

Effect of Microwave Energy on the Properties of Asphalt and Its Use as an Aging Tool

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Microwave energy causes changes in asphalt properties. Unsymmetric organic molecules with dipoles, that is, with a permanent separation of positive and negative charges, undergo excitational rotation when they are subjected to microwave radiation. The excitational rotation depends on the material's dielectric constant. Because the radiation frequency is relatively high and the dielectric constant of asphalt is low, asphalt molecules cannot rotate as fast as the applied electromagnetic field, and an out-of-phase component of the dielectric constant, called dielectric loss, is dissipated as heat. Treatment of asphalt for a short time with low-power microwave radiation decreases the dispersivity (D) and molecular size index (MSI) values obtained by high-performance size exclusion chromatography (HPSEC). Alternately, exposure for a longer time to a higher-power radiation increased both the D and MSI values for 12 asphalts studied. Microwave conditions (power level, treatment time, sample weight, and sample container material) were tailored to simulate the effects obtained after rolling thin film oven-pressure aging vessel (RTFO-PAV) aging of 18 asphalts. HPSEC gave comparable results for the two aging techniques: RTFO-PAV aging versus microwave aging. The difference in MSI amounted to ± 7.3 and ± 4.2 percent by using gravimetry and ultraviolet detection at 345 nm, respectively. The bending beam rheometer showed that microwave energy underestimates aging by a maximum of about 3°C in the limiting low temperature. Accelerated aging by microwave radiation is very simple and consumes less than 3 hr.

The electromagnetic radiation spectrum covers a wide wavelength range starting with cosmic rays and followed by γ -ray, X-ray, ultraviolet (UV), visible, infrared (IR), microwave, and then radio-frequency radiations. Cosmic rays have a very short wavelength (1.00×10^{-12} m), whereas radio waves have wavelengths greater than 1.00 m. The microwave region extends from 3.00×10^{-4} to 1.00 m. Electromagnetic radiation is described in terms of both particles and waves (I). The following equations relate the energy (E) of a particle along the electromagnetic spectrum to the velocity of light (c), frequency (ν), and wavelength λ ; h is Planck's constant (6.626×10^{-34} J·sec):

$$E = h\nu \quad (1)$$

$$\nu = c/\lambda \quad (2)$$

$$E = hc/\lambda \quad (3)$$

Equation 3 indicates that λ is inversely proportional to E . Thus, across the spectrum λ increases and E decreases. Cosmic rays and γ -radiation have high penetrating powers; γ -radiation causes exci-

tation at the nuclear level. X-rays excite inner electrons. Spectrophotometric techniques of chemical analysis make use of the energy of UV, visible, and IR radiation. Usually, the analyte is subjected to a sweep of the wavelength region of interest (UV, visible, or IR), and the difference in radiation energy is measured. UV radiation excites the outermost (valency) electrons of an atom from one energy level to a higher one. IR radiation, with its lower particle energy, can only cause molecular vibrational-rotational excitations within the same electronic state. Microwaves lead to the rotational excitation of molecules. In the rotationally excited state molecules rotate faster than they do in the ground state.

Most organic molecules have structural unsymmetry and, accordingly, possess a dipole moment as a result of the permanent separation of the positive and negative charges within the molecule. A simplified model entails an electric dipole that is contained in a spherical molecule, that is free to rotate into alignment with an applied electromagnetic field, and that is subject to the viscous drag of the surrounding medium and to collisions with other molecules (2).

At very low frequencies dipoles (molecules) are able to rotate in phase with the applied field. At higher frequencies restraints on dipole rotation become more significant and molecules are no longer able to follow the rapid oscillations of the applied field. This gives rise to an out-of-phase component of the dielectric constant representing a dielectric loss (ϵ'') (that is, a dissipation of energy as heat). Thus, the dielectric constant (ϵ') of material is related to the energy stored as electric energy (excites molecular rotations); the dielectric loss (ϵ'') is related to the energy dissipated as heat energy (heats the material). The dissipation factor or loss tangent, $\tan \delta$, is equal to ϵ''/ϵ' (3). At 25°C and a microwave radiation frequency of 3000 MHz, an asphalt cement has an ϵ' of 2.5 and a $\tan \delta$ of 1.10×10^{-3} ; under the same conditions water has an ϵ' of 76.7 and a $\tan \delta$ of 1.57×10^{-1} (3,4). Therefore, the ϵ'' for asphalt is 2.75×10^{-3} , whereas that for water is 1.20×10 . Not surprisingly, water heats more quickly than asphalt when it is subjected to microwaves. Low values of ϵ' and $\tan \delta$ for asphalt may explain the lack of studies on the effect of microwave energy on asphalt (in the absence of aggregates).

MICROWAVE ENERGY AND SHRP MODEL OF ASPHALT

The Strategic Highway Research Program (SHRP) version of a chemical model of asphalt depicts a mixture of polar materials dispersed in nonpolar materials, with polar materials forming continu-

ous, three-dimensional networks or a microstructure (5). The close proximity of polar materials allows the formation of hydrogen bonds, in which the hydrogen atom (positive end) of one molecule bonds with an oxygen or a nitrogen atom (negative end) of the same or another molecule. Other secondary bonds or intermolecular forces, for example, pi-pi bonding, dipole forces, and Van der Waals forces, are also present and, together with hydrogen bonding, determine many of the properties of asphalt. Intermolecular forces are weak and are easy to break by heat or stress; they have a low dissociation energy of 8 to 40 kJ/mol, depending on the polarizabilities and the dipole moments of the bonding molecules (6).

The SHRP chemical model of asphalt considers the breaking and reformation of weak, secondary bonds or forces between polar molecules to be responsible for many changes in the characteristics of asphalt. Because the in-phase component ϵ' can excite molecular rotations, whereas the out-of-phase component ϵ'' provides heat, microwave energy causes changes in asphalt. Once the microwave source is permanently removed, intermolecular forces again come into play, leading to different associations of molecules and, accordingly, a change in properties.

MICROWAVE CONDITIONS AND PROPERTY CHANGES

To study the effect of microwave energy on asphalt, the first stages of this work used semipreparative high-performance size exclusion chromatography (HPSEC) or high-performance gel permeation chromatography (HPGPC). Property changes were followed by measuring the molecular size index (MSI) (7-9), where

$$\text{MSI} = \text{percent first fraction} / \text{percent second fraction} \quad (4)$$

As it is known, larger molecular associations elute first from the chromatographic column followed progressively by smaller entities.

Another variable used to measure property changes was the dispersivity (D), weight average molecular weight/number average

molecular weight (\bar{M}_w/\bar{M}_n), which is a measure of the breadth of molecular weight distribution curve (6).

MICROWAVE ENERGY AND AGING

The type and magnitude of changes in MSI due to long-term exposure to a high power level of radiation are similar to the changes observed after aging: an increase in the population of larger associations (first fraction) and a decrease in the population of smaller entities (second fraction). To test the feasibility of using microwave radiation as an aging tool, 18 tank asphalts used in Kansas were selected. Each asphalt was laboratory aged by two different techniques: (a) SHRP long-term aging [rolling thin film oven and pressure aging vessel (RTFO-PAV)] and (b) microwave oven.

Comparison between the two aging techniques was studied by (a) HPSEC with a gravimetric (9) and a UV spectrophotometric finish and with a (b) bending beam rheometer (BBR), the only SHRP binder testing equipment available at this time.

Microwave aging is simple and rapid compared with RTFO-PAV aging. It requires treatment for less than 3 hr in a household microwave oven; a quartz petri dish serves as the sample container. Aging by the RTFO-PAV technique requires more operator effort, a much longer time, more equipment with accessories that are susceptible to failure, larger volumes of cleaning solvents, and hazards associated with a 2.1-MPa pressure.

EXPERIMENTAL DETAILS

Aging

1. A household microwave oven (Tappan) with an output power of 1000 W, a turntable, and a 0.037-m³ capacity was used. Power can be adjusted from high power (HP) to 10, 20, . . . , 90 percent of HP. A quartz petri dish (100 × 10 mm) served as a container for the 16-g sample. This yields a 1.5-mm-thick film of asphalt. Figure 1

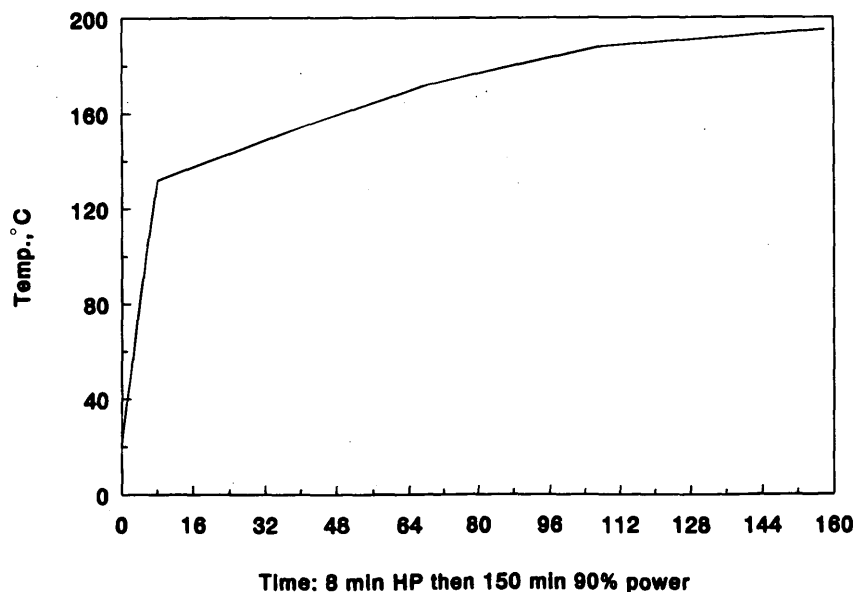


FIGURE 1 Variation of temperature with time.

shows the increase in the temperature inside the oven with treatment time and power level of radiation. A fluoroptic thermometer (Model 790 from Luxtron) was used to measure temperature.

Initial experiments used a 750-W oven with adjustable power, a turntable, and a 50-mL glass beaker as a sample container; 1.5 g of asphalt was spread over the sides and bottom of the beaker before treatment.

Sampling of 1.5- or 16-g samples was done after annealing tank asphalt for 1.5 hr at 160°C in a convection oven.

2. RTFO-PAV aging was conducted according to AASHTO T240-87; this was followed by Standard Practice for Accelerated Aging of Asphalt Binder Using a Pressurized Aging Vessel (PAV) (AASHTO PPI, Edition 1A).

Sampling was done after annealing the tank asphalt in a convection oven for 1 hr at 150°C.

Testing

1. A BBR applied test system was used. Methanol was used to fill the cooling chamber. Testing was carried out by following the Standard Test Method for Determining the Flexural Creep Stiffness of Asphalt Binder Using the BBR (AASHTO TP1, Edition 1A).

Aged material (material aged by the microwave or the RTFO-PAV technique) was allowed to cool overnight. Annealing for 1 hr at 150°C in a convection oven preceded molding. A similar annealing process, that is, 1 hr at 150°C, preceded sampling for HPSEC measurements.

2. In previous work (9) a procedure was developed to address the problems associated with the column source because HPSEC data change with every new column, even though the columns would have identical characteristics, that is, packing and dimensions. A similar procedure was used in the present work. The procedure relied on the retention time of polystyrene standards to designate fraction cut-off points, a modification that eliminated variation in HPSEC data upon replacement of a column by an identical one.

In the present work a Waters HPSEC system was used. A Shodex 6- μ m, 500- Å , KF-2002.5 semipreparative column (300 \times 20 mm) was used. A Waters R401 differential refractive index detector was used to analyze polystyrene standards. A liquid chromatography spectrophotometer (Lambda Max Model 481 from Waters) was used to analyze asphalts by UV detection at 345 nm.

- a. Analysis of standards. A set of six polystyrene standards and acetone were analyzed by using a mobile phase of 97% toluene and 3% pyridine flowing at 3.5 mL/min. The column was maintained at 70°C.
- b. Selection of cutoff points. For the analysis of asphalt cement collection of the first fraction starts at a retention time (t_R) of 7.70 min from injection. The midpoint between the t_R of standard A-2500 and that of standard A-1000 served as the cutoff point for collection of the first fraction. The cutoff point for collection of the second fraction was 21.00 min from injection.
- c. Analysis of asphalt cement. An asphalt sample in a 50-mL beaker was weighed accurately (to within 0.1 mg) in the range of 1.5 ± 0.1 g. Asphalt was spread on the sides and bottom of the beaker. About 20 mL of toluene was added, and the mixture was heated on a hot plate set at the lowest possible setting (approximately 50 to 60°C).

Dissolution takes 10 to 15 min. The contents were transferred quantitatively to a 50-mL volumetric flask, and the volume was completed with toluene. An aliquot was filtered through a 0.45- μ m-pore-size membrane.

An aliquot of 150 μ L asphalt sample solution (about 4.5 mg of asphalt) was injected in the HPSEC system. The mobile phase, flow rate, and column temperature are the same as described for the analysis of standards. The asphalt material was eluted into two, accurately weighed (to within 2 μ g) glass petri dishes (60 \times 15 mm). The petri dishes containing the two fractions were set on a hot plate maintained at 50 to 60°C. After the mobile-phase solvents evaporated, the petri dishes were heated in a convection oven for 90 min at 160°C. The petri dishes were then cooled in a desiccator to a constant weight.

A Mettler AT 20 microbalance (sensitivity of 2 μ g and capacity of 22 g) was used to weigh the glass petri dishes.

HPSEC analysis was also followed spectrophotometrically at 345 nm. The area under the chromatogram was divided at the same cutoff point used for the gravimetric finish to designate the first and second fractions.

RESULTS AND DISCUSSION OF RESULTS

HPSEC to Study Asphalt

The SHRP chemical model of asphalt emphasizes the significance of weak, secondary bonds between molecules, including dipole forces between polar sites of constituent molecules to form molecular associations. HPSEC separates constituent associations according to their effective size or, more precisely, hydrodynamic volume (V_h):

$$V_h \rightarrow M_n/N \quad \text{dL/molecule} \quad (5)$$

where

$$\begin{aligned} M &= \text{molecular weight (g/mol),} \\ n &= \text{intrinsic viscosity, (dL/g), and} \\ N &= \text{Avogadro's number (molecule/mol).} \end{aligned}$$

Previous work (8), in which HPSEC was used, has reported a perfect correlation between MSI of Corbett's fractions and polarity for 20 asphalts. For any given asphalt MSI increased progressively from the nonpolar (saturates) on the one end to the highly polar (asphaltenes) at the other end. Thus, for asphalt, the V_h of molecular entities is perfectly related to polarity; highly polar materials have high MSI values because the constituent entities are mainly made up of polar molecules leading to a predominance of larger entities with high V_h . In view of the significance of polarity in the behavior of asphalt, the use of HPSEC to study asphalts is well justified.

Toluene has been used as a mobile phase (carrier) for asphalt analysis by HPSEC because it is believed to have a solubility parameter similar to that of asphalt solvent phases (5,10,11). Furthermore, compared with other asphalt solvents, toluene has the lowest dielectric constant (2.38) and therefore causes the least disturbance to molecular associations. To avoid dissociation asphalt solutions were chromatographed rapidly (within 0 to 20 min from the time of dissolution). Inclusion of 3 percent pyridine in the mobile phase prevents the loss of some of the asphalt polar

material through adsorption on the stationary phase (column packing).

Table 1 gives the MSIs for a set of 12 tank asphalts selected randomly from those used by the Kansas Department of Transportation. It is noteworthy that the MSIs for the asphalts studied ranged between 0.26 and 0.44. This range agrees quite favorably with that of 0.15 to 0.44 obtained by Branthaver et al. (12) for the eight SHRP core asphalts, on a preparative scale, using fluorescence to 350-nm radiation to designate the cutoff points of Fractions I and II. Although the two studies used different approaches for the fractionation of yet unrelated sets of asphalts, the two MSI ranges are remarkably close.

Effect of Microwave Energy on Asphalt

Exposure of 1.5 g of asphalt to different levels of power (p) of microwave radiation for different time intervals (t) caused changes in both MSI (obtained gravimetrically) and D (obtained by using UV detection at 345 nm). A short t and a low p decreased both MSI and D (Table 2, series a to d). Alternately, a rather long t and a higher p increased both MSI and D (Table 2, series e). The two extreme conditions of microwave exposure time and power level were then applied to the whole set (Table 3).

Short-Term, Low-Power Treatment

A previous investigation (9) of the HPSEC procedure similar to the present one reported a precision of 0.02 for the MSIs of 18 asphalts.

Table 3 shows that short-term exposure to low-power radiation decreased the MSIs of five asphalts; D generally decreased for the whole set except for Sample 4729, which showed a slight increase in D . Few unsuccessful trials were performed to further decrease MSI and D .

The decrease in D is illustrated in Figure 2, in which streamlining of molecular species occurs; the very large associations as well as the rather small entities diminish (D decreased from 4.011 to 3.504; Table 3). Streamlining may be viewed as follows. The applied microwave radiation creates an in-phase component that causes the rotational excitation of molecules and an out-of-phase component that represents the portion dissipated as heat. Both components break up some intermolecular forces, leading to a relative decrease in the population with larger associations. However, there seems to be enough energy (electric and heat) for the opposite process, that is, the formation of associations through activation of rather small molecules, to also take place. The breakup of larger associations, however, predominates, as evidenced by a decrease in MSI from 0.35 to 0.32 (Table 3) and from the data in Figure 2.

Usually, the magnitude of change in D of an asphalt paralleled that for MSI. However, Samples 4190 and 4506 showed practically the same MSIs after microwave treatment, even though D suffered an obvious decrease in value. Apparently, the breakup of some large associations may have taken place at about the same rate as the formation of new associations, with no net effect on the ratio between the two HPSEC fractions.

Streamlining of molecular entities (decrease in D) occurred for all asphalts studied except for Sample 4729. The anomalous behav-

TABLE 1 MSI of Set of Tank Asphalts Using a Gravimetric Finish

Sample #	Molecular Size Index, MSI	Change in Wt, %*
2110	0.34	-3.7
3087	0.28	-2.6
3385	0.35	-6.1
3418	0.32	-7.5
3455	0.28	-7.6
3488	0.35	-6.5
3829	0.34	-9.8
4190	0.26	-7.9
4506	0.26	-7.4
4653	0.31	+1.8
4729	0.44	+0.2
4897	0.35	-2.1

Average change in Wt., % = ± 5.3

* $\frac{\text{Wt of Fractions Collected, mg} - \text{Sample Wt Injected, mg}}{\text{Sample Wt Injected, mg}} \times 100$

TABLE 2 Effect of Exposure Time t to Microwave Radiation of Power p on Tank Asphalt 4897

Series	Microwave Conditions t and p	Temp., °C*	MSI	D
a	3 min HP**; 45 min 20% p	55	0.32	3.504
b	3 min HP; 90 min 20% p	60	0.32	3.515
c	10 min HP; 15 min 60% p	125	0.32	3.675
d	10 min HP; 45 min 60% p	145	0.34	3.686
e	10 min HP; 90 min 60% p	155	0.41	4.581

[MSI = 0.35, and D = 4.011 (at 345 nm)]

* Air temperature at center of a 750-W microwave oven at the end of treatment.

** HP = High power or 100% power.

ior may be attributed to this asphalt's exceptionally high MSI (0.44) compared with those of the other asphalts studied. An asphalt with a high ratio of large associations relative to the smaller entities should encompass an abundance of a polar, three-dimensional network (5) that, on exposure to microwave radiation, causes the dielectric relaxation time τ to decrease, thus bringing $1/\tau$ closer in

value to the angular frequency $2\pi f$ (maximum ϵ'' is attained when $1/\tau = 2\pi f$) (13). A higher ϵ'' causes Sample 4729 to heat more quickly than the rest of the samples over the short exposure time used, leading to an effect similar to that observed with other asphalts only after high-power long-term treatment, that is, an increase in D (Table 3).

TABLE 3 Effect of t and p on Tank Asphalts

Sample	Tank		3 Min HP; 45 min 20% p*		10 min HP; 90 min 60% p**	
	MSI	D	MSI	D	MSI	D
2110	0.34	3.785	0.33	3.612	0.41	4.615
3087	0.26	3.953	0.24	3.733	0.33	4.695
3385	0.35	3.500	0.33	3.464	0.43	4.463
3418	0.32	4.727	0.32	4.680	0.39	6.209
3455	0.28	4.287	0.24	3.895	0.32	4.856
3488	0.35	3.525	0.32	3.439	0.43	4.299
3829	0.34	4.448	0.33	4.324	0.36	5.225
4190	0.26	4.401	0.25	4.066	0.30	5.752
4506	0.26	4.184	0.25	3.940	0.30	5.255
4653	0.31	3.743	0.28	3.468	0.34	4.444
4729	0.44	3.825	0.43	4.100	0.49	4.895
4897	0.35	4.011	0.32	3.504	0.41	4.581

* Short-term, low-power radiation treatment; air temperature at center of a 750-W microwave oven at end of treatment was 55°C.

** Long-term, higher-power radiation treatment; air temperature at center of a 750-W microwave oven at end of treatment was 155°C.

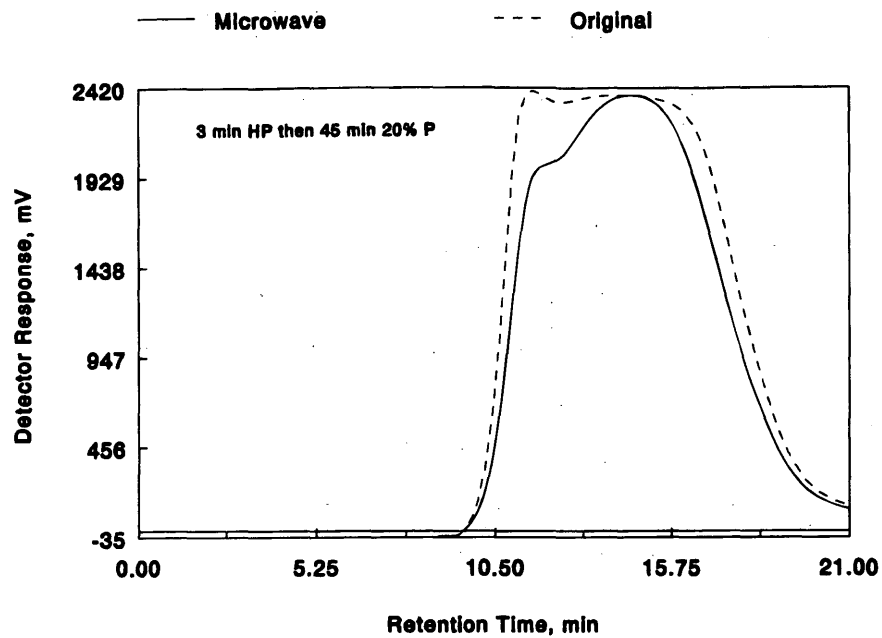


FIGURE 2 Comparison of Sample 4897 tank asphalt before and after microwave treatment.

Long-Term, High-Power Treatment

Table 3 shows that microwave energy increases the MSI and D values for asphalt cement. In contrast to short-term low-power treatment, all 12 asphalts showed increases in the values of both variables.

Microwave Energy for Laboratory Aging

Because microwave radiation increased the MSIs of a whole set of asphalts, its use is suggested for aging. To test its efficiency the effect of microwave radiation on asphalt was compared with that obtained by the SHRP long-term aging technique. A comparison of the two aging techniques, that is, the microwave versus the RTFO-PAV aging techniques, was carried out by two approaches:

(a) HPSEC (gravimetry and UV absorption), and (b) BBR. In this way an asphalt's physicochemical and physical properties are independently tested.

The aforementioned experiments used 1.5 g of asphalt for HPSEC analysis. The BBR, however, requires >12 g of sample. The data in Table 4 reveal that the preselected microwave conditions of t and p are ineffective for larger samples; MSI and D values for microwave-aged asphalt were practically indifferent from those for tank asphalt.

Experimentation with pouring of the microwave-treated asphalt from a petri dish to fill an aluminum mold for BBR testing showed that 16 g of sample was required. To cause a change in asphalt properties the following was carried out. The microwave conditions (t and p) were intensified, and a quartz petri dish was used as a sample container. Quartz is highly transparent to microwave radiation (tan $\delta = 6 \times 10^{-5}$) (13) and allows most microwave energy to affect

TABLE 4 Effect of Asphalt Sample Weight on Effectiveness of Microwave Energy

Sample	Microwave-Aged Asphalt*				Tank Asphalt	
	Sample Wt=1.5 g		Sample Wt=12 g		Sample Wt=1.5 g	
	MSI	D	MSI	D	MSI	D
2110	0.41	4.615	0.33	3.635	0.34	3.785
3418	0.39	6.209	0.31	5.057	0.32	4.727
3488	0.43	4.299	0.35	3.454	0.35	3.525

* Treated in a 750-W microwave oven for 10 min at HP then 90 min 60% p (as in Table 3).

the asphalt instead of being partially absorbed by Pyrex glass containers.

Modification of Microwave Conditions

To select the optimum microwave treatment conditions, a reference point was established. An asphalt sample was aged by the RTFO-PAV procedure and was then tested on a BBR to determine the lowest test temperature that satisfies SHRP requirements of a maximum stiffness (S) of 300 MPa and a minimum slope (m) of 0.300. Table 5 shows that a proper selection of t and p leads to an aging effect similar to that of the RTFO-PAV aging technique. Target values were practically achieved after exposure for 8 min at HP and then for 150 min at 90 percent p . These same settings were used to age a set of tank asphalts.

Comparing the Two Aging Techniques Using BBR

A set of 18 asphalts was randomly selected. Because these were viscosity-graded (AC-10 and AC-20) experimentation was necessary to determine the lowest test temperature for each asphalt that satisfied the requirements for S and m . Therefore, tank asphalt was aged by the RTFO-PAV technique. Aged material was tested on the BBR at different temperatures to determine S and m values at the limiting temperature. A 16-g sample of tank asphalt was then treated in a microwave oven for 8 min at HP and then for 150 min at 90 percent p and was tested on the BBR at the same limiting temperature. A comparison of the S and m values obtained by the two aging techniques is given in Table 6. For the set of asphalts the average difference was -16.0 percent for S and +13.6 percent for m ; the calculation was based on values obtained by the RTFO-PAV aging technique as a reference.

Microwave aging marginally underestimated the aging effect. The difference in S and m values for individual samples obtained by the two aging techniques was approximately equivalent to 1°C to 3°C, depending on the asphalt material; that is, a given asphalt passing the BBR test at -12°C after RTFO-PAV aging would pass at a temperature of 1°C to 3°C lower (-13°C to -15°C) if it was aged with microwave energy.

Trials to minimize the difference between the two aging techniques were unsuccessful. Increasing t for Samples 3418 and 4190 caused "skimming"; after cooling and annealing for 1 hr, it was practically impossible to pour the samples into a mold. On the other hand small changes in t and p did not prove to be detrimental to S and m . Table 7 shows the minor variations in S and m after microwave aging at alternative settings. The results have standard deviations of 3.0 and 0.009 and coefficients of variation of 2.6 and 2.5 percent for S and m , respectively.

As mentioned earlier, microwave action depends on the material's electrical properties. Ferry (14) reported, "The complex dielectric constant bears certain formal analogies to the complex compliance, and the frequency dependence of its real and imaginary components is determined for some polymers by molecular motions similar to those which determine the rate of response to mechanical stresses."

Comparison of the Two Aging Techniques Using HPSEC

Asphalt material aged by each technique was analyzed by HPSEC, and the MSI was determined gravimetrically and spectrophotometrically at 345 nm (Table 8). Although UV detection has its own shortcomings (15-17), it was used in the present study only to compare the effects of the two aging techniques run on the same asphalt samples rather than to compare asphalts with each other.

TABLE 5 Effect of t and p of Microwave Radiation on S and m of Sample 3829 at test temperature of -14°C (target values, $S = 139$ MPa and $m = 0.305$, obtained after RTFO-PAV aging)

Microwave Conditions*	S (MPa)	m
8 min HP; 90 min 90% p	87	0.356
8 min HP; 145 min 90% p	124	0.314
8 min HP; 150 min 90% p	132	0.309
8 min HP; 160 min 90% p	144	0.310
8 min HP; 170 min 90% p	161	0.299
8 min HP; 180 min 70% p	156	0.293
9 min HP; 150 min 90% p	125	0.311
10 min HP; 150 min 90% p	135	0.327
160 min HP	133	0.313
170 min HP	134	0.321

* A 1000-W microwave oven was used.

TABLE 6 Comparison of the Two Aging Techniques by BBR Testing at Limiting Temperature

Sample	Test Temp., °C	'RTFO + PAV'		Microwave Energy*		Difference, %**	
		S, MPa	m	S, MPa	m	S	m
3829	-14	139	0.305	132	0.309	-5.0	+1.3
3087	-12	158	0.308	136	0.316	-13.9	+2.6
3385	-13	199	0.308	177	0.371	-11.1	+20.4
3488	-12	105	0.308	90	0.350	-14.3	+13.6
4190	-12	144	0.305	118	0.333	-18.1	+9.2
4506	-12	173	0.300	149	0.324	-13.9	+8.4
4653	-16	183	0.300	145	0.353	-20.8	+18.1
4162	-12	150	0.309	116	0.358	-22.7	+15.9
4163	-12	135	0.309	107	0.361	-20.7	+16.8
3590 ^t	-12	156	0.311	121	0.362	-22.4	+16.4
4376 ^t	-12	147	0.300	130	0.315	-11.6	+5.4
4897 ^t	-10	125	0.309	98	0.365	-21.6	+18.1
4377 ^t	-10	112	0.301	101	0.361	-9.8	+19.9
3418 ^t	-11	170	0.300	130	0.349	-23.5	+16.7
4729 ^t	-11	136	0.309	112	0.349	-17.6	+12.9
3587	-13	155	0.303	125	0.350	-19.4	+15.5
3455	-17	221	0.302	200	0.359	-9.5	+18.9
2110 ^t	-12	223	0.305	197	0.350	-11.7	+14.8

* Treatment for 8 min HP then 150 min 90% p.

** The 'RTFO + PAV' is considered the reference value.

^t AC-20; the rest are AC-10.

TABLE 7 Effect of Small Changes in Microwave Conditions on BBR Results for Asphalt 4162 at -12°C

Microwave Conditions*	S, MPa	m
8 min HP; 150 min 90% p**	116	0.358
8 min HP; 170 min 70% p	116	0.356
8 min HP; 160 min 80% p	109	0.371
8 min HP; 160 min 70% p	111	0.360
8 min HP; 200 min 70% p	113	0.344
8 min HP; 200 min 60% p	116	0.362

* A 1000-W microwave oven was used.

** Conditions already applied to age the whole set of asphalts, and to generate data in Table 6.

The data in Table 8 indicate that the two aging techniques give comparable MSIs, in which the microwave energy overestimated aging for approximately half of the set and underestimated aging for the other half. This observation applies to the two finishes used. For the 18 asphalts, the average differences in MSIs between the two aging procedures amounted to ± 7.3 and ± 4.2 percent for the gravimetric and UV detection methods, respectively. The chromatogram obtained after microwave aging was identical to that obtained after RTFO-PAV aging, and as expected, both chromatograms were distinct from that of the tank asphalt (Figures 3 and 4). The HPSEC data and Figures 3 and 4 indicate that microwave energy induces molecular interactions that resemble, in type and magnitude, those taking place by the RTFO-PAV aging technique.

Because microwave radiation creates a molecular rotational-excitation component in addition to a heat component, the two components might account for the short period of time required for microwave energy to induce such molecular changes that otherwise take longer if aging is done by conductive heating (RTFO-PAV technique).

Applications of Microwave Energy

Besides its potential as an alternate tool for laboratory aging, microwave radiation can be used to cause changes in the physicochemical and physical properties of asphalt. Table 9 shows that controlling t and p can decrease or increase the MSI and D values of tank asphalt; the most microwave-resistant asphalt exhibited a 40 percent difference between extreme values of MSI.

CONCLUSION

Treatment with microwave energy causes changes in the physical and physicochemical properties of asphalt. Time of treatment, power level of radiation, amount of asphalt used, and sample container material affect the type and the magnitude of change.

With a small amount (1.5 g) of asphalt, exposure for a short period of time to a low power level of radiation decreased the MSI and D values for about half of the 12 asphalts studied. Alternately,

TABLE 8 Comparison of the Two Aging Techniques by HPSEC with Gravimetric and UV Absorption Finishes To Determine MSI

Sample	'RTFO + PAV'		Microwave Energy*		Difference, %**	
	Grav.	UV	Grav.	UV	Grav.	UV
3829	0.42	1.84	0.47	2.01	+11.9	+9.2
3087	0.46	1.86	0.53	2.12	+15.2	+14.0
3385	0.49	1.72	0.48	1.65	-2.0	-4.1
3488	0.52	2.22	0.54	2.27	+3.8	+2.3
4190	0.42	1.71	0.38	1.78	-9.5	+4.1
4506	0.37	1.49	0.38	1.49	+2.7	0.0
4653	0.40	1.88	0.43	1.81	+7.5	-3.7
4162	0.39	1.75	0.35	1.70	-10.3	-2.9
4163	0.44	2.07	0.48	2.04	+9.1	-1.4
3590	0.63	2.38	0.57	2.25	-9.5	-5.5
4376	0.49	1.86	0.51	1.98	+4.4	+6.5
4897	0.51	1.93	0.47	1.90	-7.8	-1.6
4377	0.54	2.17	0.55	2.11	+1.9	-2.8
3418	0.52	1.97	0.46	1.87	-11.5	-5.1
4729	0.60	2.42	0.59	2.41	-1.7	-0.4
3587	0.50	2.14	0.48	2.10	-4.0	-1.9
3455	0.42	1.64	0.37	1.49	-11.9	-9.1
2110	0.50	1.88	0.53	1.87	+6.0	-0.5

* Treatment as in Table 6 (8 min HP then 150 min 90% p).

** The 'RTFO + PAV' aging is considered the reference value.

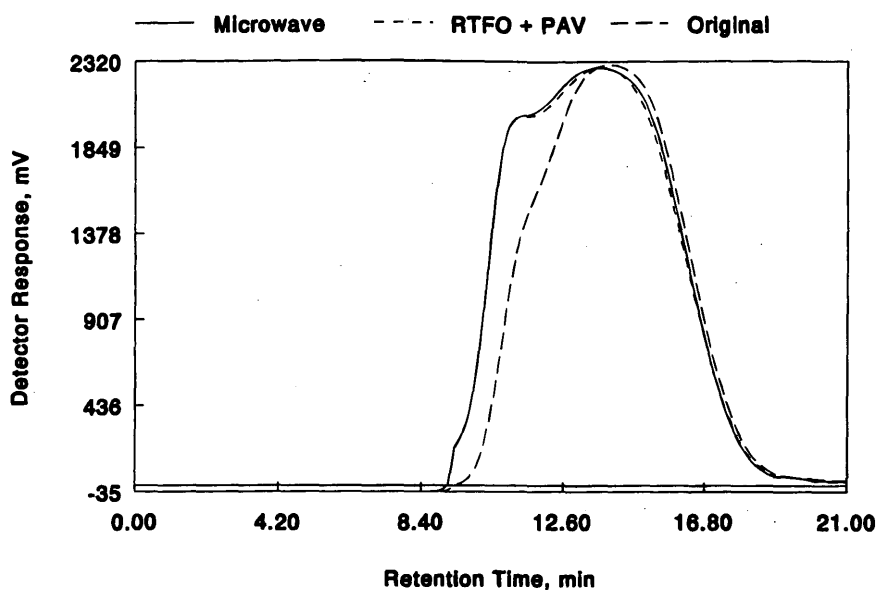


FIGURE 3 Chromatograms for microwave energy-aged asphalt, RTFO-PAV-aged asphalt, and tank asphalt (Sample 2110).

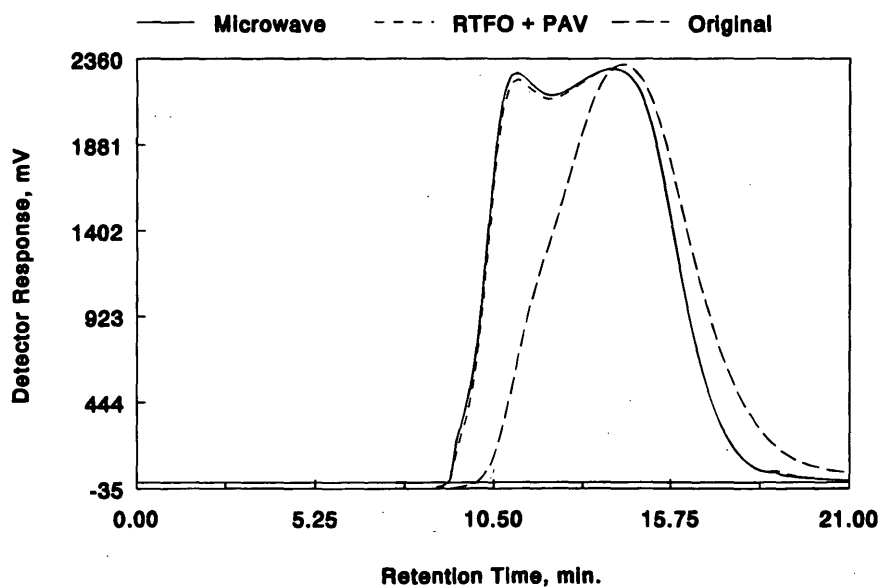


FIGURE 4: Chromatograms for microwave energy-aged asphalt, RTFO-PAV-aged asphalt, and tank asphalt (Sample 3488).

long-time exposure to a higher power level increased the MSI and D values for the set of asphalt samples.

Because of the ability of microwave radiation to increase the MSI (a behavior synonymous to aging) its use as an alternative tool for laboratory aging is promising. Microwave energy causes an extent of aging comparable to that caused by RTFO-PAV aging. Similarity between microwave aging and RTFO-PAV aging is evident from HPSEC and BBR measurements on 18 asphalts. The HPSEC procedure (which uses gravimetry and UV absorption at 345 nm) more or less gives the same MSI, regardless of the aging technique.

The chromatograms obtained after microwave aging are identical to those obtained after RTFO-PAV aging. BBR shows that microwave aging underestimates aging. The difference between the two techniques corresponds to about 1°C to 3°C in limiting low temperature; that is, a given asphalt with a limiting temperature of -12°C may pass the BBR test at -13°C, -14°C, or -15°C, depending on the asphalt material, if it is aged with microwave radiation.

A maximum difference of 3°C in limiting low temperature between microwave aging and RTFO-PAV aging may be considered in view of the following: (a) RTFO-PAV aging is nothing but

TABLE 9 Variation in MSI and D Under Two Extreme Conditions of Microwave Energy

Sample	3 Min HP; 45 min 20% P*		8 min HP; 150 min 90% P**		Difference, %	
	MSI	D	MSI	D	MSI	D
2110	0.33	3.612	0.53	4.163	60.6	15.3
3087	0.24	3.733	0.53	4.517	120.8	21.0
3385	0.33	3.464	0.48	3.798	45.5	9.6
3418	0.32	4.680	0.46	5.170	43.8	10.5
3455	0.24	3.895	0.37	4.733	54.2	21.5
3488	0.32	3.439	0.54	4.022	68.8	17.0
3829	0.33	4.324	0.47	5.211	42.4	20.5
4190	0.25	4.066	0.38	5.098	52.0	25.4
4506	0.25	3.940	0.38	4.612	52.0	17.1
4653	0.28	3.468	0.43	4.247	53.6	22.5
4729	0.43	4.100	0.59	3.878	37.2	5.4
4897	0.32	3.504	0.47	4.431	46.9	26.5

* Air temperature at center of a 750-W microwave oven at end of treatment was 55°C.

** Air temperature at center of a 1000-W microwave oven at end of treatment was 195°C.

the best estimate of the long-term aging effects, and (b) aging with microwave energy is extremely simple and rapid (less than 3 hr).

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