A Rapid Microwave-Assisted Solvent Extraction Method for Assessment of Stabilizer Concentration in Crosslinked Polydimethylsiloxane

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ABSTRACT: Crosslinked polydimethylsiloxanes were prepared containing 0.05 to 0.2 wt % of either a phenolic antioxidant (Irganox® 1010) or a hindered amine stabilizer (Tinuvin® 144). The stabilizer concentration was assessed by HPLC and UV-Vis spectroscopy of Soxhlet and microwave-assisted solvent extracts. Almost complete recovery of stabilizer was achieved with Soxhlet extraction. High stabilizer recovery was achieved when acetone was used as the solvent in the microwave-assisted extraction. HPLC was shown to be an efficient method for determining the concentration of Irganox 1010. For Tinuvin 144 the selectivity of both UV-Vis spectroscopy and HPLC was poor, leading to imprecise evaluation of the antioxidant concentration. The loss of stabilizer by migration from polymer to hot water (75 and 95°C) was monitored for the systems stabilized with Irganox 1010 and the diffusion coefficient of the antioxidant in the polymer was determined. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 2185–2192, 2004

Key words: polysiloxanes; stabilization; extraction; chromatography; migration

INTRODUCTION

The importance of composite high voltage outdoor insulators, with a shed material composed of crosslinked polydimethylsiloxane (PDMS), has grown over the last decades.[1] The advantages of PDMS insulators include good mechanical and electrical properties, low weight, environmental durability, and excellent water repellency.[2,3] Since the surface hydrophobicity of PDMS prevents the formation of a continuous water band on the surface, the flash-over potential of the insulator is raised and this improves its performance in the field.[4] During its lifetime, the surface of the insulator may be exposed to electrical discharges, such as corona discharges, resulting in a temporary loss of the surface hydrophobicity.[5] The oxidative crosslinking of PDMS at the surface is one of the most important reactions for the transformation of the surface from a hydrophobic to a wetting state.[6] This crosslinking leads to the formation of a brittle, silica-like surface layer rich in oxygen. X-ray photoelectron spectroscopy revealed that the silica-like layer consists of a mixture of PDMS (silicon bonded to two oxygen atoms) and oxidized PDMS (silicon bonded to three or four oxygen atoms).[7–9] The oxidative nature of the process was also evident in the increase in the elemental oxygen-to-carbon ratio of the immediate surface.[10–12] The brittle nature of the silica-like layer has been confirmed through studies of surface cracking. Optical and scanning electron microscopy revealed the presence of surface cracks after prolonged exposure to corona or plasma discharges. These cracks propagate into the unoxidized material and it is believed that this shortens the service life of the insulator.[13] Hence, extending the incubation time for the formation of the silica-like surface layer is beneficial for the performance of the PDMS insulator.

Fateh-Alavi et al.[11,12] reported that the incorporation of stabilizers in PDMS increased the incubation air plasma dose for the onset of surface cracking upon uniaxial elongation to 10%. A hindered amine stabilizer (Tinuvin 770) and a bifunctional antioxidant (Irganox 565) proved to be particularly efficient in increasing the plasma dose necessary for the formation of the silica-like layer.[11] It was also shown that the dose needed to form the silica-like layer increased in a linear manner with increasing stabilizer concentration.[12]

It was realized that a reliable method had to be developed for the assessment of the stabilizer concentration in PDMS to achieve a more accurate evaluation of the efficiency of different stabilizers. Furthermore, a precise determination of the stabilizer concentration is needed to make it possible to study the migration of stabilizer from PDMS to surrounding media such as water. In this paper, the microwave-assisted solvent extraction (MAE) is used to develop an efficient method for the extraction of a hindered phenol and a hindered amine stabilizer. The extracts were analyzed

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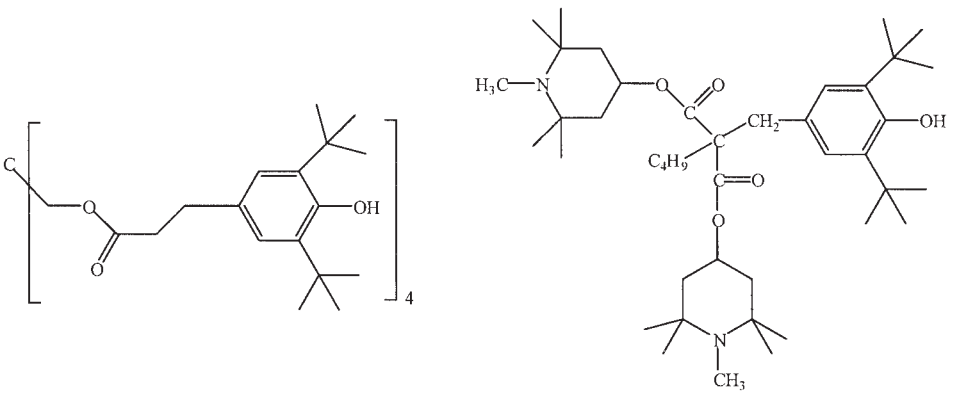

Figure 1 The chemical structures of Irganox® 1010 and Tinuvin® 144.

by UV-Vis spectroscopy and high-performance liquid chromatography (HPLC). The rate of migration of stabilizer from PDMS to surrounding hot water was determined using these methods.

EXPERIMENTAL

Materials

The stabilizers used in this study were Irganox® 1010 and Tinuvin® 144, supplied by Ciba Specialty Chemicals Inc. The stabilizers were used as received. The chemical structures of these stabilizers are shown in Figure 1.

PDMS materials were prepared containing 0.01, 0.02, 0.05, 0.1, and 0.2 wt % of the stabilizers. The stabilizers were dissolved in a small volume of chloroform and they were then added to a vinyldimethyl-terminated PDMS (M_w = 11,000 g mol^{-1}). The mixture was manually stirred to achieve a uniform distribution of the stabilizer and was placed in an oven at 80°C overnight for evaporation of the chloroform. After cooling to ambient temperature, the crosslinker (30–35%) methylhydro-(65–70%) dimethylsiloxane copolymer (M_w= 2100 g mol^{-1}) was added to the mixture. The stoichiometric ratio of hydride groups to vinyl groups was 1.5 : 1 to minimize the amount of residual unreacted chain ends in the network. A platinum divinyltetramethyldisiloxane complex at a concentration of 35 ppm was used to catalyze the vulcanization reaction. The polydimethylsiloxane resin, the crosslinker, and the platinum catalyst, purchased from United Chemicals Technologies Inc, were used as received. The components were mixed by stirring and were compression molded at 135°C in a Schwabenthan Polystat 400S press into 2-mm-thick plaques, During the molding, the pressure was maintained at 2 MPa. The cured material was cut into 30-mm-diameter discs for use in the studies.

Soxhlet extraction of stabilizers

Four PDMS disks of each stabilizer type and concentration were weighed and Soxhlet extracted in hexane for 24 h. The extracts were collected and the solvent was removed in vacuum. The precipitates were diluted with 20, 30, or 40 mL of chloroform depending on the stabilizer concentration in the PDMS. The solutions were filtered through a 0.45-μL PTFE filter purchased from Scantec Lab. The filtrates were then analyzed to assess the stabilizer concentration.

Microwave-assisted solvent extraction (MAE) of stabilizers

The microwave oven (CEM MES-1000 microwave) was operated at 700 W with a maximum pressure of 1.4 MPa. The samples were heated from 20°C to the final extraction temperature at 5°C min^{-1} and then held at this temperature for 30 min. Five MAE programs (Table I) were used to find the most effective extraction conditions. For each stabilizer type and concentration, two samples were extracted with the same MAE program.

The extracts were collected and weighed to determine the solvent loss. The extracts obtained after treatment with chloroform were filtered through a 0.45-μL PTFE filter (Scantec Lab) before the analysis. The acetone ex-

TABLE I
MAE Programs Used for Extraction of Stabilizers

Program	Solvent	Solvent volume (ml)	Extraction temperature (°C)
P1	Chloroform	20	90
P2	Chloroform	30	90
P3	Acetone	20	70
P4	Acetone	30	70
P5	Acetone	30	90

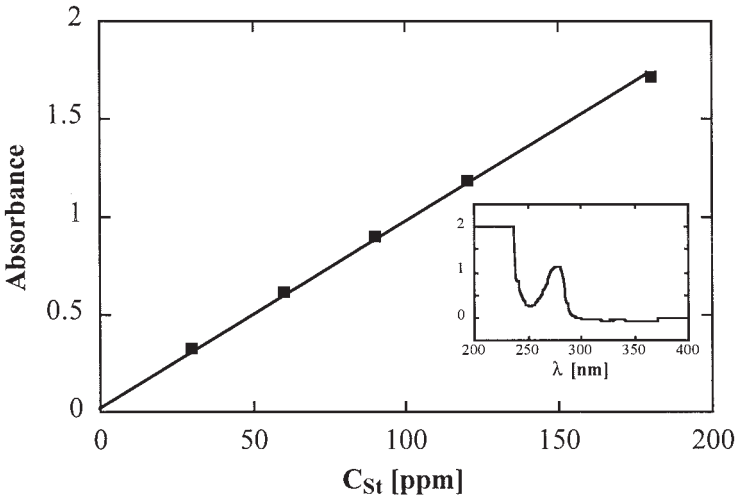

Figure 2 Calibration curve of Irganox 1010 measured as the height of the UV absorption peak at 280 nm as a function of the concentration of the stabilizer in chloroform. The coefficient of determination (r^2) is 0.996.

tracts were dried under vacuum and the residue was diluted with 10 or 20 mL chloroform depending on the actual stabilizer concentration. The solutions were filtered through a 0.45-μL PTFE filter before analysis.

UV-Vis spectroscopy

UV-Vis spectroscopy was performed using a WPA UV-Vis spectrophotometer version 1.6. Standard solutions of each stabilizer in chloroform were prepared in the concentration range from 30 to 180 ppm for Irganox 1010 and from 40 to 400 ppm for Tinuvin 144. UV-Vis spectra of the stabilizers were obtained after subtraction of the spectrum of the pure solvent. Both stabilizers showed an absorption peak at 280 nm; this was used to study the variation in the concentration of each stabilizer. For each stabilizer, the standard solution series was analyzed on three different occasions,

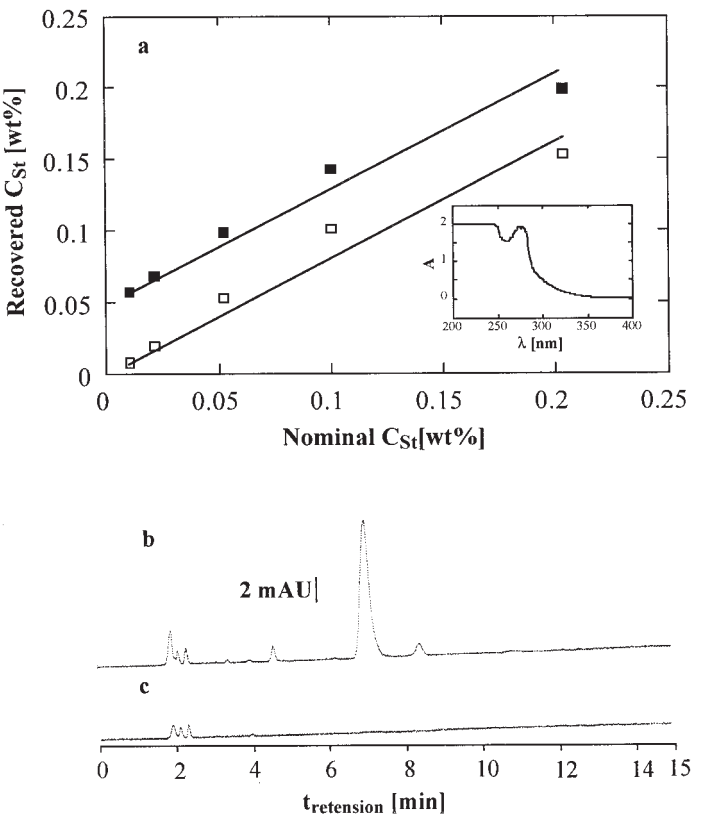

Figure 3 Soxhlet extraction of PDMS with Irganox 1010: (a) assessment of the recovery of Irganox 1010 by UV-Vis spectroscopy (■) and HPLC (□); (b) HPLC chromatogram of a standard solution of Irganox 1010 in chloroform, UV detector trace at 280 nm; and (c) HPLC chromatogram of a standard solution of Irganox 1010 in chloroform, UV detector trace at 310 nm.

TABLE II
Recovery of Irgonox 1010 from PDMS by UV-V is Spectroscopy

Extraction method	Recovery equation[a]	r^2 [b]	Recovery (%)
MAE P1	$C_r = 0.5156 \times C_n + 0.0096$	0.991	52
MAE P2	$C_r = 0.5726 \times C_n + 0.0104$	0.990	57
MAE P3	$C_r = 0.6758 \times C_n + 0.0131$	0.993	68
MAE P4	$C_r = 0.7609 \times C_n + 0.0165$	0.993	76
MAE P5	$C_r = 0.6911 \times C_n + 0.0165$	0.990	69
Soxhlet	$C_r = 0.7313 \times C_n + 0.0565$	0.978	73

[a] C_r, concentration of stabilizer (wt %) in polymer calculated from recovered amount of antioxidant; C_n, nominal concentration of stabilizer (wt %) in polymer.
[b] Coefficient of determination.

separated by at least 24 h, to assess the repeatability of the method.

High-performance liquid chromatography

Liquid chromatography was carried out in a Hewlett–Packard Chromatograph, HPLC 1090, equipped with a binary pump system, an M490 variable wavelength UV detector, a Waters Model 990 diode array detector (DAD), and a WISP autosampler. The column used for the separation of the analytes was a Supelcosil, 5 μm, 4.5 $\times$ 150 mm, LC-Si column provided with a precolumn, operated at 40°C. Both the UV detector (recording at both 280 and 310 nm) and the DAD were used for the analysis. The flow rate of the mobile phase was 1.0 mL min^{-1} and HPLC grade chloroform was used as mobile phase in the case of Irganox 1010 and HPLC grade THF was used in the case of Tinuvin 144.

Stabilizer migration to water

PDMS samples containing a nominal stabilizer concentration of 0.2 wt % were exposed to deionized water at 75°C (Irganox® 1010) and 95°C (Irganox® 1010 and Tinuvin® 144). Ten samples of each stabilizer were placed in a 1-L glass container, which was filled with deionized water and kept in a Memmert oven. Deionized water preheated to the experiment temperature was added to the container at regular intervals to compensate for the loss of water due to evaporation. Samples were analyzed after 7, 14, 21, 28, 42, and 63 days of water exposure at 95°C. In the case of PMDS with Irganox 1010 aged at 75°C, the samples were analyzed after 7, 14, 28, and 42 days of water exposure. The samples were dried for 24 h at 23°C in a desiccator before the solvent extraction of the stabilizer. The remaining stabilizer in the exposed specimens was determined on two samples per exposure time that were extracted according to MAE method P4 (PDMS with Irganox 1010) and method 3 (PDMS with Tinuvin 144).

RESULTS AND DISCUSSION

Irganox 1010

Figure 2 shows the UV-Vis spectrum of Irganox 1010 dissolved in chloroform, where the stabilizer exhibited an absorption peak at 280 nm. A linear relationship was obtained between the 280 nm absorbance and the stabilizer concentration.

The fact that the UV-Vis spectrum of the Soxhlet extracts [Fig. 3(a)] was not identical to those of the

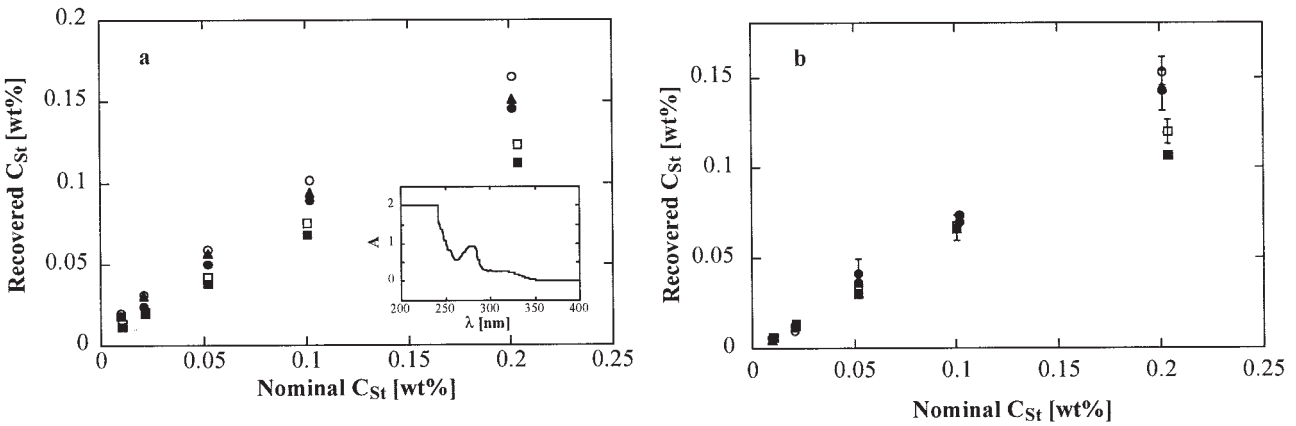

Figure 4 MAE recoveries of Irganox 1010: (a) assessment of the recovery of stabilizer by UV-Vis spectroscopy and (b) HPLC: P1 (■), P2 (□), P3 (●), P4 (○), and P5 (▲).

TABLE III
Recovery of Irganox 1010 from PDMS by HPLC

Extraction method	Recovery equation[a]	r^{2b}	Recovery (%)	Normalized recovery (%)[c]
MAE P1	$C_r = 0.5515 \times C_n$	0.978	55	68
MAE P2	$C_r = 0.6081 \times C_n$	0.992	61	75
MAE P3	$C_r = 0.7156 \times C_n$	0.996	72	89
MAE P4	$C_r = 0.7420 \times C_n$	0.994	74	91
MAE P5	$C_r = 0.7123 \times C_n$	0.999	71	88
Soxhlet	$C_r = 0.8143 \times C_n$	0.957	81	100

[a] C_r, concentration of stabilizer (wt %) in polymer calculated from recovered amount of antioxidant; C_n, nominal concentration of stabilizer (wt %) in polymer.
[b] Coefficient of determination.
[c] Recovery of stabilizer normalized with the recovery obtained by Soxhlet extraction.

standard solutions showed the presence of other species in the extracts. The HPLC chromatogram of the Soxhlet extract [Figs. 3(b and c)] was in accordance with those of the standard solutions; the peak that appeared at 6.8–7.5 min corresponded to the retention of the stabilizer. The similarity of the two chromatograms indicates that the contaminant indicated in Figure 3(a) was not retained in the column but passed through together with the mobile phase. The recovered stabilizer concentration was assessed by UV-Vis spectroscopy and HPLC of the extract as a function of the nominal stabilizer concentration [Fig. 3(a)]. It was found that the UV-Vis recovery curve had an intercept at 0.06 whereas the HPLC recovery line passed through the origin [Table II, Fig. 3(a)]. The nonzero intercept for the UV-Vis spectroscopy data suggests that impurities were present in the extracts. The absence of any residual absorption at zero concentration and the high selectivity of the HPLC method for Irganox 1010 suggest that it is a more reliable method for the assessment of the stabilizer concentration. The HPLC assessed recovery was 81% compared to the value of 73% obtained by UV-Vis spectroscopy. The difference between the nominal and the measured stabilizer concentration is probably due to loss of stabilizer during material preparation.

The UV-Vis spectrum of MAE extracts showed the same 280 nm absorption as the standard solutions and also a broad peak at ~ 300–350 nm, indicating that the extract contained other species absorbing in the UV-Vis region [Fig. 4(a)]. The HPLC chromatograms of MAE extracts showed no deviation from those of the Soxhlet extracts and the standard solutions of Irganox 1010. Figures 4(a and b) show the recovery of the stabilizer from PDMS samples assessed by UV-Vis spectroscopy and HPLC, respectively. The average degrees of recovery of the stabilizer based on the data in Figures 4(a and b) are presented in Tables II and III.

The stabilizer recovery was in all cases higher with HPLC than with UV-Vis spectroscopy. The higher selectivity of HPLC for Irganox 1010 makes it the method of choice. The lowest recovery, 55%, was ob-

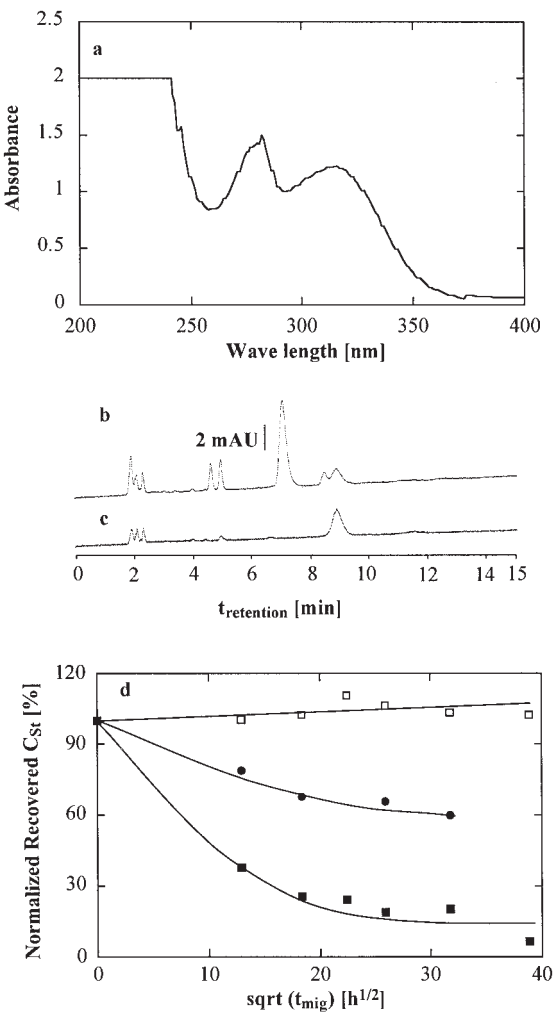

Figure 5 Samples containing Irganox 1010 exposed to water at 95°C: (a) UV-Vis absorbance of a MAE extract; (b) HPLC chromatogram of a MAE extract, UV detector trace at 280 nm; (c) HPLC chromatogram of a MAE extract, UV detector trace at 310 nm; and (d) the stabilizer concentration in polymer as a function of the square root of the exposure time at 95°C: (□) UV-Vis spectroscopy; (●) HPLC and at 75°C: (■) HPLC.

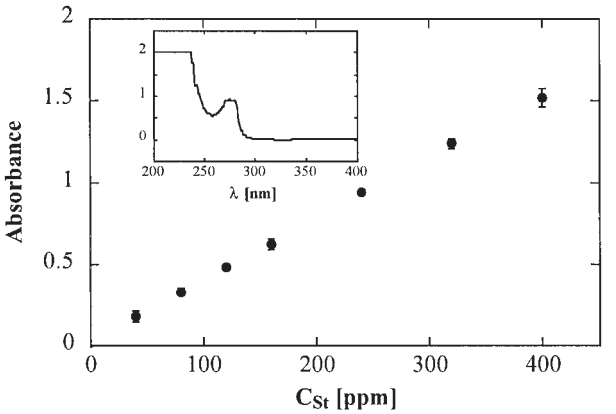

Figure 6 Calibration curve of Tinuvin 144 measured as the height of the UV absorption peak at 280 nm as a function of the concentration of the stabilizer in chloroform. The coefficient of determination (r^2) is 0.999.

tained with MAE program P1 and the highest, 74%, with MAE program P4 (Table III). The order of recovery of Irganox 1010 from PDMS samples was determined to be P1 < P2 < P3 < P5 < P4 with both UV-Vis spectroscopy and HPLC. The low recovery of MAE programs using chloroform as solvent is due to the high sorption of chloroform in PDMS. The extensive solvent uptake reduced the amount of the stabilizer in the free solvent phase and the measured recovery of the stabilizer in the subsequent analysis. The low uptake of acetone in PDMS together with the high solubility of the stabilizer in acetone are the reasons for the high recoveries obtained when using methods P3–P5 (Tables II and III). The recoveries obtained after MAE were normalized with respect to that after Soxhlet extraction; the latter method is believed to achieve complete extraction of the stabilizer. Method P4 was the most effective MAE program for extraction of Irganox 1010, giving a normalized recovery of 91%. A higher extraction temperature did not result in higher recovery (Table III).

Method P4 was used to study the changes in Irganox 1010 concentration in PDMS on exposure to deionized water at 75 and 95°C. The UV-Vis spectrum of the MAE extract of a sample exposed for 21 days in deionized water at 95°C contained an additional absorption peak at ~ 310 nm [Fig. 5(a)]. The HPLC chromatogram showed an additional peak at 8.8 min of retention time, with UV absorbance at both 280 and 310 nm, which was absent in the chromatograms of the standard solutions and of the extracts of the unexposed samples [Figs. 5(b and c)]. No significant decrease in Irganox 1010 concentration was observed with UV-Vis spectroscopy [Fig. 5(d)]. HPLC measurement of the same extracts showed a monotonic decrease in stabilizer concentration with increasing exposure time [Fig. 5(d)]. It may thus be concluded that the presence of contaminants in the extracts interfered with the UV-Vis absorption spectrum of the stabilizer. The absorption of contaminants at the selected wavelength (280 nm) drowned the effects of changes in stabilizer concentration. These problems were not present with the HPLC method.

The migration of stabilizer from PDMS to the surrounding water was analyzed in terms of Fick's second law for unidimensional penetrant diffusion, assuming constant diffusivity over the limited penetrant concentration range involved in each step:[14]

$$\frac{C_\infty - C_t}{C_\infty} = \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)}\exp\left(-\frac{D(2n+1)^2\pi^2}{4L^2}t\right)$$

where C_∞ is the stabilizer concentration in PDMS at infinite time, C_t is the stabilizer concentration at time t, D is the diffusion coefficient, and L is the half disc thickness. The diffusion constants at the two experi-

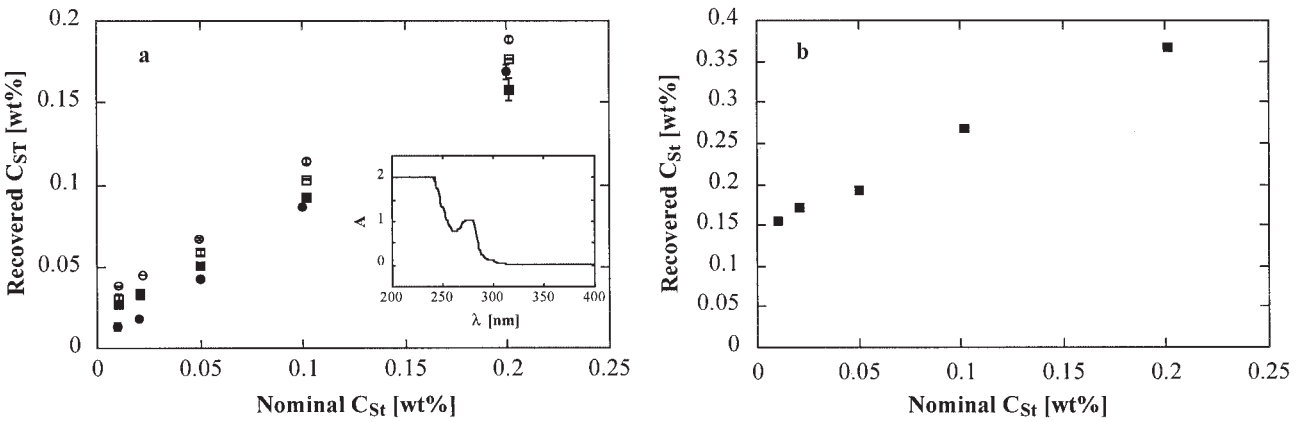

Figure 7 MAE and Soxhlet recoveries of Tinuvin 144: (a) assessment of the MAE recovery of Tinuvin 144 by UV-Vis spectroscopy and (b) assessment of the Soxhlet recovery of Tinuvin 144 by UV-Vis spectroscopy: P1 (■), P2 (□), P3 (●), and P4 (○).

TABLE IV
Recovery of Tinuvin 144 from PDMS by UV-Vis Spectroscopy

Extraction method	Recovery equation[a]	r^{2b}	Recovery (%)
MAE P1	$C_r = 0.6946 \times C_n + 0.0189$	0.998	69
MAE P2	$C_r = 0.7803 \times C_n + 0.0206$	0.998	78
MAE P3	$C_r = 0.8324 \times C_n + 0.0239$	0.999	83
MAE P4	$C_r = 0.8031 \times C_n + 0.0288$	0.999	80
Soxhlet	$C_r = 1.1131 \times C_n + 0.1457$	0.994	111

[a] C_r, concentration of stabilizer (wt %) in polymer calculated from recovered amount of antioxidant; C_n, nominal concentration of stabilizer (wt %) in polymer.
[b] Coefficient of determination.

mental temperatures were calculated using a Matlab program: $D = 3.1 \times 10^{-9}$ cm^{2}s^{-1}; SSD = 0.0523 (95°C); $D = 5.46 \times 10^{-10}$ cm^{2}s^{-1}; SSD = 0.0343 (75°C). These diffusivities correspond to an activation energy of 93 kJ mol^{-1}.

Tinuvin 144

Figure 6 shows the UV-Vis spectrum of the stabilizer in chloroform with a prominent absorption peak at 280 nm. In this case, the absorbance at 280 nm is also proportional to the stabilizer concentration in the solution.

The UV-Vis spectrum of a MAE extract is shown in Figure 7(a). The peak at 280 nm, also observed in the standard solutions, confirmed that the stabilizer was present in the extract. The MAE recoveries of Tinuvin 144 are comparable to those of Irganox 1010. The highest recovery was achieved by MAE program P3; again due to the low acetone uptake in PDMS. More alarming are the nonzero intercepts of the data shown in Figure 7(a). The intercepts are higher than for the extracts from samples stabilized with Irganox 1010. This is due to the low UV-Vis absorption of Tinuvin 144 and to the presence of other UV-absorbing species in the extracts. The UV-Vis recovery of Soxhlet extracts of this stabilizer was found to be 110%, which again indicates that other interfering species were present in the extracts [Fig. 7(b), Table IV].

Figure 8 shows HPLC chromatograms of the extracts of different PDMS samples containing Tinuvin 144. The chromatograms contained one or two overlapping peaks, showing the lack of separation between the different analytes present. Chromatogram (a) (Fig. 8) showed a split peak for a diluted standard solution in chloroform. The more concentrated standard solutions showed no splitting, i.e., the peak was "clean." The splitting at low stabilizer concentrations of Tinuvin 144 was believed to be due to impurities. The peaks of HPLC chromatograms of Soxhlet extracts were broader, suggesting the presence of more than one analyte in the solution [chromatograms (c) and (d) in Fig. 8]. The retention time was centered at 2.1 min, which is the same as that obtained for the standard solutions, which suggests that the stabilizer was the dominating analyte in the extract. The HPLC chromatogram [(e and f) in Fig. 8] of the extracts of the samples exposed to deionized water at 95°C was much broader than those of the extracts of the virgin sample and of the standard solution. The peak height at a retention time of 2.1 min was lower than that of the virgin PDMS samples, suggesting that a significant part of the stabilizer had migrated to the surrounding medium. It may be concluded that the HPLC method used was not adequate for the determination of Tinuvin 144 concentration in PDMS.

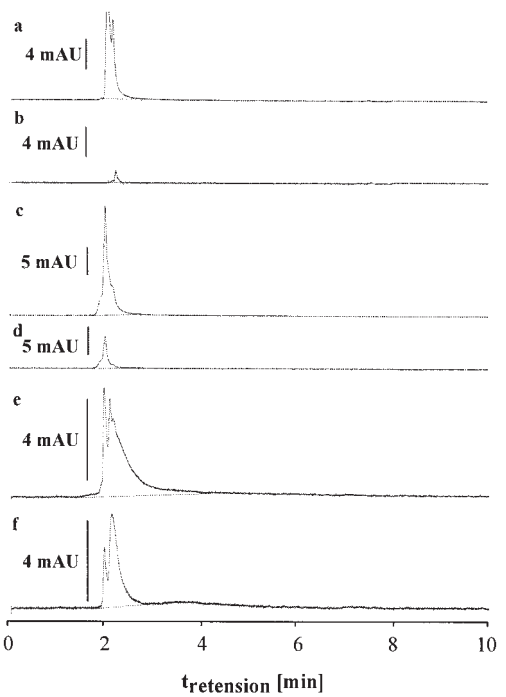

Figure 8 HPLC chromatograms of extracts/solutions of Tinuvin 144 samples: (a) standard solution (80 ppm stabilizer), UV detector trace at 280 nm; (b) standard solution (80 ppm stabilizer), UV detector trace at 310 nm; (c) MAE (P2) extract, UV detector trace at 280 nm; (d) MAE (P2) extract, UV detector trace at 310 nm; (e) MAE extract from PDMS sample exposed to deionized water at 95°C, UV detector trace at 280 nm; (f) MAE extract from PDMS sample exposed to deionized water at 95°C, UV detector trace at 310 nm.

CONCLUSION

Microwave-assisted solvent extraction can be used for close-to-complete extractions of hindered phenol and hindered amine stabilizers from silicone rubber in a shorter time than is required for a Soxhlet extraction. High recoveries were obtained using acetone as a solvent, which is a nonswelling solvent for PDMS with good solubility for the stabilizers. The recovery of stabilizers with a swelling solvent (chloroform) was significantly lower due to the high sorption of the solvent in the polymer. For precise measurement of stabilizer concentration, the stabilizer has to be separated from other species, such as oligomers, present in the extracts. HPLC was shown to be an adequate method for selectively determining the concentration of Irganox 1010 in PDMS. However, the separation and thus selective concentration determination of Tinuvin 144 was not achieved under the conditions tested. The migration of Irganox 1010 from the polymer to surrounding water at elevated temperatures was sensitively monitored by MAE followed by HPLC.

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