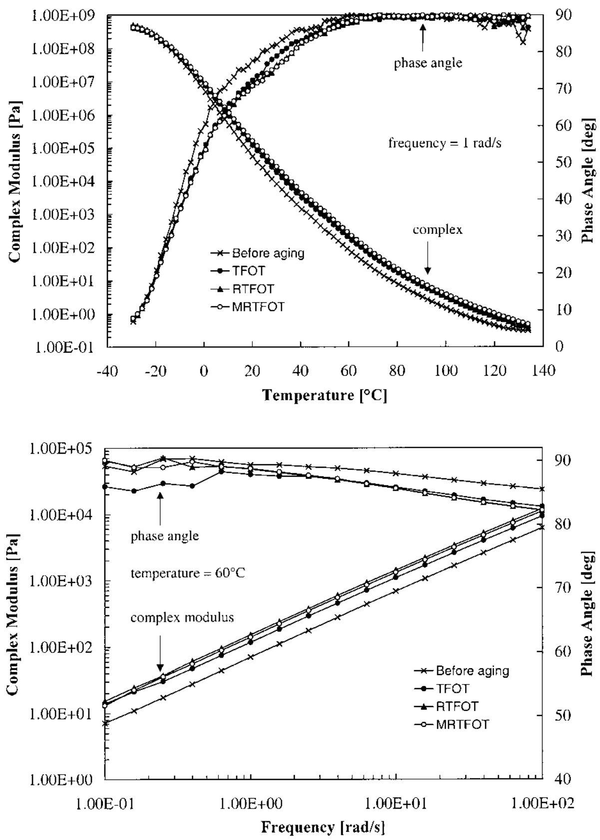

Figure 7 Complex modulus and phase angle as function of temperature and frequency for bitumen B before and after artificial aging.

of −30–50°C and 40–135°C, respectively. In the tests, a sinusoidal strain was applied by an actuator, and the actual strain and torque were measured and input to a computer for calculating complex modulus (G^*) and phase angle (δ).

RESULTS AND DISCUSSION

Chemical Characteristics

Base Bitumens

The procedures of artificial aging used in this paper involve volatilization and oxidation of bitumens. Oxidative aging can be verified and quantitatively measured by FTIR, TLC-FID, and GPC, as illustrated in Figures 1–3. In infrared spectra (Fig. 1), the bands at 1705 and 1030 cm^{-1} are assigned to carbonyl functions and sulfoxides, respectively, the group of peaks at about 750, 815, and 870 cm^{-1} attributed to substituted aromatic ring structures, while the strong band at 1375 cm^{-1} is due to C—H bending in methyl groups. When bitumens oxidize, carbonyl groups, and sulfoxides are among the most prevalent products. As indicated in Table I, carbonyl compounds and sulfoxides increase during aging, the degree of the changes being dependent on the bitumen. In most cases, minor differences are observed between TFOT, RTFOT, and MRTFOT with regard to the formation of functional groups.

The oxidation of bitumens is also evident when generic compositions are compared. As shown in Figure 2, aging reduces the content of aromatics and at the same time increases the contents of resins and asphaltenes. However, changes in the content of saturates are negligible due to their inert nature. The compositional changes imply transformation of generic fractions, which may be further confirmed by GPC (Fig. 3). During aging, the content of large bitumen molecules (peak retention time at about 18 min) increases at the expense of a decrease (oxidation) in small molecules (peak retention time at about 24 min). As a result, increases in molecular weight are observed for the whole bitumen system when subjected to aging. As an example (cf. Fig. 3), for bitumen B, after RTFOT, the contents of large molecules and molecular weight (weight average, W_w) increase by 40 and 70%, respectively.

Polymer Modified Bitumens

As described earlier, PMBs were prepared by mechanical mixing. These binders exhibit a two-phase microstructure, in which polymers may show either dispersed particles or continuous networks, depending on the characteristics of the base bitumens, and polymer type and content.[4,5] When artificial aging is performed on such systems, both the bitumen and polymer phases are influenced.[8,9] In this study, FTIR and GPC are used to determine possible compositional changes of PMBs during aging.

Figure 4 shows typical FTIR results. As can be seen, PMBs display IR bands of bitumens and polymers. For SBS and SEBS modified bitumens, the polystyrene related peak is observed at 700 cm^{-1}. The SBS modified binder also shows absorption at 965 cm^{-1}, which is due to C—H bending in the polybutadiene part of the polymer. For EVA and EBA modified bitumens, the IR bands at about 1735 cm^{-1} are attributed to C=O groups in the acetate or acrylate part of the polymers. A difference between the two types of plastomer is

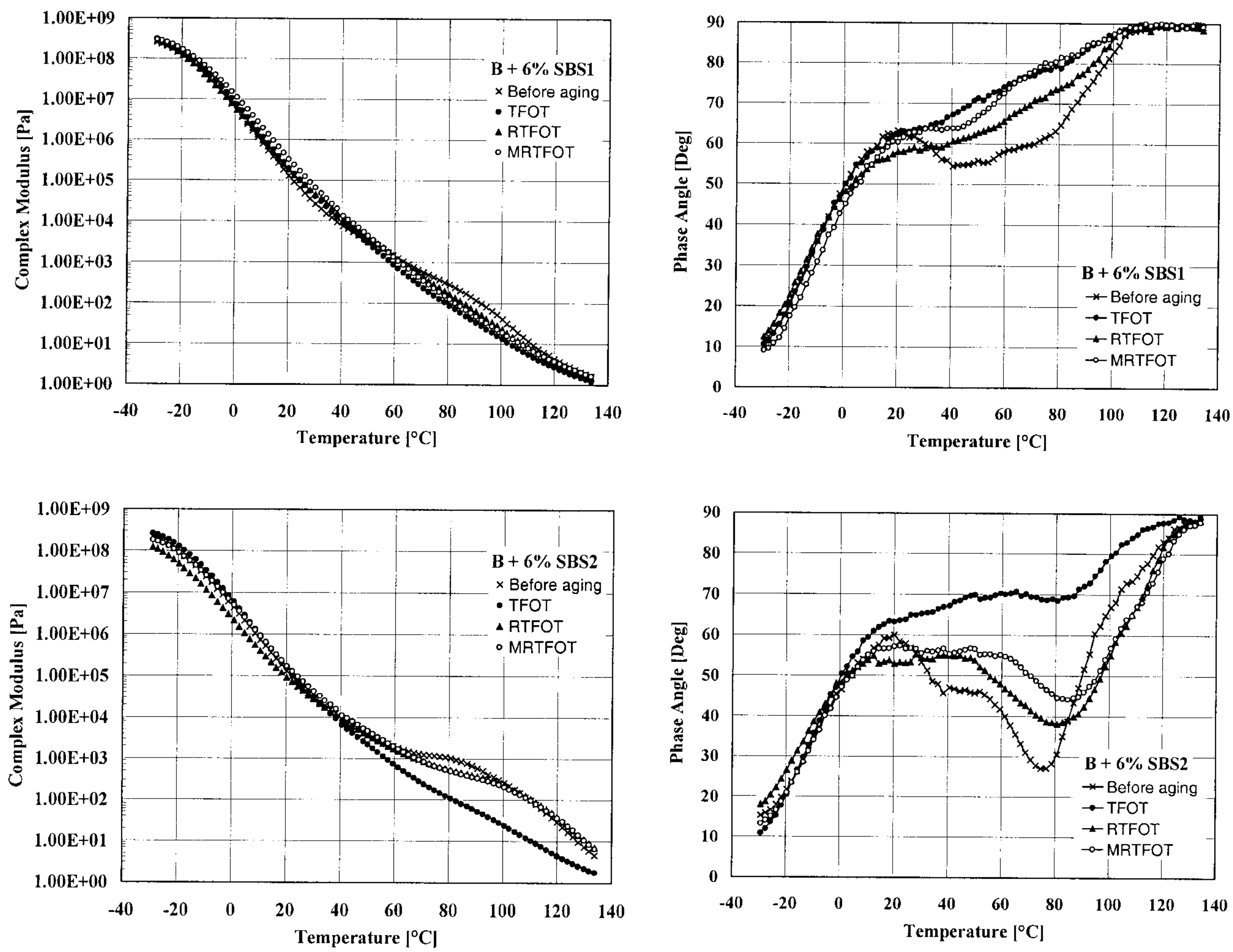

Figure 8 Effect of aging on temperature dependence of complex modulus and phase angle (SBS1 and SBS2 modified bitumen B).

that EVA displays IR absorption at 1245 cm^{-1} and EBA at 1165 cm^{-1}. It was observed that, in most cases, the above polymer-related absorption did not change during aging; however, the contents of carbonyl compounds and sulfoxides were increased by aging. Compared to the corresponding base bitumens, most of the polymer modified binders display lower formation of sulfoxides (Table II). As regards the formation of carbonyl compounds, only SEBS shows an inhibiting effect. For the other modified binders studied, determination of the carbonyl compounds of bitumens was impeded by the absorption of EVA acetate and EBA acrylate, or oxidative degradation of SBS, making examination of the effects of these polymers difficult.

In Figure 5, examples of GPC are illustrated for elastomer modified binders. Elution peaks between 20 and 32 min display a molecular weight distribution of the bitumens. The modified binders show one elution peak at 18 min for SEBS and two peaks at between 15 and 20 min for SBS. The reduction in the SBS peak indicates that the polymer undergoes degradation during aging. For aged SEBS modified binders, a very slight shift and reduction of the polymer peak are observed. Figure 5 also indicates that, during aging, the content of large bitumen molecules increases and their molecular weight shifts to a higher value (shorter elution time), while the content of small molecules decreases. The GPC changes in the bitumen phase are similar to those observed for pure bitumens. In addition, the degree of the changes is dependent on the base bitumen and polymer type. Among the four PMBs shown in Figure 5, the modified bitumen B with 6% SBS1 displays the largest changes as measured by GPC.

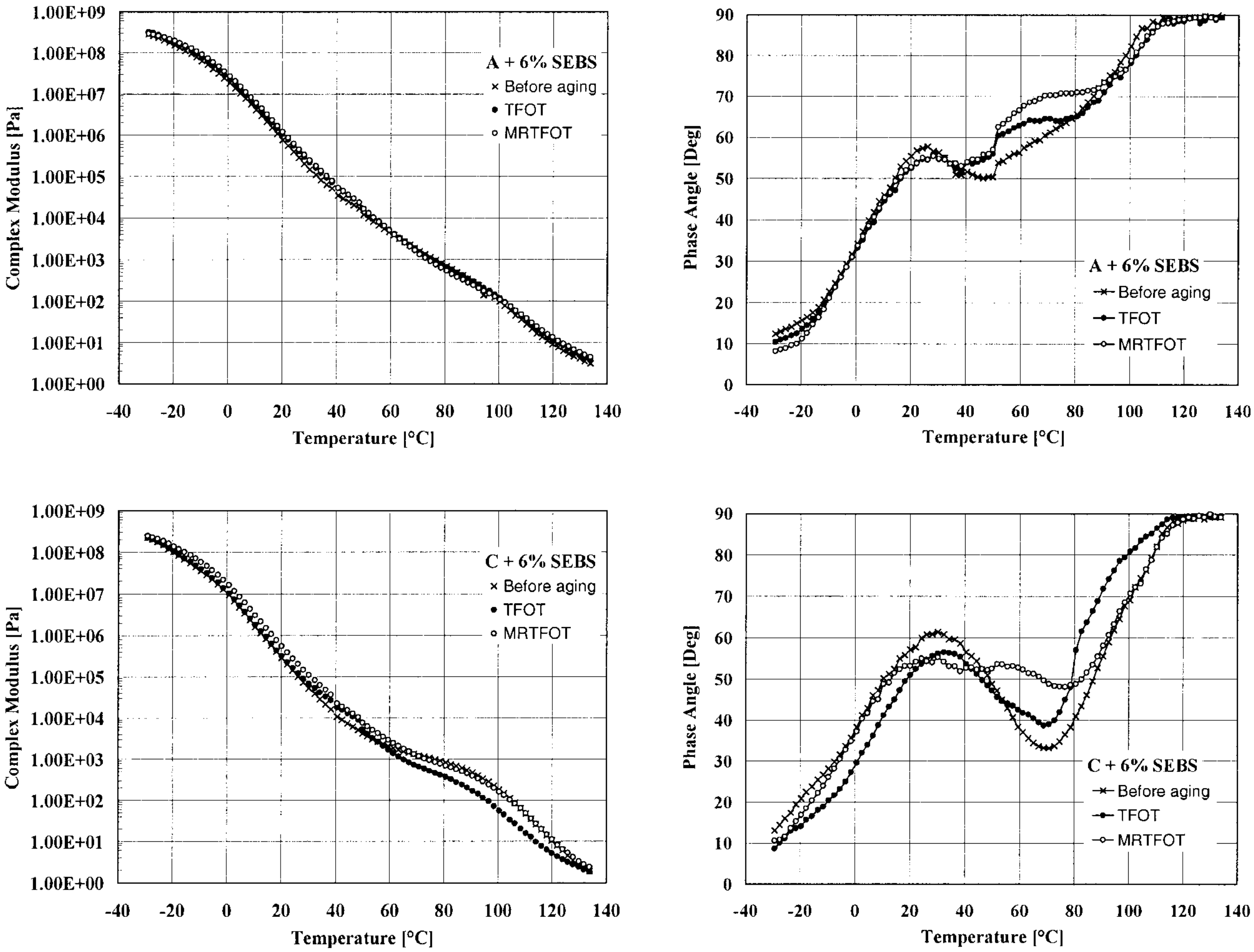

Figure 9 Effect of aging on temperature dependence of complex modulus and phase angle (SEBS modified bitumens A and C).

Typical GPC results obtained for modified binders containing EVA and EBA are shown in Figure 6. Under the GPC conditions used in this study, these polymers do not show any apparent response. However, it should be mentioned that, on preparing solutions of EVA and EBA bitumens with THF, a small amount of insoluble substances was observed. The insoluble part was removed with a 0.45 μm syringe filter before performing GPC analysis. It is uncertain whether these removed substances in any way influence the GPC characterization of EVA and EBA modified binders.

Viscoelastic Properties

Base Bitumens

As expected, the rheological properties of bitumens are influenced significantly by aging. In certain temperature and frequency regions, aging increases the complex modulus and reduces the phase angle considerably (Fig. 7). These changes imply that the aging process makes the mechanical properties of the bitumens more elastic. The shift in viscoelastic behavior is attributed to oxidation of the bitumens. As stated above, oxidative aging increases the content of functional groups, changes generic fractions, and increases molecular weight. An increasing content of oxygen-containing functional groups will increase bitumen polarity and molecular association. All these compositional and structural factors contribute to the rheological characteristics of bitumens.

Elastomer Modified Binders

Figure 8 shows the effect of artificial aging on the rheology of SBS modified bitumens. As can be

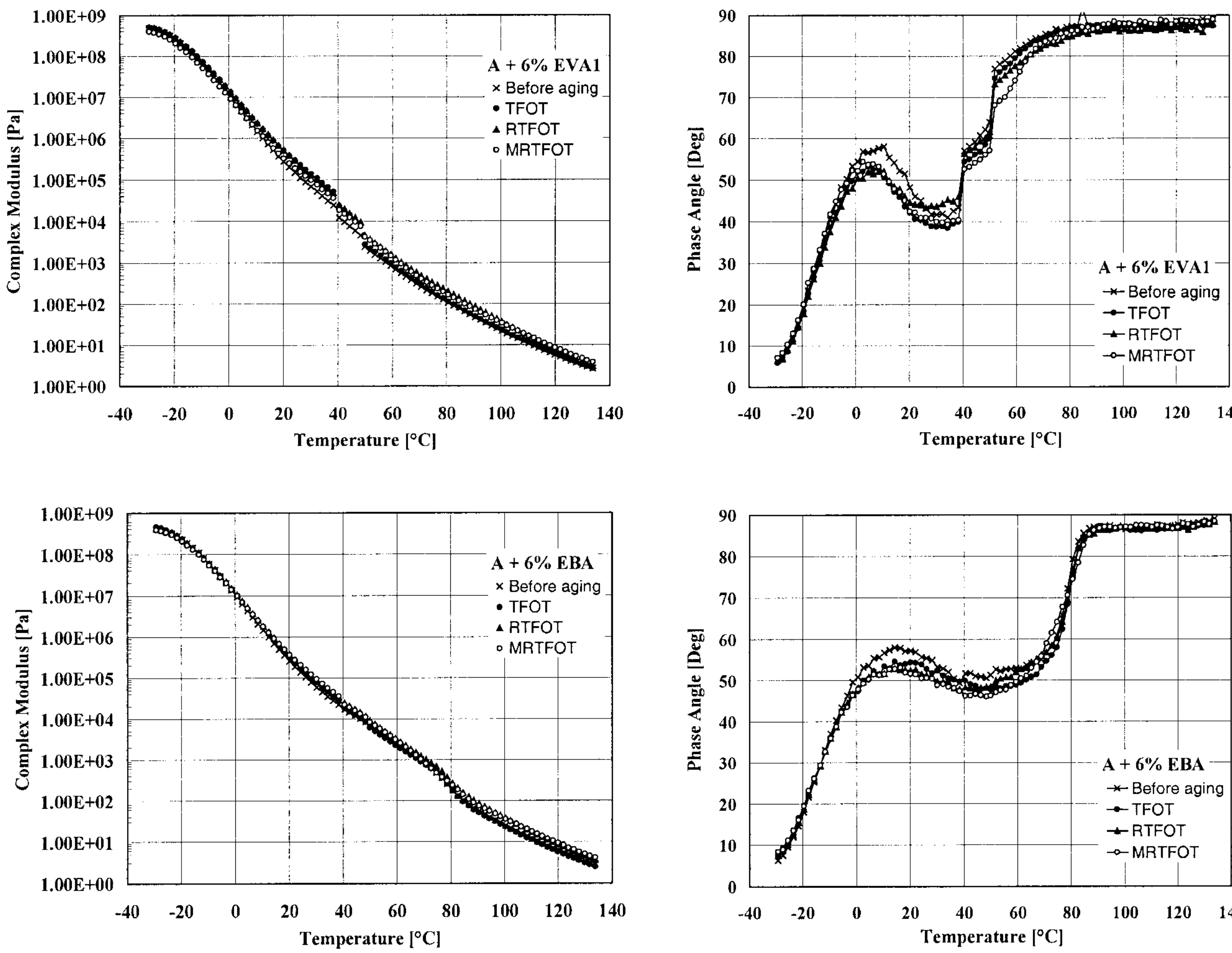

Figure 10 Effect of aging on temperature dependence of complex modulus and phase angle (EVA1 and EBA modified bitumen A).

seen, at the frequency studied (1 rad/s), the effect of aging is largely dependent on temperature. At temperatures higher than about 40°C, a decreased complex modulus (increased softness) is observed for aged modified binders. On the other hand, at temperatures lower than about 40°C, aging shows little effect on complex modulus. The effect of aging on viscoelastic properties is also evident when plots of phase angle vs temperature are examined. As indicated in Figure 8, aging increases phase angle, and consequently, reduces the depth of the phase angle minimum at high temperatures. The rheological changes are consistent with polymer degradation and bitumen oxidation. Increases in bitumen polarity and molecular association may change compatibility (molecular interaction) between the polymer and bitumen. Moreover, breakdown of SBS reduces the density of the polymer networks, and consequently, the effectiveness of the polymer in modifying bitumen rheology is reduced.

Decreased complex modulus and increased phase angle are also observed for aged SEBS bitumens (Fig. 9). As a hydrogenated SBS polymer, SEBS is highly resistant to thermal degradation. This has been shown by GPC in Figure 5. Consequently, it is not possible to relate the rheological changes of the SEBS bitumens to the composition changes of the polymer. Possible aging mechanisms of this type of modified binders need further investigation.

Plastomer Modified Binders

Figures 10 and 11 illustrate the effect of artificial aging on the rheological properties of modified binders containing plastomers (EVA and EBA). Evidently, the process of aging increases the com-

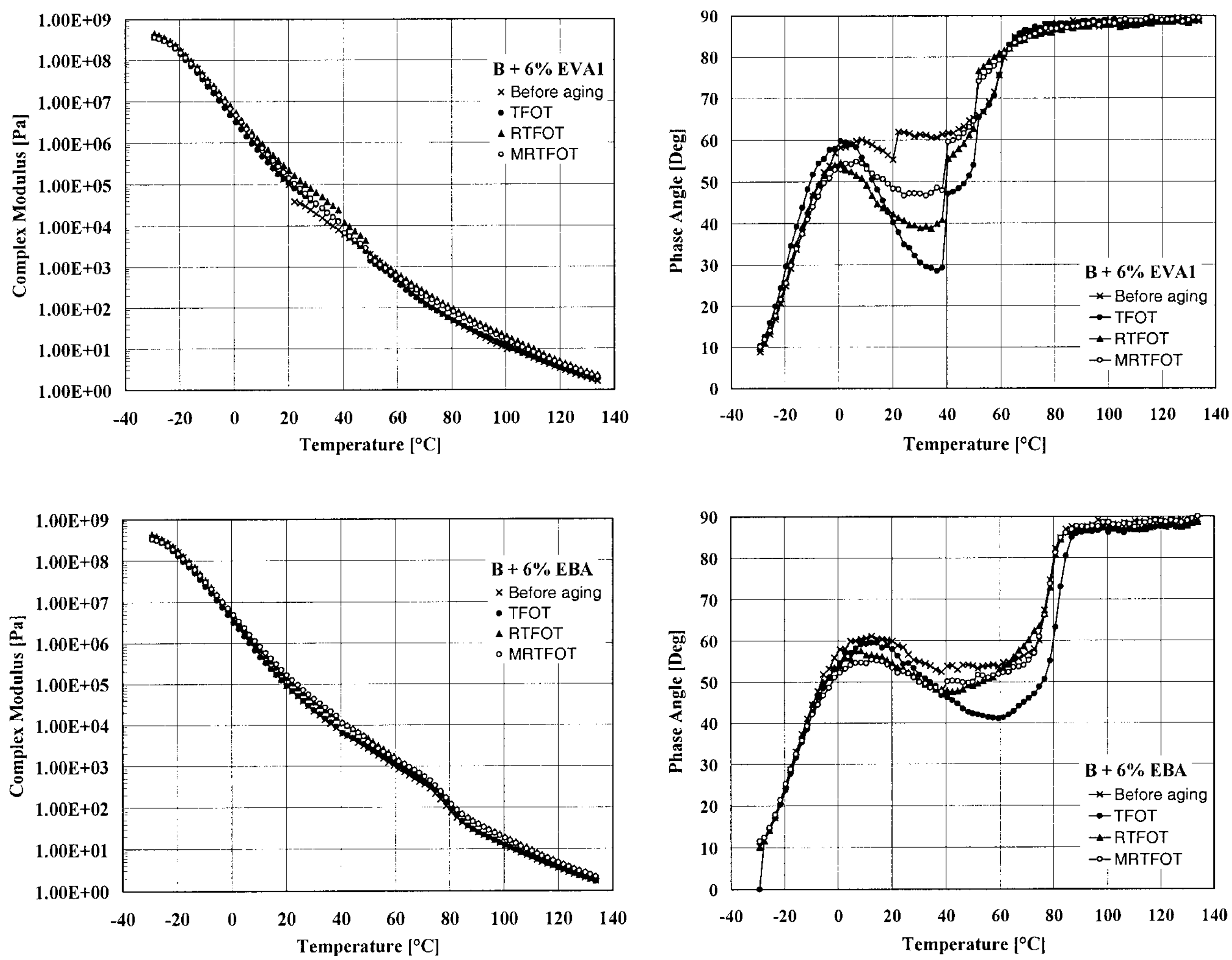

Figure 11 Effect of aging on temperature dependence of complex modulus and phase angle (EVA1 and EBA modified bitumen B).

plex modulus and elastic response (decreased phase angle). At a given content of plastomers, similar patterns of the aging effect are observed. The phenomena are mainly due to oxidative hardening of the bitumens. In other words, the addition of plastomers probably does not alter the mechanism of bitumen aging, and the degree of aging is to a great extent determined by the corresponding base bitumen. For example, bitumen B displays a higher degree of oxidation than bitumen A (Tables I and II), and as a result, the plastomer modified bitumen B displays a higher degree of aging than modified A as characterized by DMA (cf. Figs. 10 and 11). In this connection, it should be mentioned that changes in compatibility (molecular interaction) due to oxidation of bitumens may also influence the rheology.

Temperature Susceptibility

Temperature susceptibility is usually defined as the change in a binder property as a function of temperature. Since the properties of binders are characterized by various parameters, different approaches may be used to evaluate temperature susceptibility. In this paper, temperature susceptibility is calculated from the complex modulus obtained using DMA according to

$$\text{Temperature susceptibility} = [\log G^*(T_1) - \log G^*(T_2)]/(T_2 - T_1)$$

where $G^*(T_1)$ and $G^*(T_2)$ are complex moduli (Pa) at temperatures of T_1 and T_2 (°C), respectively.

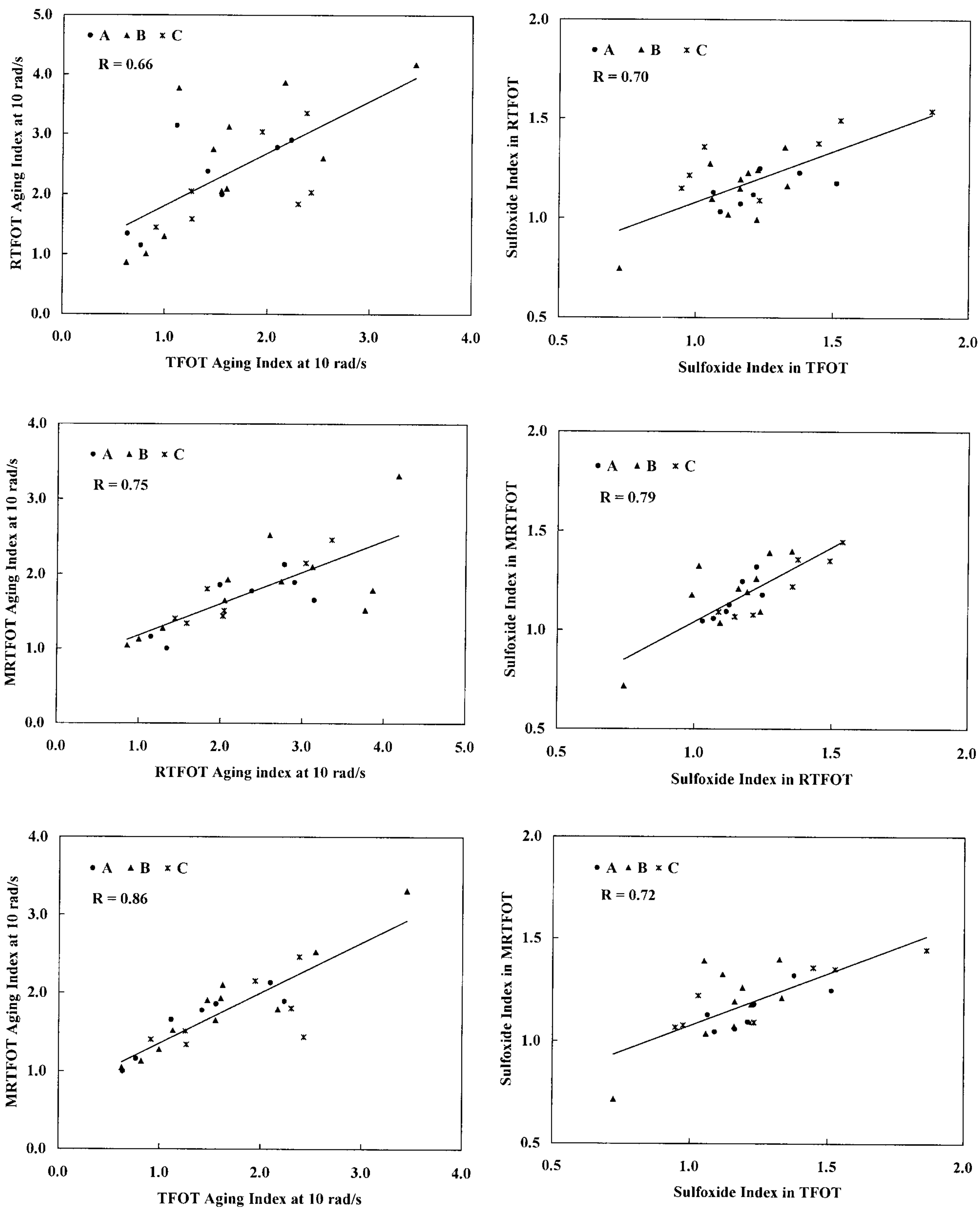

Figure 12 Correlation between different aging methods.

Table III Effect of Aging on Temperature Susceptibility (0–60°C)

Binders	Before Aging	TFOT	RTFOT	MRTFOT
Bitumen A	0.082	0.081	0.079	0.079
A + 6% SBS1	0.063	0.070	0.065	0.060
A + 6% SBS2	0.063	0.051	0.065	0.066
A + 6% SEBS	0.065	0.063	0.064	0.064
A + 6% EVA1	0.074	0.070	0.068	0.068
A + 6% EVA2	0.076	0.074	0.070	0.072
A + 6% EBA	0.066	0.063	0.060	0.061
Bitumen B	0.081	0.080	0.079	0.080
B + 3% SBS1	0.077	0.075	0.072	0.074
B + 6% SBS1	0.061	0.068	0.063	0.068
B + 9% SBS1	0.054	0.052	0.052	0.055
B + 6% SBS2	0.057	0.067	0.054	0.059
B + 6% SEBS	0.063	0.055	0.062	0.062
B + 3% EVA1	0.080	0.073	0.073	0.072
B + 6% EVA1	0.075	0.068	0.066	0.069
B + 9% EVA1	0.067	0.065	0.059	0.063
B + 6% EVA2	0.079	0.069	0.066	0.074
B + 6% EBA	0.067	0.058	0.059	0.062
Bitumen C	0.086	0.085	0.084	0.085
C + 6% SBS1	0.066	0.073	0.067	0.070
C + 6% SBS2	0.063	0.067	0.068	0.070
C + 6% SEBS	0.067	0.067	0.069	0.065
C + 6% EVA1	0.078	0.074	0.070	0.074
C + 6% EVA2	0.076	0.070	0.070	0.074
C + 6% EBA	0.068	0.075	0.063	0.064

As indicated in Table III, polymer modified binders display a lower temperature susceptibility than the corresponding base bitumen. For the base bitumens, as well as the modified binders with plastomers, temperature susceptibility is reduced by aging. However, for most elastomer modified binders, increased temperature susceptibility is observed after aging. The reduction in temperature susceptibility is attributed to increased polarity (molecular association) of the aged bitumens, while the increase in temperature susceptibility is probably due to degradation (network damage) of the polymers.

Correlation Between TFOT, RTFOT, and MRTFOT

To compare the TFOT, RTFOT, and MRTFOT, the aging index, defined as the ratio of complex modulus after and before aging, is calculated at 60°C and two frequencies (Table IV). Using aging index and sulfoxide index (Table II), correlation between the three aging methods is examined. As indicated in Figure 12, a linear relationship exists between the TFOT, RTFOT, and MRTFOT. In all the cases shown, the relationship is statistically significant at a 0.05 level of significance.

Based on the aging index, other studies have shown that the RTFOT method produces more severe aging than the TFOT method.[10,11] However, the aging index is influenced by evaluation conditions (e.g., temperature and frequency) (Fig. 13). For SBS modified bitumens, the aging index is greatly dependent on the combined effect of bitumen oxidation (hardening) and polymer degradation (lowering the consistency of PMBs). Figure 13 indicates that the RTFOT method is somewhat more severe with regard to oxidative aging of bitumen, but less severe with regard to degradation of SBS polymer, compared with the TFOT method.

CONCLUSIONS

The study has indicated that artificial aging increases the contents of carbonyl compounds and sulfoxides of conventional bitumens. Com-

Table IV Aging Indices Obtained from Complex Modulus at 60°C and Two Frequencies

	TFOT		RTFOT		MRTFOT	
Binders	1 rad/s	10 rad/s	1 rad/s	10 rad/s	1 rad/s	10 rad/s
Bitumen A	1.61	1.56	2.12	1.99	1.96	1.85
A + 6% SBS1	0.43	0.64	0.94	1.35	0.94	1.00
A + 6% SBS2	0.57	0.77	1.00	1.15	1.02	1.16
A + 6% SEBS	1.51	2.09	2.34	2.78	1.73	2.13
A + 6% EVA1	2.34	2.23	3.22	2.90	1.98	1.89
A + 6% EVA2	0.98	1.11	2.96	3.14	1.35	1.65
A + 6% EBA	1.60	1.41	2.64	2.38	2.00	1.77
Bitumen B	1.69	1.60	2.17	2.08	2.00	1.92
B + 3% SBS1	1.72	1.55	2.51	2.05	1.94	1.64
B + 6% SBS1	0.50	0.82	0.74	1.00	0.75	1.12
B + 9% SBS1	1.07	1.00	1.22	1.29	1.37	1.27
B + 6% SBS2	0.32	0.63	0.73	0.86	0.81	1.04
B + 6% SEBS	4.69	2.54	2.51	2.59	2.57	2.52
B + 3% EVA1	3.54	3.44	4.41	4.17	3.40	3.31
B + 6% EVA1	1.72	1.62	3.42	3.12	2.21	2.09
B + 9% EVA1	1.08	1.13	4.88	3.77	1.58	1.51
B + 6% EVA2	3.40	2.17	5.94	3.86	1.67	1.78
B + 6% EBA	2.21	1.47	3.15	2.74	2.00	1.90
Bitumen C	1.30	1.26	1.62	1.59	1.33	1.34
C + 6% SBS1	0.57	1.26	1.26	2.04	0.92	1.51
C + 6% SBS2	0.51	0.91	0.74	1.45	0.67	1.40
C + 6% SEBS	2.90	2.38	2.17	2.35	2.32	2.46
C + 6% EVA1	1.97	1.95	3.68	3.04	2.17	2.15
C + 6% EVA2	2.22	2.43	2.23	2.03	1.19	1.43
C + 6% EBA	1.66	2.30	1.76	1.83	1.74	1.80

pared to the corresponding base bitumens, most of the polymer modified binders display lower formation of sulfoxides. However, it is difficult to examine the effect of polymers on the formation of carbonyl compounds due to interference from polymer absorption (EVA and EBA) or degradation (SBS).

Artificial aging increases the content of large bitumen molecules and decreases the content of small molecules, leading to an increase in the molecular weight of the bitumens. For SBS modified binders, aging causes degradation of the polymer. For SEBS modified binders, a slight shift and a reduction in GPC peak of the polymer are observed after aging. The GPC responses are not observed for EVA and EBA in the modified binders.

The effect of aging on the rheology of polymer modified binders is strongly dependent on the characteristics of polymers. For SBS and SEBS modified binders, decreased complex modulus and increased phase angle are observed after aging. The rheological changes of SBS modified bitumens are associated with polymer degradation and bitumen oxidation. However, for SEBS modified bitumens, the mechanisms of aging are unclear. As regards EVA and EBA modified binders, aging increases complex modulus and elastic response (decreased phase angle). These changes are mainly due to the oxidative hardening of the base bitumens.

Artificial aging influences the temperature susceptibility of the binders. For the modified binders with EVA and EBA, this parameter is reduced by aging. For most of the SBS and SEBS modified binders, increased temperature susceptibility is observed on aging.

A statistically linear relationship exists between different aging methods (TFOT, RTFOT, and MRTFOT). However, no definite conclusion could be drawn regarding the difference in severity of aging between these methods.

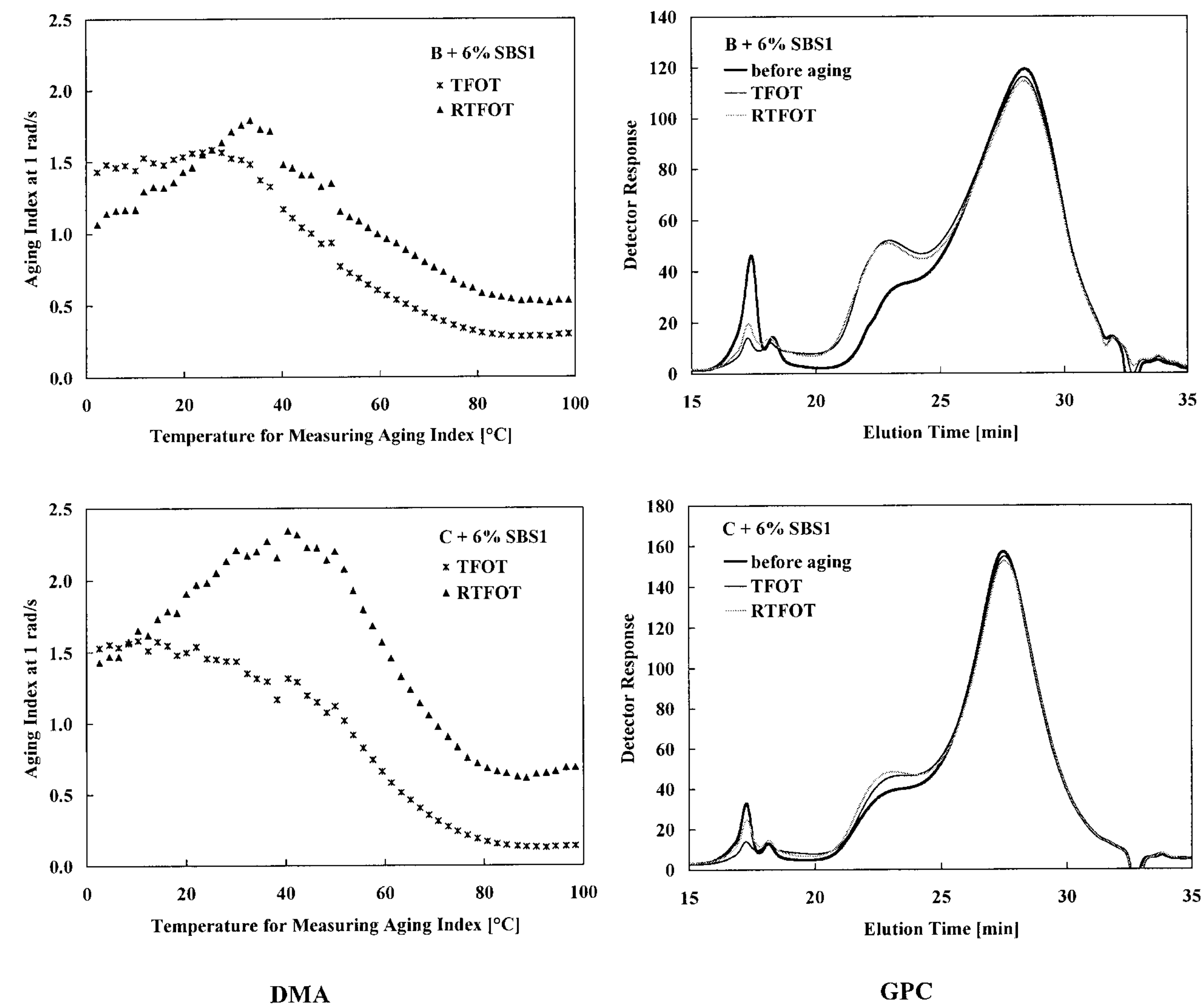

Figure 13 Comparison of the TFOT and RTFOT methods.

The authors would like to thank Jonas Ekblad, Britt Wideman, and Clarissa Villalobos for their laboratory assistance during the testing program.

REFERENCES

1. Isacsson, U.; Lu, X. Materials and Structure 1995, 28, 139–159.
2. Petersen, J. C. Transportation Research Record 999; TRB, National Research Council: Washington, DC, 1984; pp 13–30.
3. Johansson, J. S.; Lu, X.; Isacsson, U. Ageing of Road Bitumens—State of the Art; TRITA-IP FR 98-36, Royal Institute of Technology: Stockholm, Sweden, 1998.
4. Lu, X.; Isacsson, U. Materials and Structure 1997, 30, 618–626.
5. Isacsson, U.; Lu, X. J Materials Sci 1999, 34, 3737–3745.
6. Oliver, J. W. H.; Tredrea, P. F. J Assoc Asphalt Paving Technologists 1997, 66, 570–602.
7. Bahia, H. U.; Zhai, H.; Rangel, A. Transportation Research Record 1638; TRB, National Research Council: Washington, DC, 1998; pp 64–71.
8. Cotte, C.; Such, C. Proceedings of the Eurasphalt & Eurobitume Congress, E&E.5.105, Strasbourg, 7–10 May, 1996.
9. Airey, G. D.; Brown, S. F. J Assoc Asphalt Paving Technologists 1998, 67, 66–100.
10. Huang, S. C.; Tia, M.; Ruth, B. E. J Materials Civil Engineering 1996, 8, 147–152.
11. Phromsorn, C. J.; Kennedy, T. W. Transportation Research Record 1488; TRB, National Research Council: Washington, DC, 1995; pp 13–20.