THE APPLICATION OF THERMAL ANALYSIS TO THE CHARACTERIZATION OF EPDM ROOFING MEMBRANE MATERIALS AFTER EXPOSURE IN SERVICE

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This study utilized thermal analysis (TA) methods for the characterization of membrane materials sampled from roofs in service. The TA methods used were thermogravimetry (TG), differential scanning calorimetry (DSC) and thermal mechanical analysis (TMA). Three black (carbon black filled) and eight white (titanium dioxide pigmented) ethylene-propylene-diene terpolymer (EPDM) materials were analyzed after exposures ranging from 12 to 98 months in a variety of climates. The results indicated that in-service materials possessed TA properties similar to those characteristic of new membrane materials.

KEYWORDS

Differential scanning calorimetry (DSC), EPDM, Thermal analysis (TA), thermal mechanical analysis (TMA), thermogravimetry (TG).

INTRODUCTION

In 1987, more than 50 members of the U.S. roofing industry participated in a roundtable discussion to assess the needs for research to improve the performance of low-sloped roofs.[1] Two of the recommendations from the roundtable were that improved test methods were needed to characterize and evaluate new membrane materials, and more data on properties of the materials after their exposure in service were needed. Subsequently, in 1988, an international roofing committee, working under the joint auspices of CIB and RILEM,* advocated that thermal analysis (TA) methods be investigated for use in characterizing membrane materials and the changes that may occur on aging.[2] This committee acknowledged that little research had been reported on the application of TA methods to roofing and, thus, recommended that research be conducted to provide the technical basis for this application. The use of thermal analysis methods for characterization of membrane materials, as recommended by the CIB/RILEM Committee, presented one promising way for responding to the recommendation of the U.S. roofing roundtable.

Thermal analysis is a generic term for a group of measurement techniques which determine material properties as a function of temperature. These techniques can usually provide highly reproducible results with very small sample sizes.[3] The TA methods used in this study were thermogravimetry (TG), which measures changes in mass, differential scanning calorimetry (DSC), which measures relative heat flux and in turn heat capacity, and thermal mechanical analysis (TMA), which measures changes in volume or length.

Past research aimed at the application of TA methods to roofing membrane characterization includes papers by Cash,[4] Farling,[5] Backenstow and Flueler,[6] and Gaddy et al.[7,8] These papers reported thermal analysis data acquired from new and artificially aged membrane materials, but did not address the analysis of the material after in-service exposure. Cash[4] reported on the application of DSC for the characterization of ethylene- propylene-diene terpolymer (EPDM), neoprene, chlorinated polyethylene (CPE) and polyvinyl chloride (PVC). He concluded that DSC could be used to identify the type of polymer in a single-sheet, differentiate between products of manufacturers and differentiate between artificially weathered and new sheets.

Most reports on the use of TA methods for the characterization of roofing membrane materials have been along the guidelines suggested by CIB/RILEM.[5-8] Two papers [5,6] reported on the characteristics of EPDM, PVC and polymer-modified bituminous materials using TG, DSC and dynamic mechanical analysis (DMA) methods. In addition, the application of torsion pendulum analysis to the characterization

*CIB is an acronym for Conseil International du Batiment pour la Recherche, l'Etude et la Documentation (International Council for Building Research Studies and Documentation); RILEM is an acronym for Reunion Internationale des Laboratoires d'Essais et de Recherches sur les Materiaux et les Constructions (International Union for Testing and Research Laboratories for Materials and Structures).

of these membrane materials has been described.[6] Two other papers[7,8] focused on the analysis of EPDM before and after exposure to the conditions given in ASTM D 4637, "Standard Specification for Vulcanized Rubber Sheet Used in Single-Ply Roof Membrane."[9] In these four papers, it was concluded that the TA techniques studied are useful for membrane characterization, but that further study is necessary to determine the connection between TA results and in-service performance. In particular, it is desirable to determine whether changes observed by TA, following either natural or artificial exposure, are detrimental to performance.

OBJECTIVE AND SCOPE

This study reports thermal analysis data obtained on EPDM membrane materials sampled from roofs in service and compares the results with those obtained for new samples. Additionally, load-elongation measurements were conducted on specimens removed from the roofs using a standard test method often applied to membrane materials.[9] A limitation of the study was the unavailability of control (unexposed) membrane materials, which were characterized before roof installation. Consequently, changes which may have occurred due to in-service exposure could not be determined. In spite of this limitation, the authors believe that it is beneficial to report the TA results, because they contribute to establishing a data base on field performance, as recommended by the U.S. roundtable panel.[1]

EXPERIMENTAL

Three samples of black and eight samples of white EPDM sheet membrane materials removed from roofs in service were included in the study (Table 1).

All membrane samples were reported to be performing well by the individuals supplying them. Visible and microscopic examinations of the exposed surfaces provided no evidence of unacceptable deterioration.

The thermal analysis methods and procedures used in this study are described in the Appendix. Table 2 summarizes the test conditions of each of the TA methods used.

RESULTS AND DISCUSSION

Thermogravimetry

Figure 1 presents mass loss versus temperature curves which were typical for the exposed, in-service black and white EPDM membrane materials.[5,8] The curves showed specimen mass loss over two distinct temperature ranges: (1) from onset of heating to about 550°C and (2) after the addition of air at 600°C to the termination of heating at 770°C (only for the black membranes). This separated the materials into their compositional groups: (1) organic components pyrolyzed below 600°C, composed of the EPDM polymer and modifiers, (2) carbonaceous materials, primarily carbon black[5] (not present in the white samples), and (3) ash which remained after oxidation.

The compositional group of prime interest is the organics pyrolyzed below 600°C. Variations in the percent organic materials on exposure are important because they may be indicative of changes in the basic composition of the sheet including the polymer structure. The mass-loss values for the three compositional groups of the test specimens are given in Table 3. In the case of the organic components, the values for the black specimens and the white specimens ranged from 56 to 60 weight percent and 50 to 58 weight percent, respectively. As previously indicated, the unavailability of control specimens precluded determination of the extent of change of the percent organics over the service time of these specimens. Nevertheless, it was found that these data covered approximately the same range of percent-organic components determined[8] by the TG analysis of new EPDM membrane materials (Table 3).

Differential Scanning Calorimetry

DSC measures the heat capacity of a material as a function of temperature. Transitions occurring in the material are demonstrated by inflections in the temperature-heat capacity curve. Figure 2 is a DSC curve for a white EPDM specimen removed from a roof. The curve is typical for all specimens in the study. The key feature of the curve is the inflection over the temperature range from −59 to −50°C. This inflection is indicative of the glass transition temperature (T_g) range of the material. The temperature range for the inflection shown in Figure 2 is rather broad for a single transition and may reflect a series of transitions which often appear in copolymer systems.[10] The overall nonlinearity of the curve in Figure 2 is a result of the instrument baseline instability over a wide temperature range and is not reflective of the material. Additionally, the peak occurring at approximately 30°C is due to a loss of crystallinity by the semi-crystalline regions of the EPDM. For EPDM, this loss of crystallinity is known to occur over the temperature range of −40 to 40°C depending on the processing and composition.[10]

In the present study, the T_g is taken as the midpoint of the inflection in the DSC curve. Table 4 provides the values of the glass transition temperatures as determined by DSC for the EPDM roof specimens. They ranged from −63 to −56°C for the black materials, and −59 to −50°C for the white materials. Similar to the findings from TG, these data covered approximately the same range of glass transition temperature determined[8] by the DSC analysis of new EPDM membrane materials (Table 4).

Thermal Mechanical Analysis

TMA measures a change in specimen length or volume as a function of temperature. This provides a measure of the material's coefficient of thermal expansion which is the slope of the specimen length-temperature line. When a material undergoes a transition (e.g., glass transition), a change in the slope of the line occurs.[5]

Figure 3 shows a TMA plot which was typical of those obtained. The glass transition (i.e., change in the slope of the specimen length-temperature line) occurs at −37°C. Table 5 lists the glass transition temperatures determined by TMA for all specimens. They ranged from −44 to −31°C, which was as much as 10°C higher than those determined for the new materials.

Comparison of the T_g data determined by DSC and TMA (Table 4 versus Table 5) indicates that the values found using TMA were as much as 22°C higher than those measured by DSC. This was not unexpected because it is known that the value of the glass transition temperature depends upon the method of analysis.[11] Farlling[5] reported T_g determined by DMA that were 26°C higher than that obtained by DSC. The samples in the present study showed higher

T_g values using TMA in comparison to those determined by DSC because the TMA measures the change in volume of the material and DSC determines the inflection in the heat capacity curve.[5]

Load-Elongation

Elongation is a property often selected as an indicator of allowable change in the EPDM membrane material during exposure. For example, ASTM D 4637, Standard Specification for Vulcanized Rubber Sheet Used in Single-Ply Roof Membrane,[9] requires that elongation of the roofing sheets be determined after heat exposure and not be less than 200 percent. It has been reported from field data that ultimate elongation of EPDM membrane materials is affected more during exposure than is tensile strength.[12,13]

Table 6 shows the load-elongation results for the EPDM membrane materials exposed in service. As is evident, the samples showed a greater variability in the range of values of ultimate elongation, ultimate stress and modulus at 300 percent elongation than those of the properties measured using the thermal analysis techniques. For example, the ultimate elongation ranged from 230 to 810 percent.

ASTM D 4637[9] specifies 300 percent as the minimum ultimate elongation of new EPDM membrane materials. Note in Table 6 that all but one sample (7W) displayed ultimate elongations greater than this ASTM requirement.

COMMENTARY

In the introductory section of this paper, it was stated that, in using thermal analysis techniques to characterize membrane materials after exposure in service, judgments need to be made as to whether any observed changes in properties are detrimental to performance. Because control (unaged) samples of the EPDM membrane materials investigated were not available for analysis, direct commentary on this point cannot be offered. EPDMs have been described as having satisfactory weather and heat resistance,[14,15] although these properties depend on the formulation of the rubber. Indirectly, the limited TA data obtained in the present study are consistent with such descriptions of the weathering characteristics of EPDM. Obviously, additional study, particularly involving materials which are well characterized before placement on exposure, is needed to allow the development of criteria for judging whether observed changes in TA properties are acceptable or not.

On a final point, the present study, as well as previous investigations,[7,8] have shown that thermal analysis methods are readily applicable to EPDM membrane materials. The relatively small sample size and reproducibility of the methods makes them attractive for characterizing samples taken from roofs in service. Although this work has been limited to EPDM, it suggests that the methods would also be suitable to other membrane materials, and that, as recommended by the CIB/RILEM Committee,[2] investigations characterizing other membranes after exposure should be conducted.

SUMMARY AND CONCLUSIONS

This study provided data on the thermal analysis and load-elongation properties of EPDM membrane materials sampled from roofs in service. Little data are available in the literature on the characterization of these materials after field exposure. Three black and eight white EPDM membrane materials were obtained from roofs after in-service exposure ranging from 12 to 98 months. The samples were subjected to thermal analysis using TG, DSC and TMA. Load-elongation measurements were conducted to provide data on mechanical properties prescribed by a standard test method.

For the indirect comparison made between the samples taken from roofs in service and new, commercially available samples, the membrane materials did not show differences in glass transition temperature or organic component content between the in-service samples and the new samples of both carbon black filled and titanium dioxide pigmented EPDM.

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APPENDIX

A.1 Thermal Analysis Methods

Thermogravimetry—TG was performed using the Perkin-Elmer** Model TGS-2. The specimens (5 to 15 mg) were heated from 50 to 770°C at a rate of 20°C per minute. The procedure followed the CIB/RILEM recommendation.[5] Pyrolysis was conducted in nitrogen gas at a flow rate of 40 mL/min. until 600°C was reached, and then air was introduced at the same flow rate to combust the residual material. The instrument was allowed to cool to 50°C and then purged with nitrogen for about 5 minutes prior to the next run. Trials were performed prior to the test samples on a well characterized EPDM and the experimental coefficient of variation was found to be ±2 percent for TG.

Differential Scanning Calorimetry—This analysis was performed using a Perkin-Elmer DSC-2C, which was modified to operate using liquid nitrogen coolant. This allowed for stable temperatures down to −100°C.

Samples were prepared by using a paper hole punch to make round samples (dia. 7mm) that were weighed and then wedged into aluminum DSC sample holders, which were used without tops. The tight fit of the samples allowed for good thermal contact.

Preliminary tests showed that the open top did not adversely affect the results. The specimen and holder were placed in the test chamber along with an empty pan for reference, which was washed in a flow of helium gas at a rate of 40 mL/min. throughout the analysis. The specimen was stabilized at −100°C before heating at 10°C/min. to a maximum temperature of 200°C. Preliminary trials were performed on well characterized membrane material and the test method was found to have experimental variability of ±5°C.

Thermal Mechanical Analysis—TMA was performed using the Perkin-Elmer Model TMS-2. The specimens were cut from the sheets using an office hole punch yielding circles of 7mm diameter. The samples were tested over the temperature ranges of −100 to 80°C in the expansion mode and the transition was considered to be the onset of the change in coefficient of thermal expansion. Heating was performed at 20°C/min. in a helium environment to minimize condensation on the sample. All samples were allowed to equilibrate at −100°C before testing was begun. Trials were performed prior to the test samples on a chemically well characterized EPDM and the experimental coefficient of variation of the T_g was found to be ±3°C.

A.2 Load-Elongation Tests

Load-elongation testing was performed according to ASTM D 412, Test Methods for Rubber Properties in Tension, (Die C) using an Instron Series IX Automated Materials Testing System. Elongation was measured using an automated extensometer with a gauge length of 25mm. The specimens were elongated at 518 mm/min. Preliminary trials were performed on well characterized membrane material and the test method was found to have experimental variability of ±2 percent.

Sample Designation	Color	Age (months)	Location
1B	black	98	Iowa
2B	black	24	Iowa
3B	black	60	Illinois
1W	white	48	Iowa
2W	white	96	Texas
3W	white	48	Colorado
4W	white	?	Florida
5W	white	62	Illinois
6W	white	60	Kansas
7W	white	12	Kansas
8W	white	86	Ohio

Table 1 In-service conditions.

TA Method	Temperature Range (°C)	Heating Rate (°C/min.)	Atmosphere
TG	50 to 600	20	nitrogen
	600 to 770		air
DSC	−100 to 200	10	helium
TMA	−100 to 80	20	air

Table 2 Thermal analysis test conditions

***Certain trade names or company products are mentioned in the text to specify adequately the experimental procedure and equipment used. In no case does such indication imply recommendation for endorsement by The Johns Hopkins University, the National Institute of Standards and Technology or The University of Akron, nor does it imply that the products are necessarily the best available.*

Sample Designation	Compositional Group, Mass Percent		
	Organics	Carbonaceous	Ash
1B	59	31	10
2B	60	29	11
3B	56	28	14
1W	50	0	49
2W	52	0	46
3W	58	0	41
4W	57	0	43
5W	55	0	45
6W	56	0	44
7W	57	0	43
8W	51	0	49
New Black Range*	54 to 59	26 to 42	7 to 15
New White Range**	50 to 58	0	43 to 50

*Range of values determined for 3 new black membranes.[8]
**Range of values determined for 3 new white membranes.[8]

Table 3 Mass percent of each component as determined by TG for samples exposed in service.

Sample Designation	Glass Transition Temperature (°C)
1B	−63
2B	−62
3B	−56
1W	−50
2W	−51
3W	−59
4W	−56
5W	−52
6W	−58
7W	−59
8W	−50
New Black Range*	−63 to −54
New White Range**	−71 to −57

*Range of values determined for 3 new black membranes.[8]
**Range of values determined for 3 new white membranes.[8]

Table 4 Glass transition temperatures as measured by DSC for samples exposed in service.

Sample Designation	Glass Transition Temperature (°C)
1B	−43
2B	−44
3B	−41
1W	−39
2W	−31
3W	−37
4W	−41
5W	−36
6W	−42
7W	−43
8W	−31
New Black Range*	−55 to −41
New White Range**	−47 to −45

*Range of values determined for 3 new black membranes.[7]
**Range of values determined for 3 new white membranes.[7]

Table 5 Glass transition temperature as determined for samples exposed in service using TMA.

Sample Designation	Ultimate Elongation (%)	Ultimate Stress (MPa)	Modulus @300% (MPa)
1B	640	12.6	2.5
2B	350	11.3	3.8
3B	370	13.1	3.8
1W	320	9.8	1.9
2W	650	7.6	2.1
3W	710	9.3	1.5
4W	610	10.2	2.3
5W	760	9.1	1.6
6W	810	6.8	2.9
7W	230	10.5	NA
8W	520	6.8	1.8
New Black*	570-790	9.9-12.7	1.7-2.3
New White**	600-980	10.8-13.4	1.3-2.0

*Range of values determined for 3 new black membranes.[7]
**Range of values determined for 3 new white membranes.[7]

Table 6 Load-elongation results for in service materials.

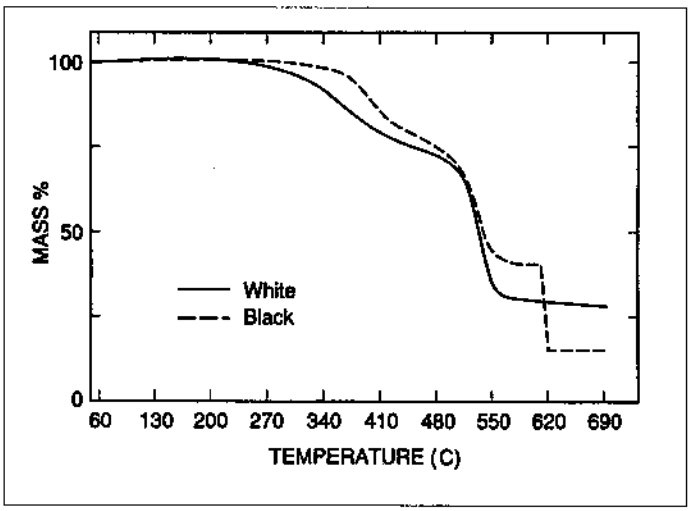

Figure 1 Typical TG curves.

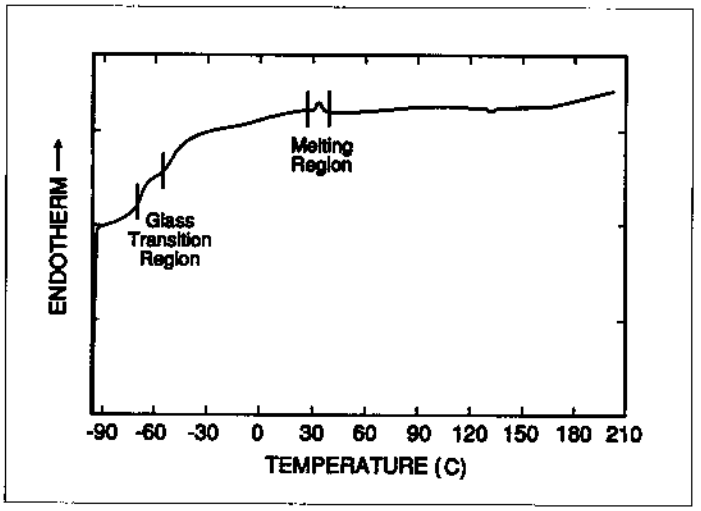

Figure 2 Typical DSC curve.

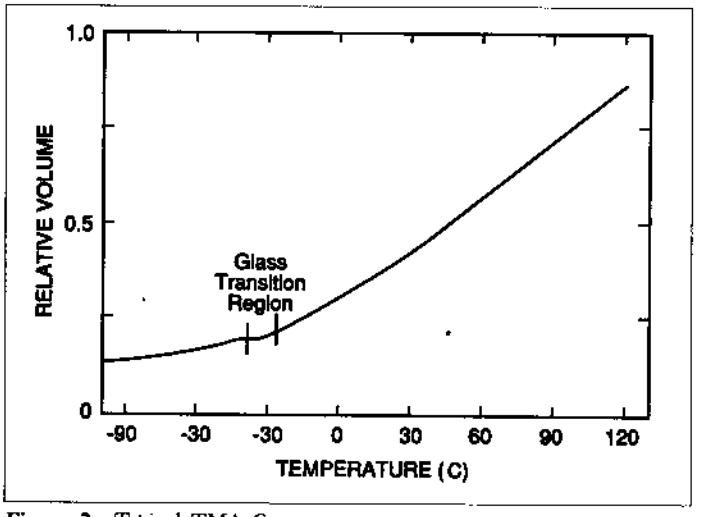

Figure 3 Typical TMA Curve.