

# Stability of Straight and Polymer-Modified Asphalts

JIM H. COLLINS AND MARK G. BOULDIN

Both short- and long-term aging can have a significant influence on the performance of hot mix asphalt pavements. This is true for polymer-modified asphalts as well as for conventional asphalt cements. The latter can undergo significant age hardening during storage, mixing, and placement in the field. This long-term aging can be dramatic and lead to premature pavement failure. The effects of aging can be exacerbated in the case of permeable pavements or in regions with extreme climatic conditions. Polymer modification is a way of overcoming these potential deficiencies by providing binders with well-balanced property sets. However, unsaturated polymers are susceptible to thermal and oxidative degradation. Thus, it is imperative to avoid prolonged storage and excessive temperatures during processing. Improved thermal and oxidative stability can be achieved by modifying asphalts with saturated polymers.

In recent years various studies have shown that polymer modification can be successful in obtaining asphalt binder systems with improved property sets. Improvements were noted in the binder properties, the properties of the hot mix asphalt (HMA), and in actual pavements in the field. In the case of permanent deformation Valkering et al. (1) found that in wheel tracking experiments the rutting rate at 40°C and 50°C could be significantly reduced by polymer modification. These results have been substantiated by Bouldin and Collins (2) with the TRRL wheel tracker for temperatures up to 60°C. Both repetitive and static creep experiments on HMA cores appear to correlate with these findings (1,3–5). Reports by Reese et al. (6) and Fleckenstein et al. (7) for example show that on heavily trafficked pavements dramatic improvements have been observed. In the case of thermal and fatigue cracking both Collins et al. (8) and Goodrich (9) have observed enhanced performance.

Such results have lead to widespread commercial use of polymer-modified asphalts. In some states, for example Nevada, polymer modification of asphalt is currently being specified for wearing courses on all major thruways.

How the long- and short-term stability of both conventional and polymer-modified asphalt influence their performance is discussed. The issues addressed are

- Asphalt cement aging,
- Polymer stability,
- Polymer-asphalt phase stability and microstructure, and
- How these influence the binder properties as well as the actual field performance.

The way these materials are handled in the field (i.e., from initial polymer-asphalt blending to laydown and compaction) can have a significant impact on the previously mentioned issues. The first section therefore primarily addresses short-term aging encountered in these operations. In the second part, we discuss how long-term field aging can affect the pavement performance.

## EXPERIMENTAL

Sample preparation, microscopy, rheological characterization, and traditional binder tests are described in detail elsewhere (10).

### Gel Permeation Chromatography

A gel permeation chromatography (GPC) technique was used similar to that described by Portfolio and Fensel (11) to determine mean molecular weight ( $M_w$ ) and molecular weight distribution. For the evaluation of field samples, the binders were extracted directly from the HMA with tetra-hydrofuran (THF). The effective amount of polymer is defined as

$$C_{\text{eff}} = \left[ \frac{C_{\text{HM,aged}} \times 100}{(C_{\text{HM,aged}} + C_{\text{LM,aged}})} \right] \div \left[ \frac{C_{\text{HM}}}{(C_{\text{HM}} + C_{\text{LM}})} \right]$$

The unaged samples have therefore by definition an effective polymer concentration of 100 percent.

### Materials

Tables 1 and 2 show the asphalts and polymers used in this study.

### Low Temperature Thermal Cracking Test

We have devised a method to determine the critical cracking temperature ( $T_{\text{cr}}$ ) of binder systems that is very similar to Hills' method (12). It is basically a visual method where  $T_{\text{cr}}$  is defined as the temperature at which the first crack in the asphalt is observed. A detailed description of the method is given by Collins et al. (8).

TABLE 1 ASPHALTS USED IN STUDY

Code	Asphalt Source	Asphalt Grade	Location
TX	W. Tx Intermediate	AC-10	TX HWY 287
WY	Wyoming	AC-10	WY I-80
NV06	California Valley	AR 1000	NV I-15
NV01	California Valley	AR 4000	NV RT 95
CA-N1	California Valley	AR 1000	CA I-40
CA-N2	California Valley	AR 4000	CA I-40
CA-C1	California Valley	AR 1000	CA RT 395
CA-C2	California Valley	AR 2000	CA RT 395
CA-S1	California Valley	AR 1000	CA Sacramento Intersection of Mack Rd. and Stockton Blvd.
CA-S2	California Valley	AR 8000	CA Sacramento Intersection of Mack Rd. and Stockton Blvd.
CV	California Valley	AR 4000	—
ET-1	East Texas	AC-5	—
ET-2	East Texas	AC-20	—
VEN-1	Venezuela	AC-7	—
VEN-2	Venezuela	AC-20	—

### Repetitive Creep Experiments

To determine the ability of a certain mix to resist permanent deformation, repetitive creep experiments were carried out. Contrary to some earlier work done by other groups (1), we did not apply a square wave but used a Haversine wave. The reasons for this are as follows:

1. It is easier to control this form of force application. The initial slope  $dF/dt$  is very small, and therefore significant force overshoots do not occur.
2. This pressure profile tends to mimic much more closely the pressures that a pavement will experience in the field (13).

The experiment is described elsewhere (14).

### Short-Term Aging

In this section we would like to focus our interest on how the following processes may affect the performance of both straight and polymer-modified asphalts. These process steps are

- Blending of the polymer with asphalt,
- Storage of straight and polymer-modified asphalts, and
- Processing of the binder in a hot mix plant.

### Asphalt Age Hardening

During the processing and storage of straight unmodified asphalt, one usually observes a so-called age hardening of the asphalt (15). Oxidation leads to more structured asphalts. In general this will result in both a higher asphaltene content and a higher average molecular weight (16–18). An example of age hardening is shown in Figure 1. The asphalt CA-S1 was stored over a period of 5 days at a temperature of 180°C (low shear agitation). As reflected in the penetration at 25°C and the penetration at 4°C the material becomes significantly harder with time. This effect is even more pronounced in crudes that are more susceptible to aging such as, for example, heavy Venezuelan crudes (9).

The most significant asphalt age hardening is normally observed when the asphalt is mixed with the aggregate in the

TABLE 2 POLYMERS USED IN STUDY

Code	Polymer Type	Oil Content	Trade Name and Grade
A	SBS	—	Shell KRATON® Rubber D1101
B	SBS	29%	D4141
C	SBS	50%	D4460X
D	(SB) <sub>2</sub>	—	D1184
E	SEBS	—	G1657
F	SEBS	—	RP6904
G	SBR	70% solids (no Oil)	Goodyear Ultrapave® 70
H	PE	—	Dow PE 2045

hot mix plant. Whereas exact temperatures are not available, the surface temperature of the aggregate can reach temperatures in excess of 260°C. Because the AC forms a thin layer on the aggregate, oxidation can be very significant.

Rolling thin film oven (RTFO) is a laboratory aging procedure (ASTM D2872) that is supposed to simulate the aging commonly observed in a hot mix plant (19). Some Western states have adopted this technique and grade all their asphalts according to the viscosity of the aged residue (AR grading system, ASTM D3381 Table III).

### Polymer Stability

Under normal conditions, no significant changes in  $M_w$  are observed during the blending process for SBS polymers. This has been established by comparing the molecular weight distribution of the neat polymer with the polymer in modified asphalt. The drop in  $C_{eff}$  due to mechanical and thermal conditions in the blending process is generally less than 4 to 5

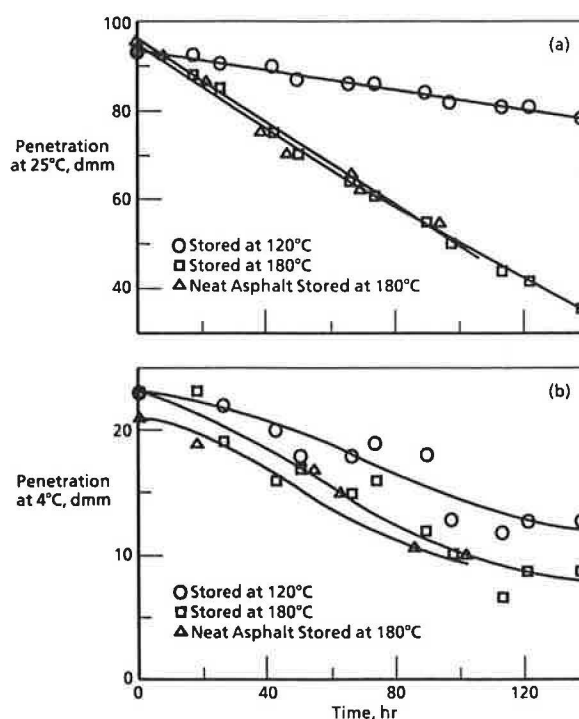


FIGURE 1 Influence of storage time and temperature on penetration (a, 25°C; b, 4°C) for 4 percent weight SBS (Polymer D) in CA-S1.

TABLE 3 GPC RESULTS ON POLYMER-MODIFIED BINDERS

Asphalt	Polymer	Hot Mix Plant Type	Conditioning	C <sub>eff</sub> %
TX	3%w A	Drum	Original <sup>2</sup>	89.3
			RTFO	51.0
	6%w A	Drum	loose mix <sup>3</sup>	0.0
			Original	70.6
WY	6%w C <sup>1</sup>	Drum	RTFO	40.1
			loose mix	14.8
	6%w C <sup>1</sup>	Drum	Loose mix	~100
			field aged sample (after ~4 years)	87.5
NV01	6%w C <sup>1</sup>	Drum	Original	100
			RTFO	62.9
	6%w C <sup>1</sup>	Drum	loose mix	89.9
			field aged sample (after ~3.5 years)	80.8
CA-N1	D	Drum	Original	74.9
			CATOD	0.0
CA-S1	4%w F	Drum	Original	95.2
			RTFO	93.4
			CATOD	93.2
			loose mix	96.4

<sup>1</sup>Actual neat polymer content.<sup>2</sup>Polymer/asphalt blend prior to use at hot mix plant.<sup>3</sup>Loose mix samples were taken prior to compaction at job site.

percent (compare Table 3). This is valid for both low and high shear mixing. However, sufficient temperature control is necessary to avoid excessive viscous dissipation during high shear mixing.

At the polymer levels used in standard paving applications, virtually only chain scission is observed. Gelation does not occur as shown in Figure 2 (no ultrahigh molecular weight species even after RTFO). A potential exception is when a concentrate is formulated that may contain up to 15 percent weight polymer. In these cases recombination and cross-linking can result in ultrahigh molecular weight species, and the latter may precipitate during solvent extraction.

A more likely source of polymer degradation is hot storage. It is not uncommon in the industry to hold asphalts over

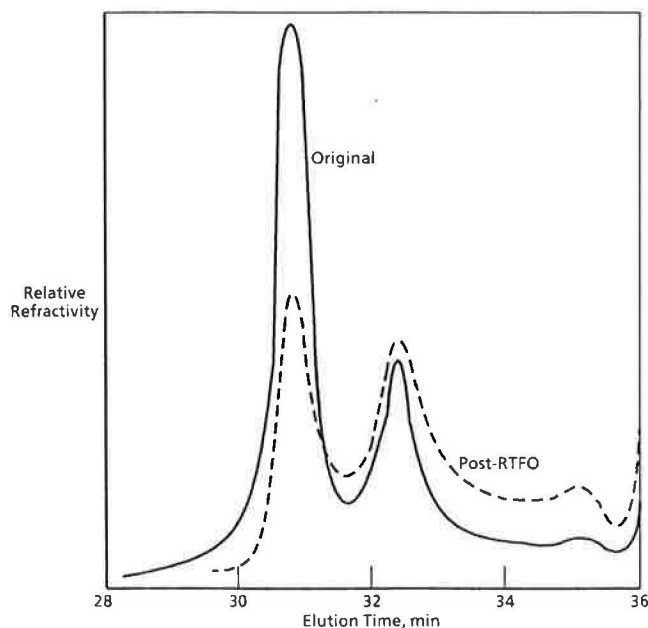


FIGURE 2 Typical chromatographs of 3 percent weight of SBS (Polymer A) in ET-1 before and after RTFO aging.

periods of weeks, and less frequently over months. If this is done with styrene-butadiene (unsaturated) polymers, one should take care to ensure that the storage temperature is well below 135°C to maximize polymer stability. Two laboratory samples were blended both containing 4 percent weight SBS. The first one was held at a temperature of 180°C (356°F), and the second sample was held at a more moderate temperature of 120°C (248°F). In both cases the samples were gently agitated and were exposed to air. As shown in Figure 3 at 120°C, the polymer stability is significantly enhanced relative to storage stability at 180°C. Stability can be further improved by blanketing with nitrogen.

This stability has a potentially significant impact on the resulting rheological properties of the asphalt blend, and thus its relative performance in the field. In general one would

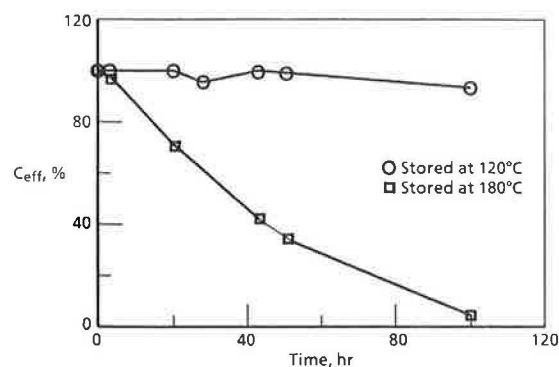


FIGURE 3 Degradation of 4 percent weight SBS (Polymer D) in CA-S1 as a function of storage time and temperature.

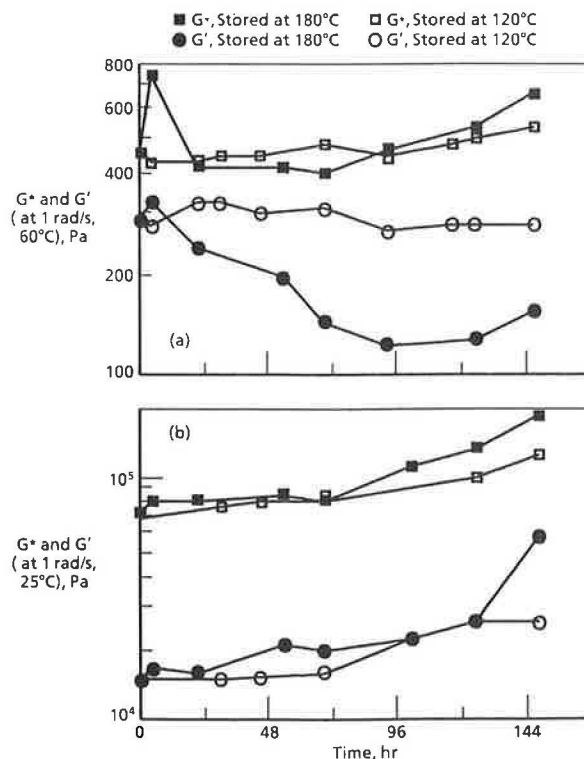


FIGURE 4 Change of storage and complex modulus as a function of storage time and storage temperature for 4 percent weight SBS (Polymer D) in CA-S1.

want a material that exhibits high resistance to deformation at elevated temperatures and that is not prone to exhibit cracking at low temperatures. A measure of the ability of a material to resist deformation is the complex modulus,  $G^*$ . The elasticity of a material is measured with the storage modulus,  $G'$ , which indicates the portion of the energy that is restored elastically. The loss modulus,  $G''$ , is an indicator of the amount of energy that dissipates in the form of viscous flow (20). Straight unmodified asphalts are at elevated temperatures virtually only viscous,

$$G'' \gg G'$$

$$G'' \sim G^*$$

whereas polymer-modified asphalt may be even more elastic than viscous at high temperatures (2,10). The ideal binder should have a large value of  $G^*$  and  $G'$  at 60°C.

On the other hand, to prevent premature fatigue cracking  $G^*$  at 25°C should be as low as possible (21–23). In Figure 4 the values of  $G^*$  and  $G'$  are plotted as a function of storage time for the two samples of the asphalt CA-S1 containing 4 percent weight SBS (Polymer D). It is interesting to note that the sample stored at 180°C exhibits a rather significant drop of  $G'$  over the storage period, whereas the sample stored at 120°C shows a much smaller decrease in elasticity. Fragmentation of the SBS copolymer to lower molecular weight species thus results in a reduction of the material's ability to resist permanent deformation. By the same token the complex mod-

ulus of the material at 25°C increases when stored at 180°C. Hence, polymer-modified asphalt stored at an excessively high temperature of 180°C will be more susceptible to fatigue cracking and thermal cracking due to asphalt age hardening (high  $G^*$ ). Best overall property retention is achieved by storing the samples at temperatures not exceeding 120°C and by minimizing the duration of storage.

As previously mentioned, the RTFO is a standard testing technique to approximate what will happen to the material in the hot mix plant. In Table 3 a series of SBS and SEBS modified asphalts was compared to see whether RTFO is a good indicator for polymer stability. In general we find that the RTFO is more severe to the polymer than the "real-world" hot mix plant. In most cases RTFO significantly over-predicted polymer stability. This appears to be independent of the plant type, continuous or batch. In addition, saturated polymers (Polymers F and H) show virtually no change following RTFO, long-term storage, or hot mix plant processing. Thus we conclude that RTFO aging is probably only an indicator if particular polymer/asphalt systems are potentially unstable.

In the case of the SEBS modified asphalt, RTFO aging was more severe than that observed in the loose mix (compare Table 3, CA-S1 4 percent weight Polymer F). The degradation was, however, for SEBS insignificant and led actually to enhanced high temperature properties of the binder as shown in Table 4 (compare CA-S1 4 percent weight Polymer F). It is interesting to note that only one of the six SBS samples showed a decrease in elasticity at 60°C after RTFO. This reduction of  $G'$  is a direct result of polymer fragmentation.

TABLE 4 RHEOLOGICAL PROPERTIES OF BINDERS USED IN STUDY

Asphalt	Polymers	Conditioning	$G^*$ (25°C), @ 1 rad/s	$G^*$ (60°C), @ 1 rad/s	$G'$ (25°C), @ 1 rad/s	$G'$ (60°C), @ 1 rad/s	Repetitive Creep <sup>2</sup> # Cycles to Failure	$T_{cr}$ , °C
TX	3%w A	Original	67,800	250	22,800	120	1900 ± 40	-37.2
		RTFO	213,000	460	88,600	77		-34.1
	6%w A	loose mix	615,000	1,160	250,000	210	1740 ± 85	-33.2
		Original	88,300	1,160	45,100	840		-47.5
		RTFO	294,400	1,930	176,500	1,130		-43.3
		loose mix	123,900	1,060	62,800	525		-39.3
NV06	2.5%w D	Original	82,000	330	20,800	30	2025 ± 240	-39.8
		loose mix	245,200	710	113,800	108		-37.3
	3.8%w D	Original	100,000	670	29,500	365	4480 ± 320	-37.3
		loose mix	317,800	1,170	194,800	730		-37.0
CA-S1	4%w F	Original	114,700	570	24,500	430		-30.7
		RTFO	344,700	920	69,000	515		-25.6
		CATOD	$3.8 \times 10^6$	10,600	600,000	2,880		-23.4
		loose mix	220,000	1,050	54,000	700		-
CA-32 (AR 8000)	-	Original	697,000	420	21,600	~2		-18.3
		RTFO	$1.5 \times 10^6$	1,065	35,000	11		-17.2
		CATOD	$5 \times 10^6$	14,300	$1.3 \times 10^6$	1,590		-13.2
		loose mix	495,000	454	33,200	16		-20.4
CV (AR 4000)	-	Original	266,400	245	6,100	1		-24.1
		RTFO	681,000	495	263,000	3		-23.1
ET-2 (AC-20)	-	Original	266,500	270	28,000	~1		-25
		RTFO	496,000	463	46,800	5		-24.9
VEN-1 (AC-7)	-	Original	34,500	94	15,180	~1		-41
		RTFO						-41.5
VEN-2 (AC-20)	-	Original	84,150	190	27,500	11	200	-34
		RTFO	194,000	571	87,500	40		-
CA-S1 (AR 1000)	-	Original	46,300	75	1,140	~0.01		-30.2
		RTFO	99,200	125	5,070	~0.5		-

<sup>1</sup>Loose mix samples were taken prior to compaction at job site.

<sup>2</sup>Repetitive creep on mix; all other tests on binders.

Asphalt age hardening, on the other hand, generally gives an increase in  $G^*$  (and a decrease of the penetration). In all the loose mix samples in this study no reduction of  $G'$  or  $G^*$  was observed, again indicating that RTFO is more severe than the actual processing.

### Case Histories—Short-Term Aging

#### Texas Highway 287

In spring 1989 the Texas State Department of Highways and Public Transportation, District 25, constructed HMA test sections using various polymer-modified asphalts on HWY 287 near Memphis, Texas. Two test sections were put down containing 3 percent weight and 6 percent weight SBS (Polymer A). The base asphalt was given in Table 1, an AC-10 (TX). However, in the case of the binder containing 6 percent weight polymer, an extender oil was added. Hence, the resulting base asphalt was, according to Table 5 (compare TX 6 percent

weight Polymer A 4°C pen), relatively soft and resembled more an AC-5.

Infrared pyrometer measurements on the 3 percent weight Polymer A section taken on the mat directly behind the paver gave excessively high temperatures,  $\sim 180^\circ\text{C}$ . Normal mat temperatures should be in the neighborhood of  $150^\circ\text{C}$  or lower. The results of the excessively high temperatures can be seen in the material properties. In Table 4 compare the values of both the complex modulus and the storage modulus of the original binder with those of the binder recovered from the loose mix and the more moderate increases due to RTFO. The increase in  $G^*$  at  $25^\circ\text{C}$  is almost an order of magnitude, from 67,800 to 615,000 Pa. This value is actually higher than values typically found for an AC-30 grade asphalt (i.e., the asphalt had dramatically age hardened). As one may expect under these severe conditions the polymer/asphalt blend was largely degraded. No triblock material could be detected by GPC for the blend containing 3 percent weight SBS. For the blend containing 6 percent weight SBS serious stability problems were observed and  $C_{\text{eff}}$  was reduced to 14.8 percent. In

TABLE 5 PROPERTIES OF BINDERS USED IN STUDY  
(CLASSICAL TESTS)

Asphalt	Polymers	Conditioning	Penetration, dmm 100g, 5s @25°C	Penetration, dmm 200g, 60s @4°C	Absolute Viscosity Pa.s @ 60°C	Kinematic Viscosity cm <sup>2</sup> /s @135°C
TX	3%w A	Original	66	21	840	6.6
		RTFO	32	13	910	8.7
		loose mix	35	13	1,600	9.7
	6%w A	Original	90	31	no flow	12
		RTFO	47	24	no flow	12.3
		loose mix	51	25	3,750 @ $0.4\text{s}^{-1}$	12.3
NV06	2.5%w D	Original	64	18	391	8.5
		loose mix	44	19	854	7.5
	3.8%w D	Original	56	18	25,840 @ $0.06\text{s}^{-1}$	12.1
		loose mix	22	9	5,448 @ $0.09\text{s}^{-1}$	3.6
CA-S1 (AR 1000)	—	Original	136	35	55	1.4
		RTFO	95	25	92	1.7
		CATOD	11	—	5,000	—
CA-S2 (AR 8000)	—	Original	29	5	450	3.5
		RTFO	19	4	866	4.6
		CATOD	5	1	14,000	20
		loose mix	37	12	600	4.2
CV (AR 4000)	—	Original	45	13	237	2.8
		RTFO	31	7	441	3.2
ET-2	—	Original	50	14	209	3.4
		RTFO	28	7	443	5.3
CA-S1	4%w F	original	61	17	6,570	11.1
		RTFO	42	14	13,850	14.5
		CATOD	9	3	17,860	41.9
		loose mix	48	16	6,840	16.5
CA-N2* (AR 4000)	—	Original	48	11	172	2.6
		RTFO	32	10	388	3.65
		CATOD	10	—	9,840	13.4
CA-N1*	D	Original	248	114	185	2.7
		RTFO	201	70	212	2.38
		CATOD	40	—	1,000	5.9
	E	Original	126	45	196	—
		RTFO	85	28	344	—
		CATOD	36	—	1,200	—
CA-C2* (AR 2000)	—	Original	75	20	124	1.8
		RTFO	50	11	226	2.6
		CATOD	12	—	3,030	7.7
CA-C1*	E	Original	145	43	143	5.1
		RTFO	103	30	223	6
		CATOD	38	—	910	7.9

<sup>1</sup>Loose mix samples were taken prior to compaction at job site.

\*Data taken from reference 11.



this case RTFO predicted a significantly higher degree of polymer stability (Table 3). However, note that the absolute amount of degradation is nonetheless unusually high in this asphalt. This implies that certain asphalts lead to less stable polymer/asphalt binder systems. Hence, RTFO coupled with GPC and rheology is a good tool in predicting polymer stability.

As indicated in Table 4, the results for repetitive creep are actually slightly higher for the binder system with less polymer. The reason for this is that polymer content has virtually no influence on the performance because of the high degree of degradation in both instances. Moreover, the base asphalt stiffness is in these cases the overriding factor.

On the other hand, premature rutting could have occurred if the polymer degradation had not been accompanied by significant asphalt age hardening. Therefore it is of particular importance to ensure polymer integrity when modifying soft base asphalts with low levels of polymers.

#### *Nevada I-15*

In 1989 the Nevada Department of Transportation (NDOT) placed a series of polymer-modified asphalts on I-15 near Mesquite, Nevada. The department was seeking improvements in resistance to permanent deformation and long-term pavement durability, which are common problems throughout the deserts of the southwestern United States. In these regions the average daily high temperatures of the hottest month exceed 40°C, and pavement temperatures up to 80°C have been measured by NDOT (L. Quilici, personal communication).

The asphalt binder system consisted of a California Valley AR-1000 (soft base; NV06) modified with Polymer D at 2.5 percent weight and 3.8 percent weight SBS. The binders exhibit very high elasticity ( $G'$ ) and resistance to deformation ( $G^*$ ) at high temperatures. In addition, low temperature properties are outstanding. This is reflected in the relatively low values for  $G^*$  at 25°C (soft material is less susceptible to fatigue cracking) and the very low critical cracking temperatures. This best balance of properties results from using a soft base asphalt and sufficient polymer to establish a polymeric network. The effectivity of this network formation is demonstrated by the exceptionally high numbers of loadings until failure in repetitive creep of the HMA (Table 4). Increasing the polymer concentration from 2.5 percent weight to 3.8 percent weight more than doubles the resistance to permanent deformation of the HMA. A more detailed description of how the rheology of these binders influences their performance is given elsewhere (2,14).

#### *Sacramento Mack Road/Stockton Blvd.*

The city of Sacramento was concerned about the severe shoving and rutting at the intersection of Mack Rd. and Stockton Blvd. To evaluate how an SEBS modified asphalt would perform in comparison with a very hard AR-8000 (CA-S2) two pavements were laid down in October 1990.

Virtually no degradation was observed in the original, the RTFO aged residue and in the extracted binder (Table 3). In general saturated polymers are relatively immune from deg-

radation problems. Therefore, plant operating windows can be much wider. Yet, good handling practices are still imperative to avoid the consequences of serious asphalt age hardening.

With regard to the mechanical properties of the binder systems, the polymer-modified asphalt exhibits superior performance at both high and low temperatures (i.e., higher values of both  $G^*$  and  $G'$  at 60°C and lower values at 25°C). The critical cracking temperature of the SEBS modified material is significantly lower than that of the AR 8000. The pavement is still too new to draw any conclusions.

#### **Long-Term Aging**

Following laydown and compaction there has to be concern with the long-term durability of the pavement and how this affects the performance of the HMA. This aging process is exacerbated by the severe desertlike climates that prevail throughout large areas of the southwestern United States.

In the case of straight unmodified asphalts the experience in these areas has been that ACs embrittle within 2 to 4 years. Subsequently the pavements fail because of cracking. In permeable mixes, for example open-graded friction courses or gap-graded mixes, aging may be of concern even in moderate climatic regions. A possible avenue in obtaining long-term aging resistant binder systems is polymer modification. Polymer modification allows the use of soft base asphalts, and, therefore, the bitumen itself will not govern the viscoelastic behavior of the blend. Moreover, the polymeric network is the determining factor. Therefore, polymer stability is of critical concern.

Various attempts have been made to devise laboratory simulations for long-term aging. A detailed evaluation of simulated age hardening of asphalt mixtures has been published by Chollar et al. (17) and Chari et al. (24). Chari reported on the effects of UV and elevated temperatures on the aging rate of a number of straight asphalts. More recently the Strategic Highway Research Program (SHRP) has been evaluating the so-called pressure air vessel (PAV) method (25,26). However, to our knowledge this work has not been extended to include polymer-modified systems. Also further field validation is required.

A simple and straightforward technique to simulate long-term field aging (as it occurs in desert regions) has been developed by Kemp and Predoehl at Caltrans (27). This test uses the standard rolling thin film oven to age the asphalt at a temperature of 111°C for 7 days. The procedure of this so-called California Tilt Oven Durability Test (CATOD) is given in California Test Method 374. Both Kemp and Predoehl (27) and Reese and Predoehl (6) have been successful in correlating field data with CATOD laboratory results. There is insufficient data currently available to determine the general applicability of this test to other climatic regions. At present polymer modified asphalts are being evaluated using this technique.

#### **Polymer Stability**

As in the case of short-term aging polymer integrity is to be considered in long-term aging. Here also we find GPC to be

an excellent tool to track the molecular weight and molecular weight distribution of the block copolymers through time. Two samples were taken from roads that were modified with SBS and are located in Nevada (NV-01) and Wyoming (WY). Both pavements were placed in relatively moderate climates. After 3 to 4 years in service we found effective polymer contents of 80.8 percent and 87.5 percent, respectively (Table 3). Thus, one can expect a continued contribution of the polymer to the binder performance over an extended period of time.

We also studied the stability of SEBS (Polymer F), which because of the saturation of the rubber midblock is expected to give superior long-term performance. Using the previously mentioned CATOD, samples of the binders used in the Sacramento job (CA-S1 with 4 percent weight Polymer F and CA-S2) were aged. Virtually no polymer degradation was found (Table 3). In the case of the straight CA-S2 (AR 8000) we found an extreme increase of the moduli (Tables 4 and 5). This implies that after some years of service, this pavement is expected to embrittle and exhibit fatigue and thermal cracking. After CATOD aging, the modified material is significantly less brittle and therefore should not experience fatigue and thermal cracking (in this climatic region). Where extreme long-term stability is required saturated polymers such as Polymer F give better results.

### Case Histories—Long-Term Aging

In 1987 Caltrans embarked on a program to find improved binders for desertlike conditions (16). Some examples will be discussed.

#### California Interstate 40

For this evaluation Caltrans placed a series of test sections near Needles, California, on I-40. Needles has a typical low desert climate with an average daily high during the hottest month of 41.7°C and an average low during the coldest month of 0°C. As a control, an AR 4000 (CA-N2) was placed (Figure 5). Three polymer-modified sections were placed in the west-bound travel lane, which were separated by control sections. The polymers compared were Polymers D, E, and G. The base asphalt was AR 1000 in each case. However, as shown in Table 5, the low temperature pens indicate that varying amounts of extender oils were used.

To simulate the aging the binders would experience over a period of 4 years in the field the samples were CATOD aged and subsequently rheologically characterized. The results are given in Table 6. On the basis of these results, fatigue cracking would be expected to occur with the binders exhibiting the higher moduli at 25°C. On a relative basis one would therefore predict the following resistance to reflective and fatigue cracking:

$$CA-N1/D \sim CA-N1/E > CA-N1/G \gg CA-N2$$

A measure of the binder's ability to mitigate permanent deformation is  $G^*$  and  $G'$  at 60°C. The largest potential for rutting is directly after placement before the binder has aged hardened. Therefore, it is better to look at the moduli of the unaged material. All materials have a value of  $G^*$  in the range between 200 and 360 Pa. However, the unmodified asphalt CA-N2 has virtually no elasticity ( $G' \sim 2$ ) at 60°C and, hence, should be much more susceptible to permanent deformation. On a relative basis one would therefore predict the following resistance to permanent deformation:

$$CA-N1/G \sim CA-N1/D \sim CA-N1/E \gg CA-N2$$

A summary of the actual field performance is shown in Figure 5. All the control sections are showing reflective and wheel-path cracking. As predicted the controls in the heavily trafficked driving lane are also showing rutting and bleeding (28). All polymer-modified sections have shown excellent resistance to permanent deformation. Only in the CA-N1/G section has reflective cracking been observed. Thermal cracking has not been detected in any of the sections. The field performance confirms the predictions offered on the basis of the rheological findings on the CATOD aged samples.

#### California U.S. Route 395

A cold climate test section was placed on U.S. Rt. 395 at Crestview, approximately 50 mi north of Bishop, California. This test section does not experience the high temperatures that the Needles test sections receive. The average daily high for the hottest month is 32°C, according to Caltrans. The winters are colder with an average low for the coldest month of -15°C.

As a control an AR 2000 (CA-C2) was chosen. The polymer-modified system was AR 1000 (CA-C1) containing Polymer

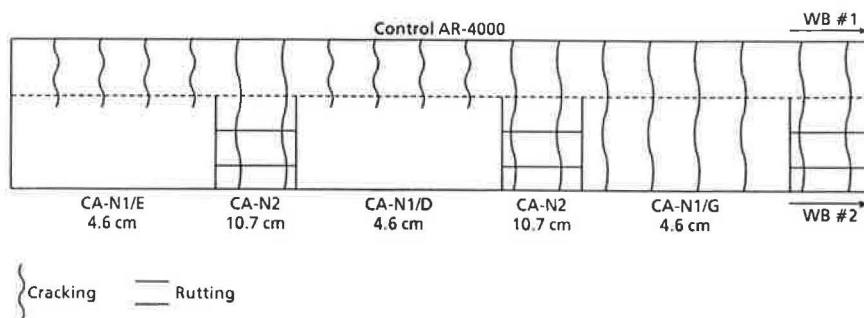


FIGURE 5 Needles test section, I-40 (status April 1991).

TABLE 6 RHEOLOGICAL PROPERTIES OF BINDERS USED IN STUDY FOR LONG-TERM AGING

Asphalt	Polymers	Conditioning	G* (25°C), @ 1 rad/s	G* (60°C), @ 1 rad/s	G' (25°C), @ 1 rad/s	G' (60°C), @ 1 rad/s	T <sub>cr</sub> , °C
CA-N2 (AR 4000)	—	Original	362,000	235	134,000	—2	—24.4
		CATOD	3.6 × 10 <sup>6</sup>	13,900	25 × 10 <sup>6</sup>	2950	—16.5
CA-N1	D	Original	8,300	210	3,260	170	—
		CATOD	530,000	2,180	360,000	610	—34.6
	E	Original	36,200	300	13,900	75	—
		CATOD	570,000	1,600	155,000	300	—37.6
	G	Original	122,700	364	36,900	50	—
		CATOD	960,000	7,180	785,000	2,040	—35.6
CA-C2 (AR 2000)	—	Original	223,400	260	162,000	~1	—29.5
		CATOD	3.6 × 10 <sup>6</sup>	6,350	2.3 × 10 <sup>6</sup>	530	—19.4
CA-C1	E	Original	27,100	180	8,300	22	—36.9
		CATOD	630,000	1,210	300,000	140	—30.9

E. As shown in Table 5, the system contained a significant amount of extender oils, which is reflected in the very high 4°C pen.

Because of the low traffic volume and the fact that it does not experience excessively high pavement temperatures, fatigue and rutting were not expected. However, thermal cracking should occur in the CA-C2 which, according to Table 6, has a critical cracking temperature of  $-19.4^{\circ}\text{C}$  after CATOD aging. The polymer-modified system has a  $T_{cr}$  of  $-30.9^{\circ}\text{C}$  after CATOD aging and, therefore, should not exhibit thermal cracking.

The field observations agree very well with the laboratory findings. The control has already shown thermal cracking after the exceptionally cold winter of 1990–1991. The polymer-modified test section is not showing distress.

## CONCLUSIONS

Both short- and long-term aging can have a significant influence on the performance of HMA. This is true for polymer-modified asphalts as well as for conventional ACs. The latter can undergo significant age hardening during storage, mixing, and in the field. This long-term aging can be dramatic and lead to premature pavement failure. The effects of aging can be exacerbated in the case of permeable pavements or in regions with extreme climatic conditions.

Polymer modification is a viable route in overcoming these potential deficiencies by providing binders with well-balanced property sets. This is generally achieved by modifying soft, compatible asphalts. Improvements are noted in both the binder's resistance to permanent deformation and its ability to mitigate thermal and fatigue cracking. However, unsaturated polymers may exhibit thermal and oxidative instabilities. Thus, it is imperative to avoid prolonged storage and excessive temperatures. This is especially important in hot mix plant operations. GPC and dynamic mechanical analysis are excellent tools in evaluating the stability of polymer (SBS) modified asphalts. Likewise, RTFO can be useful in indicating potentially unstable polymer/asphalt blends. The results presented here indicate that different asphalt chemistries can lead to varying degrees of polymer degradation in the case of unsaturated polymers. In general, we found RTFO aging to be more severe than actual field operations. With regard to long-

term aging Caltrans and our findings appear to support the notion that CATOD is a reasonable simulation for field aging in hot desertlike climates. In more moderate climates we observed less than 20 percent reduction of  $C_{eff}$  even after 3 to 4 years in the field.

Improved thermal and oxidative stability can be achieved by modifying asphalts with saturated polymers. However, good handling practices are still necessary to preclude the consequences of serious asphalt age hardening. GPC, rheological characterization, and field data demonstrate the superior performance of these blends even in severe climates.

## NOMENCLATURE

Symbol	Meaning	Units
A.I.	aging index [ $\eta(\text{RTFO})/\eta(\text{original})$ ]	
AC	asphalt cement	
AR	asphalt residue	
C	concentration	kg/m <sup>3</sup> or %w
CATOD	California tilt oven durability test	
G*	complex dynamic shear modulus	Pa
G'	storage modulus	Pa
G''	loss modulus	Pa
HMA	hot mix asphalt	
M <sub>w</sub>	Weight average mean molecular weight	g/mol
P	pressure	P <sub>a</sub>
PE	polyethylene	
P <sub>0</sub>	static pressure	Pa
RTFO	rolling thin film oven	
SBR	styrene-butadiene rubber random copolymer	
SBS	styrene-butadiene-styrene block copolymer	
SEBS	styrene-ethylene-butylene-styrene block copolymer	
t	time	sec or hr
t <sub>0</sub>	duration of loading	sec
T	temperature	°C
T <sub>cr</sub>	critical cracking temperature	°C
%w	percent weight	
$\eta$	viscosity	Pa



$\omega$	angular velocity	rad/sec
aged	aged polymer	
eff	effective	
HM	high molecular weight species, (SB) <sub>x</sub> , where $x \geq 2$	
LM	low molecular weight species	

## REFERENCES

1. C. P. Valkering, D. J. L. Lancon, E. de Hilster, and D. A. Stoker. *Proc., Association of Asphalt Paving Technologists*, Vol. 59, 1990.
2. M. G. Bouldin and J. H. Collins. Polymer Modified Asphalt Binders. *ASTM STP 1108* (K. R. Wardlaw and S. Shuler, eds.), ASTM, Philadelphia, 1990.
3. D. N. Little. Polymer Modified Asphalt Binders. *ASTM STP 1108* (K. R. Wardlaw and S. Shuler, eds.), ASTM, Philadelphia, Pa., 1990.
4. A. A. Tayebali, J. L. Goodrich, J. B. Sousa, and C. L. Monismith. *Proc., Association of Asphalt Paving Technologists*, Vol. 60, 1991.
5. R. J. Salter and M. Y. O. Al-Shakarchi. *Transportation Research Record 1228*, TRB, National Research Council, Washington, D.C., 1989.
6. R. Reese and N. Predoechl. Caltrans Report 65324-633383. Sacramento, Calif., 1989.
7. L. J. Fleckenstein, K. Mahboub, and D. L. Allen. Polymer Modified Asphalt Binders. *ASTM STP 1108* (K. R. Wardlaw and S. Shuler, eds.), ASTM, Philadelphia, Pa., 1990.
8. J. H. Collins, M. G. Bouldin, R. Gelles, and A. Berker. *Proc., Association of Asphalt Paving Technologists*, Vol. 60, 1991.
9. J. L. Goodrich. *Proc., Association of Asphalt Paving Technologists*, Vol. 60, 1991.
10. M. G. Bouldin, J. H. Collins and A. Berker. Rheology and Microstructure of Polymer/Asphalt Blends. *Rubber Chem. Tech.*, Vol. 64, No. 4, 1991.
11. D. C. Portfolio and F. A. Fensel. *Proc., 3rd International Symposium Roofing Techn.*, Montreal, Canada, 1991.
12. J. H. Hills. *Inst. Petr. Tech.* 74-014, 1974.
13. J. B. Sousa, J. Craus, and C. L. Monismith. SHRP-A/IR-91-104. Washington, D.C., 1991.
14. M. G. Bouldin. *Shell Development Company Technical Bulletin*. Houston, Tex., 1991.
15. J. C. Petersen. In *Transportation Research Record 999*, TRB, National Research Council, Washington, D.C., 1984.
16. A. S. Noureldin and L. E. Wood. In *Transportation Record 1228*, TRB, National Research Council, Washington, D.C., 1989.
17. B. H. Chollar, J. A. Zenawitz, J. G. Boone, K. T. Tran, and D. T. Anderson. In *Transportation Research Record 1228*, TRB, National Research Council, Washington, D.C., 1989.
18. J. A. S. Pribanic, M. Emmelin and G. N. King. In *Transportation Research Record 1228*, TRB, National Research Council, Washington, D.C., 1989.
19. F. N. Hveem, E. Zube, and J. Skog. *Proc., Association of Asphalt Paving Technologists*, Vol. 32, 1963.
20. J. D. Ferry. *Viscoelastic Properties of Polymers* (third edition). John Wiley & Sons, New York, 1980.
21. S. C. S. R. Tangella, J. Craus, J. A. Deacon, and C. L. Monismith. SHRP-A/IR-90-011. Washington, D.C., 1990.
22. J. B. Sousa, G. Rowe, and A. A. Tayebali. (Submitted for publication.)
23. W. van Dyke and W. Visser. *Proc., Association of Asphalt Paving Technologists*, Vol. 46, 1977, pp. 1-40.
24. C. T. Chari, B. E. Ruth, M. Tia, and G. C. Page. *Proc., Association of Asphalt Paving Technologists*, Vol. 59, 1990, pp. 176-239.
25. C. J. Glover, R. R. Davison, S. M. Ghoreishi, H. B. Jemison, and J. A. Bullin. In *Transportation Research Record 1228*, TRB, National Research Council, Washington, D.C., 1989.
26. C. A. Bell. SHRP-A/IR-89-004. Washington, D.C., 1989.
27. G. R. Kemp and N. H. Predoechl. *Proc., Association of Asphalt Paving Technologists*, Vol. 50, 1981.
28. M. G. Bouldin and M. A. Berggren. *Shell Development Company Technical Bulletin*. Houston, Tex., 1991.

Publication of this paper sponsored by Committee on Characteristics of Bituminous Materials.