THE APPLICABILITY OF MODERN ANALYTICAL TECHNIQUES TO DETECTION OF CHANGES IN ROOFING MEMBRANE MATERIALS BROUGHT ABOUT BY HEAT AGING

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1. INTRODUCTION

The U.S. Army Construction Engineering Research Laboratories (CERL) has been investigating the development of a test methodology for evaluating the service life of roofing membrane materials. As part of this effort, CERL conducted a study to investigate the applicability of strain energy (a mechanical test) and Fourier transform infrared (FTIR) spectroscopy (a chemical analysis) as methods for characterizing changes that roofing membrane materials may undergo upon exposure to elevated temperatures [1]. In the case of FTIR, the intent was to evaluate whether changes in the carbonyl index as a function of thermal exposure could be used as an indicator of the stability of the membrane materials. The carbonyl index is the ratio of the intensity of the carbonyl absorption band (i.e., C=O) to that of another band (such as C-H stretching or bending) in the spectrum. Increases in a material's carbonyl index after exposure may be an indication that oxidation occurred during the exposure. Measurements of both strain energy and carbonyl index have been used for specific types of membrane materials. Neither has been applied universally to the variety of membrane materials currently available [1].

CERL requested the U.S. National Institute of Standards and Technology (NIST) assist in its study and conduct analytical tests of heat-exposed membrane materials. This paper summarizes the results of the analyses. CERL selected the heat-exposure conditions and made arrangements for previously heat-exposed membrane materials to be sent to NIST. The types of samples were ethylene propylene diene terpolymer (EPDM), poly (vinyl chloride) (PVC), atactic polypropylene modified bitumen (APP), styrene-butadiene-styrene modified bitumen (SBS), and conventional built-up roofing (BUR).

The analyses conducted were: thermogravimetry (TG), differential scanning calorimetry (DSC), FTIR spectroscopy, secondary ion mass spectroscopy (SIMS), and nuclear magnetic resonance (NMR) spectroscopy. These modern analytical techniques were selected because they have been used successfully in characterizing organic materials and changes that occur during exposure to a variety of environments including heating. Note that the TG and DSC techniques are among those methods referred to as thermal analysis [2]. At present, a joint CIB/RILEM task group, under the auspices of CIB W.83/RILEM 120-MRS on Membrane Roofing Systems, is undertaking a study on the applicability of thermal analysis to characterizing roofing membrane materials [3]. The results of the present study should complement the efforts of the CIB/RILEM Committee.

In a another phase of the CERL study, Cash and Bailey [4] determined the strain energy-to-maximum load and also the carbonyl index for each sample. The results of the strain energy measurements were that, in general, few samples showed little change due to the heat exposure. Consequently, these authors questioned whether the heat exposure alone was sufficient to accelerate the deterioration process to produce changes evident in a practicable exposure period.

2. OBJECTIVE

The objective of the study was to apply modern methods of analysis, i.e., TG, DSC, FTIR, SIMS, and NMR, to the heat-exposed roofing membrane materials to determine whether the thermal exposure produced changes in the materials properties which could be quantified.

3. TEST SAMPLES

Table 1 summarizes the types (i.e., EPDM, PVC, APP, SBS, and BUR) and number of samples received from CERL. All were commercially available products. Controls were samples that had been maintained at room temperature (i.e., unaged or not subjected to heat exposure). The number of plies of each sample reflected their typical use in service. The EPDM and PVC samples were single-ply products. The SBS and APP modified bitumen samples were two-ply materials having the modified bitumen material adhered to a glass fiber felt with bitumen. Both the glass fiber felt and organic fiber felt BUR samples contained four plies.

Note in Table 1 that some samples were designated as having been exposed for 3000 hours at 23 °C. Reference to these samples is included in Table 1 to list fully the samples received. For purposes of this analytical study, there was no difference between samples "exposed" under those conditions and the controls, because neither had been subjected to elevated temperature. In the mechanical property phase of the CERL study [4], the strain energy of the samples exposed for 3000 hours at 23 °C had been determined.

The plan for analysis was to characterize first those samples that were heat exposed for 3000 hours at 80 °C. This was the most severe of the exposure conditions. If these initial analyses showed major differences between the control and the heat-exposed samples, then further analyses of samples exposed at the less severe conditions were to be conducted. In general, the results of the analyses showed no major differences between the controls and the samples exposed for 3000 hours at 80 °C. The following sections of this paper provide overviews of the analysis methods, descriptions of the test specimens, and typical results found for each method.

Table 1. Roof membrane samples in the study

Membrane Designation	Membrane Type	Exposure Condition[1,2]	
		Time, hours	Temp., °C
A	EPDM	672	80
		2000	80
		3000	23, 40, 80
B		3000	23, 40, 80
C		3000	23, 40, 80
D	PVC	672	80
		2000	80
		3000	23, 40, 80
E		3000	23, 40, 80
F		3000	23, 40, 80
G	SBS Mod-Bit[3]	672	80
		2000	80
		3000	23, 40, 80
H		3000	23, 40, 80
I		3000	23, 40, 80
J	APP Mod-Bit[3]	672	80
		2000	80
		3000	23, 40, 80
K		3000	23, 40, 80
L		3000	23, 40, 80
M	BUR-fiberglass	672	80
		2000	80
		3000	23, 40, 80
N	BUR-organic	672	80
		2000	80
		3000	23, 40, 80

[1]In addition to the exposure conditions listed, a control sample of each material was also received.
[2]Exposure conditions other than time and temperature were not known.
[3]The modified bitumen samples had a granule surfacing.

4. THERMOGRAVIMETRIC ANALYSIS

Thermogravimetry (TG) is a technique that measures the mass (or change in mass) of a specimen as a function of temperature. In the present study, specimens (generally 25 to 35 mg) were heated from 30 to 770 °C at a rate of 20 °C per minute. Pyrolysis was conducted in nitrogen gas at a flow rate of 40 mL/min from 30 to 600 °C. Then air was introduced at the flow rate of 40 mL/min to combust the residual organic material while continuing to raise the temperature to 750 to 800 °C. The instrument was allowed to cool to 30 °C and purged with nitrogen for about 5 minutes prior to the next analysis. Mass loss of the specimen was recorded as a function of temperature. Each analysis was conducted in duplicate.

The EPDM and PVC test specimens consisted of a small piece (diameter about 5 mm) taken across the entire thickness of the sheet material. In the case of the modified bitumen samples, granules on the surface were removed and test specimens were taken from both the surface and bulk of the sheet material. Similarly, for the BUR samples, test specimens of the conventional bitumen were taken from both the first layer of asphalt and within its bulk after removal of the first ply of felt.

Figs. 1 and 2 illustrate typical results of the TG analyses. In considering the curves presented, the temperature range from initial heating to 600 °C, over which pyrolyzable organic materials are liberated, is of interest. For the synthetic single-layer sheets (i.e., EPDM and PVC), the pyrolyzable organic materials include the base polymer and additives such as processing oils, stabilizers, and plasticizers. For the modified bitumens, the pyrolyzable organics include the asphalt and the polymer modifiers. Variations which occur in the percent pyrolyzable organics due to thermal exposure may be indicative of basic changes in the composition of the sheet including base polymer.

In reviewing Fig. 1, it is evident that the thermogravimetric curves for the PVC samples were essentially the same for the control and heat-exposed specimens. This indicated that the exposed samples did not significantly lose material (often called volatiles) during heating for 3000 hours at 80 °C.

Fig. 2 provides a comparison of an analysis of the bulk and surface of a modified bitumen sample. In the case of either the bulk or surface analysis, the percent mass remaining after heating to 600 °C was somewhat greater (2 - 4 %) for the heat-exposed specimens. This implied that some volatile components were lost from the samples during the heat exposure. This is not unexpected for bituminous materials which are known to have volatile components. However, this small difference (2 - 4 %) may be within the experimental error of the measurement. Analyses of some of the other bituminous samples in the study showed scatter in the mass loss data (spread between the replicate curves) which were of the order of 2 - 4 percent. Note in a comparison of Figs. 1 and 2 that more scatter was found for the curves of the bituminous materials than for the curves for the synthetic PVC materials. This was generally the case for all analyses, as the replicate analyses of any of the EPDM and PVC products showed more reproducibility than those for the bituminous products.
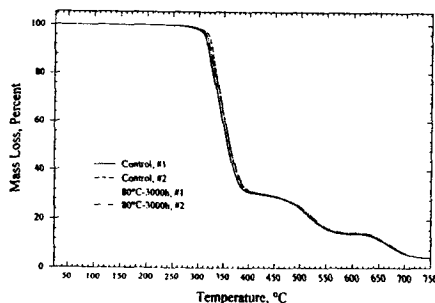

Fig. 1. TG analysis of the control (unaged) and heat-exposed (3000 hours at 80 °C) PVC Sample D.
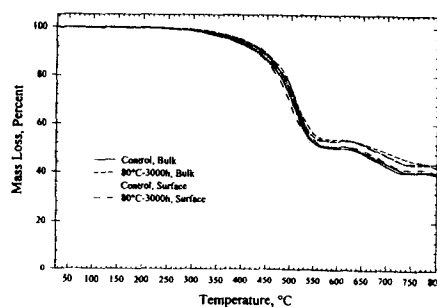
Fig. 2. TG analysis of the surface and bulk of the control (unaged) and heat-exposed (3000 hours at 80 °C) SBS modified bitumen Sample H.

5. DIFFERENTIAL SCANNING CALORIMETRY

Differential scanning calorimetry is a technique in which the difference in energy input into a material and a reference material is measured as a function of temperature. In this study, a modulated differential scanning calorimetry (MDSC) procedure was used for the analysis. In the MDSC method, the specimen is exposed to a steady rising temperature modulated by small-amplitude, sinusoidal temperature oscillations. In addition to providing a determination of the total heat flow into or from the specimen, the MDSC method allows for the mathematical separation of the total heat flow into reversing and non-reversing components. Reverse heat flow is associated with reversible thermal phenomena that occur within a specimen regardless of its thermal history, for example, heat capacity. A benefit of MDSC technique is enhanced capability for investigating the structure and behavior of materials.

The MDSC specimens (generally 12 to 20 mg in mass) were heated from -50 to 100 °C at a rate of 5 °C per minute with a reverse heat flow modulation of 0.5 °C/min. The analysis was performed in nitrogen gas at a flow rate of 30 mL/min. Prior to the next analysis, the heating chamber was allowed to cool to -50 °C and then purged with nitrogen for about 5 minutes. Total heat flow and reverse heat flow were recorded as a function of temperature. In general, only one analysis was conducted for each sample.

In conducting the analyses of the EPDM and PVC samples, the test specimen consisted of a small piece (diameter about 5 mm) taken across the entire thickness of the sheet material. In the case of the modified bitumen samples, granules on the surface were removed. Test specimens of the modified bitumen were taken from both the top of the sample and within its bulk. Similarly, for the BUR samples, test specimens of the conventional bitumen were taken from both the first layer of asphalt and within its bulk after removal of the first ply of felt.

In general, for all MDSC analyses, no differences were observed between the controls and heat-exposed samples. This finding was, in part, the reason why replicate specimens were not subjected to analysis. Figs. 3 and 4 illustrate typical results. In each figure, three curves are plotted: (1) heat flow, (2) reverse heat flow, and (3) derivative of the reverse heat flow. Fig. 3 is for the EPDM Sample A before and after heat exposure for 3000 hours at 80 °C. A major peak in the derivative curve for the reverse heat flow was found to occur at about 2 °C higher temperature (about -53 versus -55 °C) for the heat-exposed specimen. This peak corresponds to an inflection in the reverse heat flow curve associated with the glass transition temperature of EPDM roofing membrane materials. No significance was attributed to the 2-degree difference as previous experience with DSC measurements of EPDM roofing membrane materials have shown such scatter in replicate data on the same sample [5].

Similarly, Fig. 4 is for the SBS Sample I before and after heat exposure for 3000 hours at 80 °C. As was the case for the EPDM Sample A, the curves for these control and heat-exposed SBS specimens showed little difference.
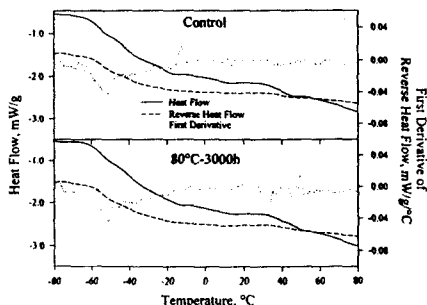

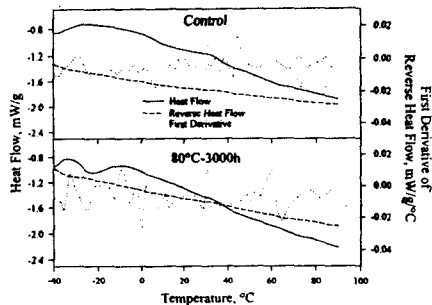Fig. 3. MDSC analysis of the control (unaged) and heat-exposed (3000 hours at 80 °C) EPDM Sample A.

Fig. 4. MDSC analysis of the control (unaged) and heat-exposed (3000 hours at 80 °C) SBS modified bitumen Sample I.

6. FOURIER TRANSFORM INFRARED SPECTROSCOPY

Fourier transform infrared spectroscopy (FTIR) is an analytical method that determines a material's absorbance of infrared radiation as a function of frequency. Analysis of the spectrum obtained provides information on a material's chemical structure, particularly the presence of functional groups. In the present study, the attenuated total reflectance (ATR) technique was used to analyze the surface of the specimen directly (granule surfacings on modified bitumens were removed). In the ATR technique, the specimen surface is brought into contact with an infrared-transparent prism. The infrared beam is reflected on the specimen-prism interface. If the specimen is an infrared absorber, the total reflection is attenuated in the corresponding frequency regions.

A spectrum consisted of the average of 1000 scans at a resolution of 4 cm^{-1} and was obtained in purged dry air using an incident angle of 45°. In general, one analysis was conducted for each of the controls and samples aged for 3000 hours at 80 °C. In this study, the carbonyl peak was of interest, because its presence after exposure may provide evidence that oxidation of the sample occurred. To quantify the analysis, the intensity of the carbonyl absorption peak (at about 1700 cm^{-1}) was normalized with respect to that of a carbon-hydrogen stretching absorption (at about 2919 cm^{-1}). In normalizing each spectrum, the intensity of all absorption bands was divided using computer software by the intensity of the 2919 cm^{-1} band; i.e., the absorption at 2919 cm^{-1} was set to one. After normalization, difference spectra (where the control spectra were subtracted from those of the companion spectra of the heat-exposed samples) were generated using computer software. A positive peak in a difference spectrum such as that associated with a carbonyl group is indicative of an increase of a functional group during exposure.

The general results of the FTIR analyses were that major differences were not seen between the carbonyl absorption in the spectra of the control and the specimens heat-exposed for 3000 hours at 80 °C. In the case of two PVC Samples (D and F), some differences were observed, but were difficult to interpret. Figs. 5 and 6 show typical FTIR spectra. They were obtained from EPDM Sample A and SBS Sample G, respectively. Note the absence of a positive carbonyl peak in the 1700 cm^{-1} region of the difference spectra, indicating that carbonyl containing species were not greater in the heat-exposed specimens than in the controls.

Fig. 7 presents two difference spectra for PVC Sample D: (a) heat-exposed for 3000 hours at 80 °C minus the control, and (b) heat-exposed for 3000 hours at 40 °C minus the control. The former analysis was first conducted and a positive carbonyl absorption was observed at 1725 cm^{-1} in the difference spectrum (Fig. 7a). The type of chemical species (e.g., aldehyde, ketone, or ester) and its origin were not assigned. PVC roofing membrane materials contain ester plasticizers. Thus, the observed positive carbonyl peak in the difference spectra could be due to differences in the amount of ester in the control and heat-exposed samples or, possibly, to oxidation of the heat-exposed sample which may or may not be accompanied by loss of plasticizer. Because of this complexity, it was not possible in this limited study to determine the reason for the observation. More detailed investigation would be required.
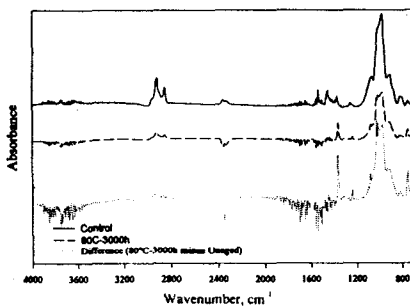

Fig. 5. FTIR spectra for EPDM Sample A: (a) control), (b) heat-exposed for 3000 hours at 80 °C, and the difference (normalized on 2919 cm^{-1}) between spectrum b minus spectrum a.
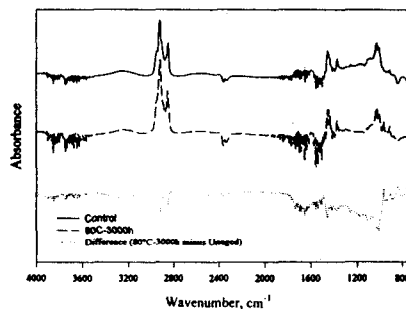
Fig. 6. FTIR spectra for SBS modified bitumen Sample G: (a) control), (b) heat-exposed for 3000 hours at 80 °C, and the difference (normalized on 2919 cm^{-1}) between spectrum b minus spectrum a.
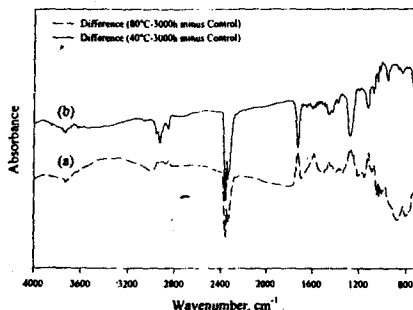
Fig. 7. FTIR difference spectra normalized on 2919 cm⁻¹ for PVC Sample D: (a) heat-exposed for 3000 hours at 80 °C minus control and (b) heat-exposed for 3000 hours at 40 °C minus control.

Because of the appearance of the positive carbonyl peak in the difference spectrum for the specimen exposed for 3000 hours at 80 °C, the analysis of the specimen exposed for 3000 hours at 40 °C was performed. It was of interest to determine whether the difference spectrum for the specimen exposed at the lower temperature also showed a positive carbonyl peak. In this case, the difference spectrum showed a pronounced negative peak at 1725 cm⁻¹ (Fig. 7b), indicating more carbonyl containing species in the control than in the heat-exposed specimen. No interpretation as to why the difference spectrum of the specimen exposed at the higher temperature displayed the positive carbonyl, while that exposed at the lower temperature displayed a negative carbonyl is given. These limited observations illustrate the complexity of characterizing exposed plasticized PVC materials using FTIR analysis and the carbonyl index.

7. SECONDARY ION MASS SPECTROSCOPY

Secondary ion mass spectroscopy (SIMS) is a general surface analysis technique that provides information on chemical composition. It is sensitive to foreign species in solids, particularly in the top monolayer. In SIMS, the surface of the specimen is sputtered (i.e., bombarded with an energetic ion particle) and surface layers are eroded as ions. Collection and analysis of the sputtered ionic species (i.e., secondary ions) provides an indication of the molecular structure of the material removed. The analysis of the sputtered species is conducted using mass spectroscopy. Both positive and negative ions sputtered from the surface can be analyzed but in separate runs.

In the present study, sputtering was conducted for 60 seconds using a gallium positive ion source at a nominal energy of 25 keV. The secondary ions were analyzed using a time-of-flight mass spectrometer. The section of analyzed surface area of the specimen was about 0.2 by 0.2 mm.

As a preliminary step in determining whether the SIMS method had applicability to the analysis of roofing membrane materials, controls and heat-exposed specimens of EPDM A and of PVC D were analyzed. If these analyses had shown differences between the comparable control and heat-exposed specimens, then further analyses of other EPDM and PVC samples would have been conducted. The technique was not considered applicable to the bituminous samples because, during analysis, the specimens might possibly release volatile components that could contaminate the apparatus.

Figs. 8 and 9 show the results of the positive ion SIMS analyses of the EPDM Sample A. These plots give the mass to charge ratio (m/z) of the ionic species versus the relative abundance (counts) of each ion. Note on the plots that notations have been made as to either the type of ionic species or the mass number. As evident in Figs. 8 and 9, the results of the EPDM analysis showed that, in general, little difference was observed between the mass spectrograms of the comparable pairs. The same was true for the PVC analysis. The implication of the findings was that the surfaces of the EPDM and PVC samples were not altered by the heat exposure. A notable difference was for the relatively greater abundance of the $C_4H_{11}^+$ species in the
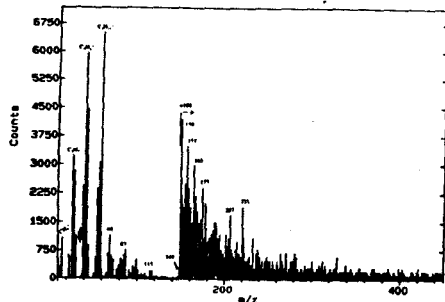
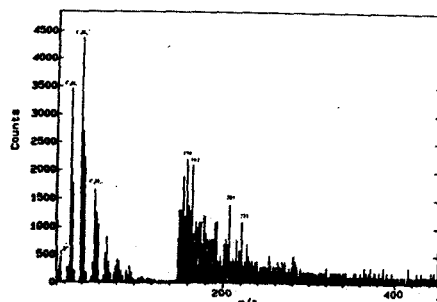Fig. 8. SIMS analysis of the control (unaged) EPDM Sample A.

Fig. 9. SIMS analysis of the heat-exposed (3000 hours at 80 °C) EPDM Sample A.

mass spectrogram of the control EPDM specimen (Fig. 8) versus that of the heat-exposed specimen (Fig. 9). Reasons for the observation were not ascertained.

Further SIMS analysis were not conducted after completing the preliminary analyses of the EPDM Sample A and PVC Sample B. One reason was that major differences between the controls and heat-exposed specimens were not seen. Also, it was felt that the application of the SIMS technique to roofing membrane materials is somewhat premature at this time. In general, the SIMS technique has had relatively little application to synthetic organic materials, and the lack of experience makes interpretation of the mass spectrograms difficult. Also, the present analysis used formulated membrane products that contain a variety of components such as carbon black, plasticizers, processing oils, and heat and UV stabilizers in addition to the base polymer. Changes in the mass spectrograms upon heat exposure could be associated with any of these components including the base polymer. Knowledge of the performance of the individual components in a SIMS analysis, where possible, is needed to complement the analysis of the formulated product.

8. NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

Nuclear magnetic resonance (NMR) spectroscopy is a technique for determining the chemical structure of organic compounds. The method provides information on the chemical environment of the atoms (e.g., hydrogen or carbon) in the molecules under analysis. Analyses may be conducted on specimens in the liquid state or solid state. In addition to obtaining information on the chemical environment of the atoms under analysis, solid state NMR provides information on the mobility of the molecules in the solid.

In this study, solid state carbon nuclear magnetic resonance (CMR) was performed on control and heat-exposed (3000 hours at 80 °C) EPDM Sample A, PVC Sample D, and SBS Sample G. The EPDM and PVC specimens had rectangular dimensions of about 6 by 10 mm; whereas the SBS specimen had cylindrical dimensions of about 6 mm diameter and 10 mm length. The granular surfacing and layer of felt were removed from the SBS specimen. As was the case with the SIMS analyses, if this preliminary NMR analyses showed major differences between the control and exposed samples, further analyses of other samples were to be conducted.

NMR spectroscopy has had little use for characterization of roofing membrane materials [6]. In conducting the present analysis, it was found to be applicable to these materials but time-consuming. Consequently, the technique may be considered more applicable for research purposes and not for general analysis of membrane products.

Figs. 10 and 11 illustrate the results of the NMR analyses. They were obtained for the EPDM Sample A and PVC Sample D, respectively. The figures show plots of the intensity of the absorptions versus chemical shift expressed in ppm (parts per million) from a relative standard (taken as 0 ppm). Chemical shift is the expression of the separation of the resonance frequencies of the various nuclei (in this case, carbon) in
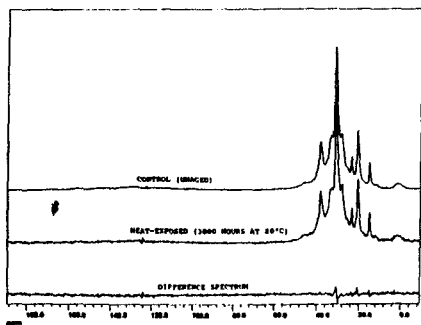
Fig. 10. NMR analysis of the control (unaged) and heat-exposed (3000 hours at 80 °C) EPDM Sample A; a difference spectrum of the two is also shown.
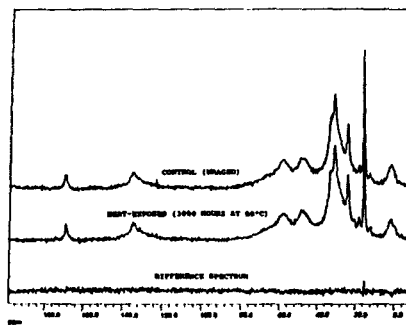

Fig. 11. NMR analysis of the control (unaged) and heat-exposed (3000 hours at 80 °C) PVC Sample D; a difference spectrum of the two is also shown.

different structural environments from an arbitrarily chosen standard. Figs. 10 and 11 show three spectra: (1) the control, (2) the heat-exposed specimen, and (3) the difference between these two. No difference in the spectra for the control and heat-exposed specimens was observed. Note in both figures that the difference spectra are essentially horizontal lines. The minor peaks in the 20 to 30 ppm region of Fig. 10 were considered insignificant. This suggested no major compositional differences between the control and heat-exposed specimens. Similar results indicating no major heat-exposure effects on the composition for the SBS sample were found. However, in this case, the NMR results hinted that aromatic molecules in the specimens may have become less mobile after heat-exposure. The finding was qualitative and reasons for its observation were not investigated.

9. SUMMARY

Samples of commercially available EPDM, PVC, SBS modified bitumen, APP modified bitumen, and BUR membrane materials were submitted to NIST by the U.S. Army Construction Engineering Research Laboratories. Both controls (unaged) and heated-exposed samples were included. Analyses using TG, MDSC, FTIR, SIMS, and NMR methods were conducted to determine whether heat exposure of the membrane materials produced deterioration that could be quantified. The TG, MDSC, and FTIR analyses were applied to all samples heated for 3000 hours at 80 °C; SIMS and NMR were applied to a limited number of specimens.

The results of the study were positive in that the objective to analyze heat-exposed roofing membrane materials using modern analytical methods was met. The study demonstrated that the SIMS method could be applied to synthetic membrane materials such as EPDM and PVC, although the interpretation of the method's findings may be difficult because of a lack of experience in applying the method to these materials. Additionally, the study illustrated that the NMR method was applicable to both synthetic and bituminous membrane materials, although the analysis can be time-consuming and, thus, not yet practicable for routine use.

Results of the analyses conducted on the roofing membrane materials indicated that, in general, no major differences were found between comparable pairs of the controls and heat-exposed samples. The most severe exposure condition was 3000 hours at 80 °C. Apparently, the membrane samples were stable under these conditions to the extent that no major changes occurred that were detectable by the five analytical methods employed. These analytical methods have been well established as being sensitive for characterizing polymeric materials and changes they may undergo during various environmental exposures. Consequently, if major compositional changes had been brought about by the heat-exposure, it would have been expected that the changes would have been observable by one or more of these methods.

10. ACKNOWLEDGMENTS

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