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Applications of Thermogravimetry and PAS-FTIR in the Characterization of Silicone Sealants

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Abstract

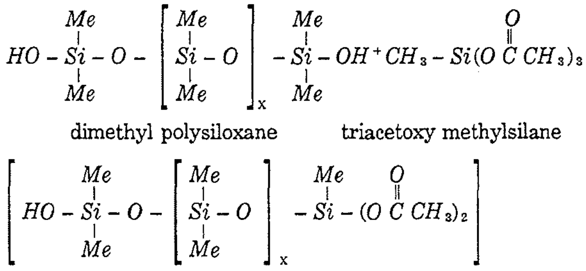
Fourier transform infrared photoacoustic (PAS-FTIR) spectroscopy and thermogravimetry (TG) have been used to study the effects of exposure of silicone sealants to water in the presence and absence of UV-radiation. The silicone sealants were found to be fairly resistant to the two types of weathering conditions for the duration of the exposure (8000 hours). Only a small increase in the hydroxyl absorption band was observed by PAS-FTIR. No substantial changes in weight loss were observed using thermogravimetry.

Résumé

La spectroscopie photo-acoustique infrarouge par transformée de Fourier (PAS-FTIR) et la thermogravimétrie (TG) ont été utilisées afin d'étudier l'effet de l'exposition à l'eau de produits silicones scellants, en présence ou en l'absence de radiations UV. Ces produits ont montré une bonne résistance aux conditions décrites ci-haut pendant toute la durée de l'exposition (8000 heures). Seule une légère augmentation de la bande d'absorption correspondant au groupe hydroxyle a été observée par PAS-FTIR. La thermogravimétrie n'a révélé aucune perte de masse significative.

Introduction

Silicone sealants are the leading type of sealants currently being used in the construction industry. They are preferred because of their properties which are directly linked to their chemistry. Silicone sealants normally contain polydimethylsiloxane rubber (PDMS) which has a very flexible backbone (1). PDMS is a polyorganosiloxane with high thermal stability. The chemical bonds -Si-O-, -Si-C- and -Si-H are very stable. For example, the -Si-O-Si- bond has a bond dissociation energy of 364 KJ mol^{-1} and can tolerate up to 300°C without decomposing (2). Furthermore, the backbone is not affected by ultraviolet radiation and therefore, silicone sealants weather very well. The silicone sealants also contain additives (which provide strength and resistance to various environmental factors) and a crosslinking system. The crosslinking system is required to form the linear silicone elastomer and the mechanism usually involves a free-radical pathway. The curing process for one-part systems requires atmospheric moisture because it is a condensation curing process during which acetic acid is given off (see eq. [1]).



$$HO-\overset{\overset{Me}{|}}{\underset{\underset{Me}{|}}{Si}}-O-\left[\overset{\overset{Me}{|}}{\underset{\underset{Me}{|}}{Si}}-O\right]_x-\overset{\overset{Me}{|}}{\underset{\underset{Me}{|}}{Si}}-OH+CH_3-Si(O\overset{\overset{O}{\|}}{C}CH_3)_3\rightarrow$$

dimethyl polysiloxane triacetoxy methylsilane

$$\left[HO-\overset{\overset{Me}{|}}{\underset{\underset{Me}{|}}{Si}}-O-\left[\overset{\overset{Me}{|}}{\underset{\underset{Me}{|}}{Si}}-O\right]_x-\overset{\overset{Me}{|}}{Si}-(O\overset{\overset{O}{\|}}{C}CH_3)_2\right]$$

base polymer

+ acetic acid [1]

Some of the advantages of the silicone sealants include(1): their one component nature, colour stability, high temperature resistance (up to 200°C), great flexibility (down to about −60°C), UV and ozone resistance, good chemical resistance. The disadvantages include: cost, difficult in painting, unpleasant odour (during cure), critical importance of surface preparation.

In many industrial applications it is necessary to determine the durability of a product. If the product has been in-use for many years then the durability can be

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predicted from historical data. This, however, is not feasible for new products since it is unrealistic to expect a company to wait 25 years prior to releasing a product. Also, it is unacceptable to expect a consumer to accept a new product which has no track record. Since natural weathering takes too long, accelerated weathering is used. Accelerated aging can vary from a simple heat-aging test to more elaborate systems which simulate combined UV-radiation, temperature, humidity and atmospheric pollutant effects. Accelerated weathering is faster because harsher conditions are used. These harsh conditions can generate unnatural responses in the material and hence, care must be taken when defining the weathering conditions.

Various mechanical and chemical properties can be monitored to study aging phenomena (3). The mechanical properties include tensile strength, elongation, flexural strength, impact, etc. Some of the chemical techniques used to study the weathering effects include thermal analysis (TG, DMA, DSC, TMA) and spectroscopy (FTIR, NMR, MS, SEM, ESCA, *etc.*).

Thermal Analysis

Thermal analysis encompasses a number of techniques which are useful to characterize polymeric building materials. These techniques include thermogravimetry (TG), differential thermal analysis (DTA), differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), thermomechanical analysis (TMA), and simultaneous thermal analysis (STA or TG/DTA or TG/DSC). In STA, data from two thermoanalytical techniques, thermogravimetry (TG) and differential thermal analysis (DTA), are acquired simultaneously, by the same instrument on a single specimen. Since TG provides information on any reaction involving mass change as a function of temperature and/or time (4), information on the heat stability and composition of the sample can be obtained. Differential thermal analysis (DTA) provides information on the temperature difference between a reference and a sample while they are subjected to a common temperature program (4). The main application of DTA is in the determination of thermal events such as oxidative stability, chemical reactions, phase transitions, enthalpies, melting point, decomposition, *etc.* All chemical changes can be studied by DTA since heat is either absorbed (endothermic reaction) or evolved (exothermic reaction). In endothermic reactions such as melting, the temperature of the sample should be lower than in the reference, since no heat was absorbed in the reference. Simultaneous TG/DTA technique is a very useful technique since physical and chemical changes of the sample are recorded simultaneously. This combination has many advantages over the individual TG and DTA techniques. Firstly, the two measurements are taken at the same temperature and time, thereby eliminating the problem of homogeneity. Secondly, it saves time since only one sample has to be prepared, which minimizes experimental errors.

The STA technique is not always sufficient to characterize all types of materials such as construction materials, which have very complex composition. In many cases, complementary techniques (*e.g.*, FTIR) are required to fully characterize the material.

Fourier Transform Photoacoustic Infrared (PAS-FTIR) Spectroscopy

Photoacoustic-FITR spectroscopy has been used for a number of years in many different fields, including, food, pharmaceutical, biomedical, coal, semi-conductors, environmental, and coatings. (5), Minimal sample preparation is a definite advantage of the PAS-FTIR technique (6). The KBr pellet technique often presents problems with samples which are difficult (if not impossible) to grind. Diffuse reflectance (DRIFT) is not feasible if the sample has low diffuse-reflectance components. Internal reflection also known as attenuated total reflectance (ATR) is a good technique when information is required of the top surface (1 to 10 μ-m in depth) (7). This technique cannot, however, be used with samples of irregular morphology since it is difficult to obtain good optical contact between the sample and the ATR crystal. These problems are surmountable with the aid of PAS-FTIR. Photoacoustic spectroscopy renders possible the simultaneous study of sample surface and bulk and it has been demonstrated to be a useful technique for obtaining mid-infrared spectra of solid samples with minimal preparation (8-13). Moreover, the presence of up to 25 wt% carbon black, a highly absorbing filler used in many construction products, does not cause any interference (14). PAS-FTIR is particularly useful for measuring the spectra of materials, such as construction sealants, that suffer from a change in morphology during weathering. The applications of this technique are quite widespread and include the analysis of catalytic surfaces, (15-17), electrode surfaces (18), polymer films (7, 19, 20), evaluation of accelerated weathering for polyester-urethane coatings (20), cured paint media and weathering of alkyd paints (21).

It is clear that polymeric construction materials are very complex. In addition to the resin used as a modifier, plasticizers, stabilizers, fillers (carbon black or mineral) are also added. Construction materials, such as weathered sealants, cannot always be characterized by transmission or reflection techniques because they are black, grey or opaque, thick, and, as previously mentioned, change morphology with weathering. PAS-FTIR technique is known to be capable of providing spectral information for this type of material with minimal sample preparation. For this reason, PAS was considered useful for this investigation.

In this study, PAS and STA are used to monitor the chemical changes that occur in silicone-based sealants during exposure to water, both alone and in combination with UV-radiation. This work is part of a larger project which attempts to compare the weatherability of different sealants such as polyurethanes, polysulfides and silicones. The overall objective is to compare and correlate the various chemical and mechanical properties of these caulking materials using both natural and accelerated aging.

Experimental

Five commercially available silicone sealants were obtained from different manufacturers and cast as free-films (see Table I). The free films were placed back-to-back in a frame which separated the films with an aluminum divider. All of the free films were loaded into a xenon-arc Weather-o-meter (Atlas Electric Devices Company) for weathering. One series of films was thus exposed to light and water while the other was exposed to water only. Samples were removed every 1000 hours and stored for further analysis. The total time of exposure was 8000 hours.

Table I. Sample Description

Sample	Colour
S1	Off-white
S2	White
S3	Black
S4	Grey
S5	White

The weathering conditions used for the samples were as follows:

Irradience: 0.37 W m^{-2} nm^{-1}
Black panel temperature: 63°C
Relative humidity arc on: 50%
Light cycle: 3.5 hours on; 0.5 hours off
Specimen spray cycle (deionized water): 118 min off; 20 min on
Rack spray cycle: when arc off

Thermal analysis

Thermoanalytical studies of unweathered and weathered sealants were performed using a Seiko Simultaneous Thermal Analyzer (STA) model TG/DTA320. This module was interfaced to a Seiko SS5200H disk station. A specimen, weighing between 7 and 8 mg, was heated under a nitrogen atmosphere (100 mL min^{-1}) from 40°C (no weight loss observed before 40°C) to 900°C at 10°C min^{-1}. All samples were run in duplicate.

Fourier transform infrared photoacoustic spectroscopy

Fourier transform infrared spectra were measured on a Nicolet 170SX spectrometer as well as a Nicolet 800 spectrometer. Both systems were equipped with an MTEC photoacoustic cell (model 200). For sampling, disks of 8 mm diameter were cut with a cork borer. In a few cases, where the samples were too thick, the thickness was reduced by slicing with a scalpel. Conditions used for recording the spectra were: resolution 8 cm^{-1}; mirror velocity setting 4; number of scans 512; helium purge; Happ-Genzel apodization; standard phase correction. In addition to the weathered samples, specimens of each material before exposure were analyzed and used as controls. In all cases, no significant difference was observed between the duplicate specimens tested, and only one of the two spectra is included here. All spectra were ratioed against a background recorded earlier the same day with carbon lampblack (Fisher Scientific, Cat. No. C-198) or with a carbon membrane standard reference. The spectra obtained were generally of good quality, but a higher noise level below 600 cm^{-1} meant that only large features could be discerned in this region. The ratioed spectra were corrected for nonlinear response in PAS-FTIR by using the Nicolet macro CPA. Spectra were recorded for unexposed samples and samples exposed for 2000, 4000, 6000 and 8000 hours. The samples corresponding to odd-numbered multiples of 1000 hours of exposure were not analyzed because so little difference was observed between samples corresponding to even-numbered periods.

Results and Discussions

Simultaneous thermal analysis (STA)

STA data provided simultaneous DTA and TG/DTG data of the silicone sealants. A typical STA plot (TG, DTG and DTA) is shown in Figure 1. In this case, however, only weight loss (TG) and the associated derivative

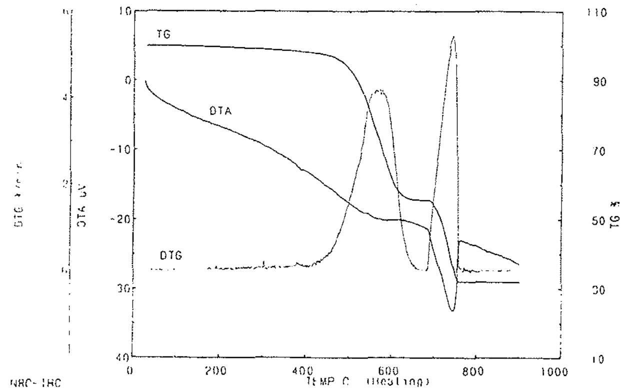

Figure 1. Typical STA plot for an unaged silicone sealant.

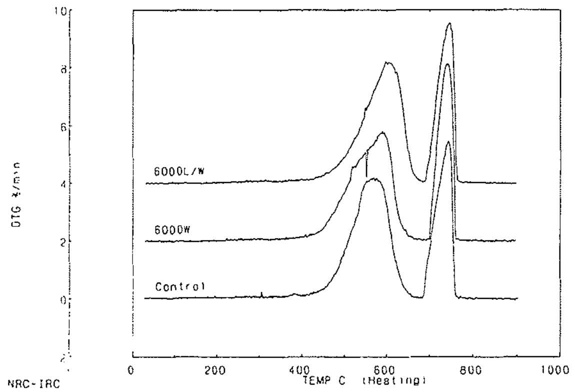

Figure 2. Derivative thermogravimetric (DTG) curves for the S1 sample; unexposed (control), exposed to water only (6000 W) and exposed to both water and ultraviolet light (6000 L/W).

(DTG) data will be discussed since it is these values which yielded the most information. Two endothermic events can be observed in the DTA curve shown in Figure 1. The first (between approximately 300 and 600°C) is related to the decomposition of the polymer while the second event (between 700 and 800°C) is most likely due to the decompostion of the filler (*e.g.*, $CaCO_3$). The onsets of TG and DTG curves were also established in an attempt to determine if they could be used in a routine fashion. Unfortunately, this was found to be a tedious process and is operator dependent, therefore the data are presented but will not be discussed further. All of the data are summarized in Tables II to VI.

In general, two major weight losses are recorded for the silicone sealants. The first weight loss occurs in the 200-685°C region and is most likely due to the decomposition of the siloxane polymer. The second weight loss, observed between 685°C and 800°C, arises from the breakdown of calcium carbonate. Weight losses for the sealants at 0 and 6000 hours are summarized in Table II.

As shown in Table II, the S1 silicone sealant does not undergo significant changes with weathering. The samples start to lose weight at ~300°C (Figure 2) and the total weight loss is 67-69% for both the unexposed and UV/water exposed samples. The weight loss in the 300°C-685°C region for the weathered samples is only 1-2% lower than that of the control sample, whereas the second weight loss (685°C-800°C) remains unchanged.

Table II. Onset Temperatures and Weight Losses for S1 Silicone Sealant

Sample	T_{onset} (°C)		T_{max}	Wt. loss	T_{onset} (°C)		T_{max}	Wt loss	Residue
S1	TG	DTG	(°C)	(%)	TG	DTG	(°C)	(%)	(%)
Control	494	474	571	44.8	707	688	743	23.8	31.4
6000L/W	520	469	609	44.3	723	697	749	24.2	31.5
6000W	489	434	584	42.5	713	692	741	24.4	33.2

The total weight loss for the series was merely 3% less for the sample exposed to water only. This variation may be attributed to inhomogeneity in the sealant or experimental errors rather than being due to weathering.

The S2 sealant series (Table III and Figure 3) has a total weight loss of 64-65%. This series starts to lose weight at a lower temperature than the S1 samples (~200°C). Hence, it is thermally less stable. The TG and the DTG curves of the S2 samples (control and exposed) show similar trends to those observed for S1 sealants.

Table III. Onset Temperatures and Weight Losses for S2 Silicone Sealant

Sample	T_{onset} (°C)		T_{max}	Wt. loss	T_{onset} (°C)		T_{max}	Wt loss	Residue
S2	TG	DTG	(°C)	(%)	TG	DTG	(°C)	(%)	(%)
Control	411	349	591	42.0	708	688	745	22.9	35.1
6000L/W	456	347	554	40.9	702	674	739	23.0	36.1
6000W	465	347	573	40.7	705	682	740	22.9	36.4

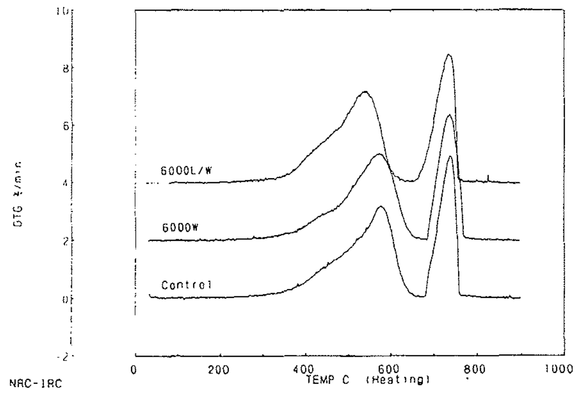

Figure 3. Derivative thermogravimetric (DTG) curves for the S2 sample; unexposed (control), exposed to water only (6000 W) and exposed to both water and ultraviolet light (6000 L/W).

However, the peak temperature of the two weight losses for the samples exposed to light and/or water are lower than that of the control. Therefore, the weathering appears to affect thermal stability. A shoulder can also be observed between 200°C and 500°C. In the 685°C to 800°C region, the weight loss was 23% for both the unweathered and weathered samples.

The peak height of the DTG curves for the S3 control sample is similar for both weight losses. A similar trend is observed in the sample exposed to water. The first peak of the DTG curve for the control sample (Figure 4, control) has a small shoulder between 400°C and 550°C, which is not observed for the exposed samples (Figure 4, 6000 and 6000 L/W). The first weight loss for the sample exposed to water only is 3% lower than that of the control and the sample exposed to light and water (see Table IV). The latter does not seem to be affected by weathering, however, the same peak becomes sharper and an increase in peak height of 40% is observed. Although only the sample exposed to water shows a 3% lower weight loss, the shoulder in the control sample is not observed in either of the exposed samples. This may be due to the loss of a component in the sample during exposure to water. The sharpness of the first derivative weight loss of the DTG curve for the sample exposed to light, as well as its increase in peak height, shows that this sample is thermally less stable.

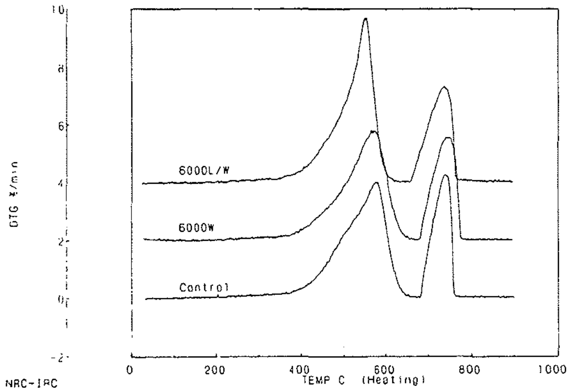

Figure 4. Derivative thermogravimetric (DTG) curves for the S3 sample; unexposed (control), exposed to water only (6000 W) and exposed to both water and ultraviolet light (6000 L/W).

Table IV. Onset Temperatures and Weight Losses for S3 Silicone Sealant

Sample S3	T_{onset} (°C)		T_{max} (°C)	Wt. loss (%)	T_{onset} (°C)		T_{max} (°C)	Wt loss (%)	Residue (%)
	TG	DTG			TG	DTG			
Control	457	407	565	46.9	699	670	740	21.6	31.6
6000L/W	483	397	555	46.9	691	659	738	21.6	31.6
6000W	486	405	569	44.3	703	679	747	22.7	33.0

The DTG curve for the S4 control silicone sample (Figure 5) shows that the sample starts to lose weight at a similar temperature (300°C) as the S1 and S3 series. From the data in Table V, it can be observed that the S4 series shows the largest total weight loss (75%) of all series studied, and that the control and exposed samples show similar weight losses. A comparison of the weight losses for this sample with those for the previous samples reveals that S4 loses more weight in the first region and less in the second. The peaks of the DTG curves for the control sample in both weight loss regions (Figure 5, control) have similar peak heights. UV radiation and/or water exposure seem to have an opposite effect on the shape of the peaks of the DTG curves for this series. Both exposed samples (Figure 5, 6000 and 6000 L/W), show two unresolved peaks for the first weight loss, but this peak becomes sharper for the sample exposed to water. In addition, the peak height of the second peak decreases slightly for the sample exposed to water, whereas it becomes sharper for the sample exposed to light. Although the DTG curves for the control and exposed samples have different shapes, the series does not seem to be significantly affected by the two types of weathering conditions used. However, it is more affected than S1, S2, and S3.

Table V. Onset Temperatures and Weight Losses for S4 Silicone Sealant

Sample S4	T_{onset} (°C)		T_{max} (°C)	Wt. loss (%)	T_{onset} (°C)		T_{max} (°C)	Wt loss (%)	Residue (%)
	TG	DTG			TG	DTG			
Control	542	496	620	56.1	723	712	750	19.1	24.8
6000L/W	530	477	619	55.5	730	719	753	19.3	25.3
6000W	498	439	593	54.8	702	685	741	19.3	25.9

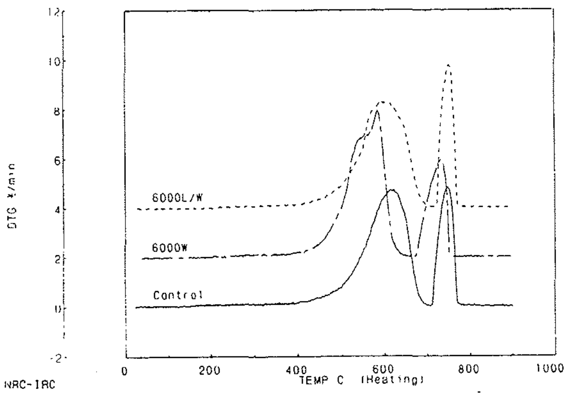

Figure 5. Derivative thermogravimetric (DTG) curves for the S4 sample; unexposed (control), exposed to water only (6000 W) and exposed to both water and ultraviolet light (6000 L/W).

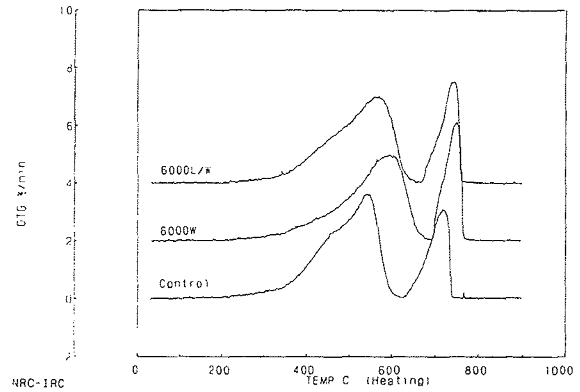

Figure 6. Derivative thermogravimetric (DTG) curves for the S5 sample; unexposed (control), exposed to water only (6000 W) and exposed to both water and ultraviolet light (6000 L/W).

Table VI. Onset Temperatures and Weight Losses for S5 Silicone Sealant

Sample S5	T_{onset} (°C)		T_{max} (°C)	Wt. loss (%)	T_{onset} (°C)		T_{max} (°C)	Wt loss (%)	Residue (%)
	TG	DTG			TG	DTG			
Control	447	338	586	47.0	710	682	747	17.9	33.7
6000L/W	425	331	560	47.9	693	656	739	17.4	35.0
6000W	436	338	561	48.2	692	657	729	17.6	35.3

The TG/DTG curves for control and exposed S5 silicone series are displayed in Figure 6 while the data are summarized in Table VI. A shoulder between 250°C and 500°C is observed for the control sample. It can also be seen that the first peak of DTG curve for the control sample is higher than the second one. Samples exposed to UV-radiation and/or water, do not show the shoulder on the first peak and the two weight losses occur at temperatures slightly higher than that of the control sample. They also show a slight decrease in the peak height of the first peak, with a proportional increase on the peak height of the second peak.

FTIR Analysis

Generally, there was very little change in the FTIR spectra for the five different sealants after 8000 hours of weathering. All of the sealant spectra contained the general peaks characteristic of the siloxane polymer.

The spectrum of the unexposed S1 specimen (Figure 7) shows a number of peaks characteristic of calcium carbonate: a broad band from 1600-1300 cm^{-1}, sharper peaks at 879 and 712 cm^{-1}, and weak peaks at 2513 and 1796 cm^{-1}. These are due to calcite (a type of calcium carbonate). The remaining bands are characteristic of a polydimethylsiloxane polymer. They include (10) the C-H stretching peaks at 2966 and 2904 cm^{-1}, the broad Si-O-Si band at 1200-1000 cm^{-1}, the Si-CH$_3$ peaks at 1267 and 822 cm^{-1}, and the peak at 700-660 cm^{-1}.

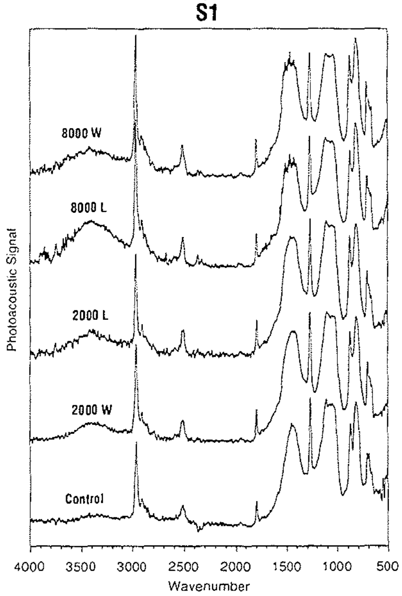

Figure 7. PAS-FTIR spectra for the S1 silicone sealant prior to weathering, after 2000 and 8000 hours of exposure in a weathering device.

Spectra of samples exposed for 2000, 4000 and 8000 hours to water and UV radiation/water spray closely resemble Figure 7 control. The only significant difference is the appearance of a broad OH band near 3400 cm^{-1}, which could be due simply to absorbed water.

The spectrum of the control S2 sample shows the same peaks observed in S1, corresponding to calcium carbonate and polydimethylsiloxane. The slightly different shape of the carbonate band at 1600-1300 cm^{-1} may indicate a different type of calcium carbonate (*e.g.* precipitated). Spectra of samples exposed for 2000, 4000 and 8000 hours to water and UV radiation/water spray resemble the spectrum of the unexposed sample, except for the appearance of a broad OH band near 3400 cm^{-1}. In addition, the sample exposed to water for 2000 hours displayed peaks at 2919, 2850, and 1579 cm^{-1}. The first two peaks are typical of long hydrocarbon -(CH$_2$)$_n$- chains, and the third could be due to carboxylate ions -COO-. Peaks at these positions are characteristic of calcium salts of fatty acids, for example calcium stearate. Originally, it was unclear whether these peaks originate from the sample itself (surface enrichment in calcium stearate additive) or from contamination.

Unlike the previous two materials, the S3 sealant is black. The presence of carbon black is probably responsible for the somewhat stronger baseline absorption observed in the spectra (about 5% as compared to less than 1% in the previous cases). Otherwise, the spectra show the same peaks as S1, arising from calcium carbonate and polydimethylsiloxane. Again, exposure to water or UV radiation/water spray for 2000, 4000 and

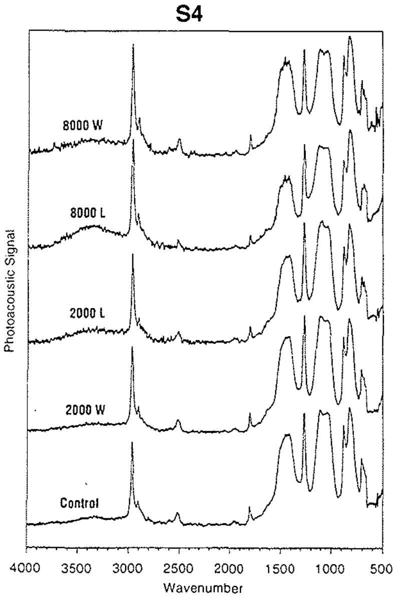

Figure 8. PAS-FTIR spectra for the S4 silicone sealant prior to weathering, after 2000 and 8000 hours of exposure in a weathering device.

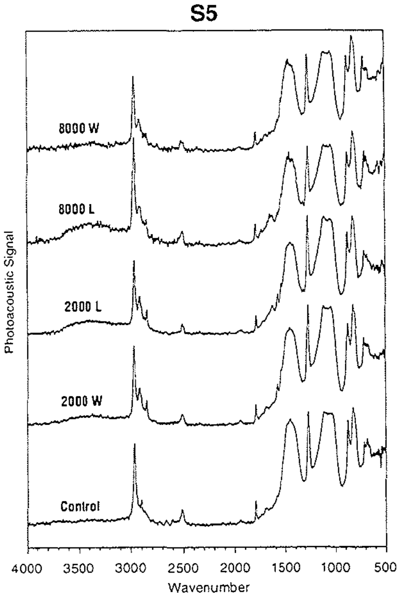

Figure 9. PAS-FTIR spectra for the S5 silicone sealant prior to weathering, after 2000 and 8000 hours of exposure in a weathering device.

8000 hours has little effect on the spectrum. The increase in OH absorption on exposure is less pronounced than in the previous two cases, but the samples exposed to UV radiation/water spray show signs of a decrease in the intensity of the carbonate peak at 1450 cm^{-1} with respect to the silicone peak at 1266 cm^{-1}. It is not clear whether this is due to loss of carbonate, a change in the nature of the carbonate species, or simply to compositional variations within the material.

The S4 spectra (Figure 8) showed the same peaks as before, namely calcium carbonate and polydimethylsiloxane. Once again, exposure to water or UV radiation/water spray for 2000, 4000 and 8000 hours had little effect on the spectrum.

The spectra for the S5 sealant showed once again the same components: calcium carbonate and polydimethylsiloxane (Figure 9). However, there is a weak shoulder near 1690 cm^{-1} not observed in the previous cases. Also, the notably higher absorption in the 700-500 cm^{-1} range could indicate the presence of another pigment such as titanium dioxide. The shape of the carbonate band is similar to that seen in S2. The samples exposed to water and UV radiation/water spray show an increase in OH absorption near 3400 cm^{-1}. The effect of water can be seen more clearly after subtraction of the unexposed sample spectrum (Figure 10). It is interesting to note that all four of the exposed samples show the peaks (in the subtracted spectra) at 2918, 2850, 1578, 1540 cm^{-1} characteristic of calcium stearate, as mentioned earlier in connection with S2.

The possibility was considered that the "calcium stearate" observed in some of the spectra could be transferred from the plastic bags used to store the samples. To check this, the bag used for the S5 sample exposed to water for 4000 hours was rubbed against a clean KBr window and the spectrum measured in transmission. The resulting weak spectrum corresponded to a fatty amide such as oleamide or erucamide. Such products are commonly used in the processing of polyethylene. There was no evidence of calcium stearate. Calcium carbonate is available in a form treated with stearic acid. It is possible that this type of calcium carbonate was used and that the weathering resulted in surface enrichment in stearate.

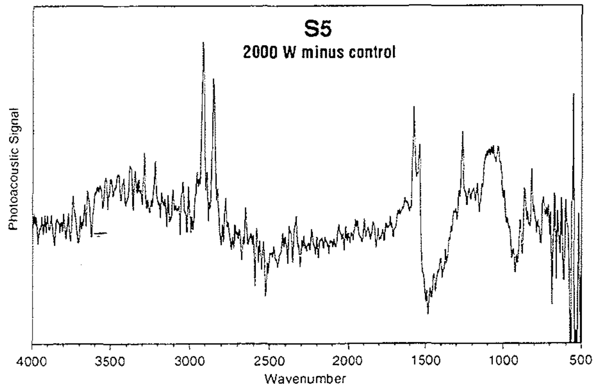

Figure 10. PAS-FTIR difference spectrum for the S5 silicone sealant (2000 hours exposure to water only - control). See text for explanation.

Conclusions

The five silicone-based materials all have a similar composition. The main components are a polydimethylsiloxane polymer and calcium carbonate; the S5 may also contain some titanium dioxide. Up to 8000 hours of exposure, all five materials are fairly resistant to the two types of weathering conditions employed. Only minor changes were observed using TG/DTG and PAS-FTIR spectroscopy. In some cases there is an increase in hydroxyl absorption (possibly signifying an increase in water absorption). Furthermore, the weathering of specimens S2 and S5 resulted in surface enrichment in calcium stearate. The main weight losses observed by TG/DTA are most likely due to the siloxane polymer and calcium carbonate. Additional work using a hyphenated technique such as TG/DTA-FTIR or quenching the sample at various temperatures would facilitate the identification of the various components.

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