Thermochimica Acta, 226 (1993) 77–84
Elsevier Science Publishers B.V., Amsterdam

Evaluating the effects of aging on the thermal properties of EPDM roofing materials [1]

James J. Penn [a] and Ralph M. Paroli [b,*]

[a] *Seiko Instruments USA, Inc., 981 Busse Road, Elk Grove Village, IL 60007 (USA)*
[b] *Institute for Research in Construction, National Research Council of Canada, Ottawa, Ontario K1A 0R6 (Canada)*

(Received 6 August 1992; accepted 11 May 1993)

Abstract

Two ethylene–propylene–diene monomer (EPDM) roofing membranes (111 and 112) were artificially aged in air-circulating ovens set at 130°C for 7 and 28 days. The effects of aging were studied by comparing various chemical data obtained by thermoanalytical techniques. The techniques used were dynamic mechanical analysis (DMA), thermomechanical analysis (TMA), differential scanning calorimetry (DSC) and simultaneous thermogravimetry/differential thermal analysis (TG/DTA). These techniques were found to be useful in monitoring and characterizing the influence of aging on the chemical and physical properties of EPDM roofing materials. Heat aging induced a significant change in T_g, the coefficient of thermal expansion (CTE), and the chemical composition for EPDM 111. This was not the case for EPDM 112. Based on these results, it was found that EPDM 112 was less affected by heat aging than EPDM 111.

INTRODUCTION

The availability of a wide range of roofing membranes, e.g. PVC, atactic polypropylene (APP)- styrene–butadiene–styrene (SBS)-modified bitumens, has changed the approach that must be used to characterize these materials. In the past, the main indicator of quality and/or performance was mechanical testing. The variety of roofing membranes and reinforcement makes it difficult to predict the durability of materials exclusively on mechanical properties. The mechanical characteristics of these materials are also related at the molecular level which is controlled by chemical composition and molecular arrangement.

EPDM (ethylene–propylene–diene monomer) is an elastomeric material that is used frequently in the construction industry as a roofing material. One of the common concerns of EPDM and other materials is the

* Corresponding author.

[1] Presented at the 21st Annual NATAS Conference, Atlanta, GA, 13–16 September 1992.

durability of the material in end-use application. To reduce the time required to evaluate the durability of roofing membranes, accelerated aging by artificial weathering is used. The artificial weathering systems simulate temperature, humidity, and solar radiation; often the individual parameters are more intense than the average values under general exposure conditions. Following the aging process, the material is tested and the results are compared with those obtained for control samples. Although this simulation is helpful, it is important that the behavior of the material be understood.

It is well known that a thermoanalytical approach affords a means of measuring the degradative factors [1–5]. This can lead to the correlation between accelerated aging and actual field performance. The objective of this study is to demonstrate the utility of TG/DTA, DSC, TMA and DMA in characterizing roofing membranes. Although these techniques have been applied to polymers [1] and other construction materials, they have only recently been used in the roofing field [4]. TG/DTA can be used to determine how the chemical composition has been altered by heat aging, while DSC, TMA, and DMA can provide information on changes in glass transition temperatures T_g, coefficient of thermal expansion (CTE), storage modulus (a measure of hardness) and the loss modulus (a measure of the ability of the material to dissipate mechanical energy).

EXPERIMENTAL

The thermoanalytical characterization was performed on control and heat aged EPDM roofing samples. Two commercially available, non-reinforced EPDM roofing membrane samples (111 and 112) were obtained. One piece of each sample was used as a control. Another piece was placed in an air-circulating oven preheated to 130°C for heat aging. One piece of each sample was removed from the oven after 7 and 28 days.

The thermal characteristics of the as-received, 7-day and 28-day exposures where analyzed on the following instrumentation: DSC210, TG/DTA220, TMA/SS120C and DMS110 manufactured by Seiko Instruments USA, Inc. The TG/DTA and TMA/SS experiments were carried out at the Seiko and IRC sites.

The DSC experiment was conducted by placing a sample of 15–20 mg in an aluminum pan and an appropriate amount of inert material was used in the reference pan to counterbalance the specific heat capacity. The sample was tested between −150°C and 100°C at a rate of 20°C min^{-1} under a static air environment. The temperature calibration of this module was done by using the melting points of indium and tin.

The TG/DTA experiment was run by placing 10–13 mg of sample in a platinum pan. An empty pan was used for the reference side. The module was heated from 25 to 800°C at a rate of 20°C min^{-1} under a purge of 4.8

grade nitrogen gas at a flow rate of 300 ml min^{-1}. At 550°C, the gas was changed to dry air at a matching flow rate to establish the amount of carbon black. The temperature calibration of the TG/DTA was carried out by using indium and tin.

The TMA/SS parameters required a small piece of size 1 mm × 7 mm × 7 mm to be placed on a quartz platform inside the module. The quartz expansion prove was positioned on the sample under a compressive force of one gram. The analysis was run from −100°C to 20°C at a rate of 2°C min^{-1} under static air environment. The temperature calibration of the TMA/SS was achieved by using the melting points of indium and mercury.

The Seiko DMS110 was configured with an 8-mm dual-cantilever mode of deformation to characterize the rheological properties of the EPDM material. The sample size was 30 mm long, 3 mm wide, and 1 mm thick. The temperature range was from −160°C to 100°C at a rate of 1°C min^{-1} using a constant amplitude of deformation of 30 μm at frequencies of 1, 2, 5, 10 and 20 Hz.

RESULTS AND DISCUSSION

A typical DSC thermal curve of the EPDM 111 roofing membrane is displayed in Fig. 1. The average onset of the T_g of the as-received sample was at −78.5°C, while the average T_g established by the half-height technique was found to be −66.0°C. After heat aging for 7 and 28 days at 130°C, the T_g was found to shift to higher temperatures. This trend was not observed for the EPDM 112 sample where the T_g was found to remain

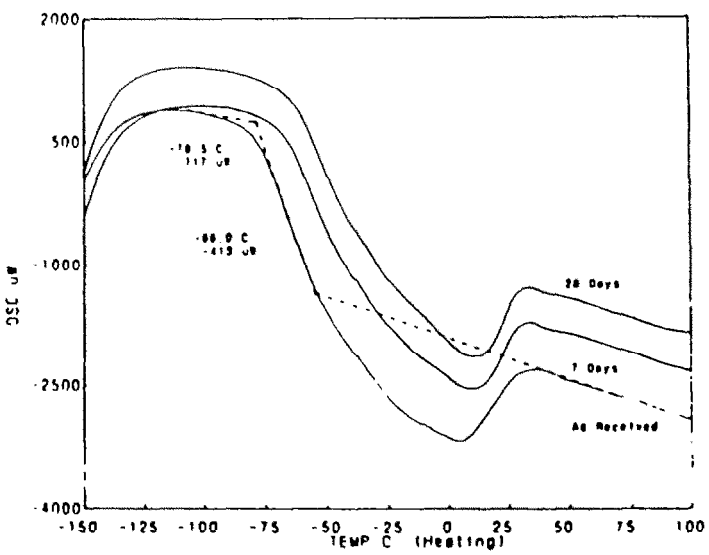

Fig. 1. DSC curves for EPDM 111: as-received; 7 days at 130°C; and 28 days at 130°C.

TABLE 1
DSC data

	EPDM 111		EPDM 112	
	Onset of T_g/°C	T_g/°C	Onset of T_g/°C	T_g/°C
As-received	−78.5	−66.0	−61.6	−54.0
7 Days	−70.4	−58.9	−60.8	−53.5
28 Days	−66.6	−52.8	−60.6	−52.9

relatively constant with the aging process. The DSC results are summarized in Table 1.

The TMA results (Table 2) indicate a similar behavior with respect to the glass transition temperature of the roofing membranes. Moreover, the T_g determined by TMA matched the T_f measured by DSC using the half-height technique. For example, the average T_g as determined by TMA for the as-received EPDM 111 was found to be −66.2°C, while the average T_g determined by DSC using the half-height method was found to occur at −66.°C. In addition, the coefficient of linear thermal expansion (CTE) decreased with increased aging. In the case of EPDM 112, the T_g did not shift significantly with aging; however, the CTE values did decrease with increased heat aging.

The TG/DTA technique was used to study the effect of aging on the chemical composition of the roofing membranes. A typical TG/DTA scan is shown in Fig. 2 and the TG/DTA results are summarized in Tables 3 and 4. As can be seen, three events are recorded for both EPDM membranes. The first mass loss is due to the loss of extender oil and/or plasticizers. It would appear that the 112 material contains an oil which is less volatile than that used for the 111 material. As a result, the 112 undergoes a weight loss at a higher temperature. The second weight loss is due to the decomposition of the EPDM resin. The two membranes experience this loss in the same temperature range, between 430 and 455°C. The third thermal event is

TABLE 2
TMA data

	EPDM 111		EPDM 112	
	T_g/°C	CTE above T_g ($\times 10^{-6}$ per °C)	T_g/°C	CTE above T_g ($\times 10^{-6}$ per °C)
As-received	−66.2	342	−54.6	319
7 Days	−59.2	235	−53.4	300
28 Days	−52.8	202	−52.4	284

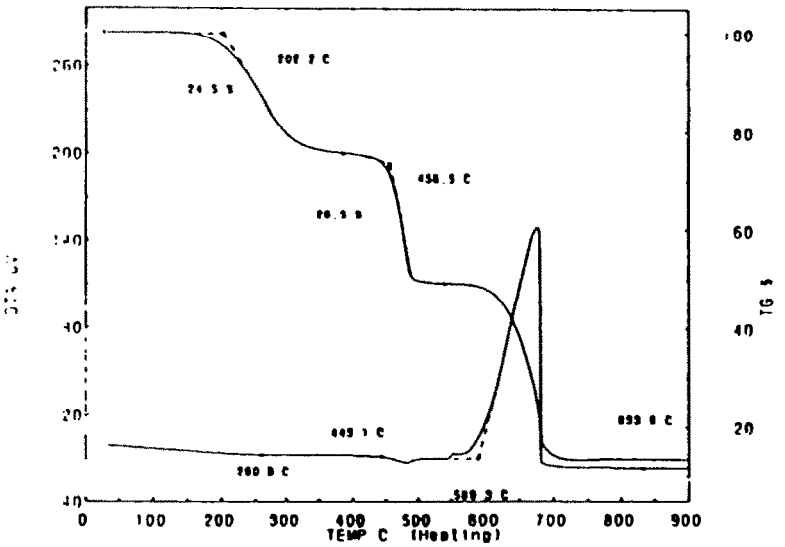

Fig. 2. Typical simultaneous TG/DTA curves for as-received EPDM 111.

encountered only if the atmosphere is changed from nitrogen to air. This causes the combustion of carbon black. Based on these results, it can be noted that the chemical composition of EPDM 112 is not significantly affected by the heat aging process. In the case of the 111 sample, less oil is detected in the aged samples than in the unaged samples. Thus, it would appear that the 111 sample loses oil during the aging process.

TABLE 3

TG/TA data for EPDM 111

TG	1st mass loss (%)	Onset temp. of decomp. of 1st event/°C	2nd mass loss (%)	Onset temp. of decomp. of 2nd event/°C	3rd mass loss (%)	Onset temp. of decomp. of 3rd event/°C	Ash (%)
As-received	24.5	202	26.5	455	36.8	639	12.2
7 Days	12.8	212	30.3	454	42.4	643	14.4
28 Days	9.2	213	32.1	452	44.7	635	14.2

DTA	Onset temp. of 1st event/°C	Onset temp. of 2nd event/°C	Onset temp. of 3rd event/°C
As-received	202 (endo)	443 (endo)	587 (exo)
7 Days	212 (endo)	444 (endo)	586 (exo)
28 Days	213 (endo)	445 (endo)	584 (exo)

TABLE 4
TG/DTA data for EPDM 112

TG	1st mass loss (%)	Onset temp. of decomp. of 1st event/°C	2nd mass loss (%)	Onset temp. of decomp. of 2nd event/°C	3rd mass loss (%)	Onset temp. of decomp. of 3rd event/°C	Ash (%)
As-received	12.0	400	42.5	430	30.1	634	15.0
7 Days	11.8	407	42.5	430	30.5	634	15.2
28 Days	11.6	407	42.5	429	30.9	623	14.8

DTA	Onset temp. of 1st event/°C	Onset temp. of 2nd event/°C	Onset temp. of 3rd event/°C
As-received	399 (endo)	446 (endo)	588 (exo)
7 Days	406 (endo)	447 (endo)	587 (exo)
28 Days	405 (endo)	443 (endo)	582 (exo)

Typical DMA (E') curves for the two EPDM samples at a frequency of 2 Hz are shown in Fig. 3. Three rheological properties are recorded: storage modulus (E'), loss modulus (E'') and tan $\delta(E''/E')$. The storage modulus, a measure of the stiffness or rigidity of the material, does not show any

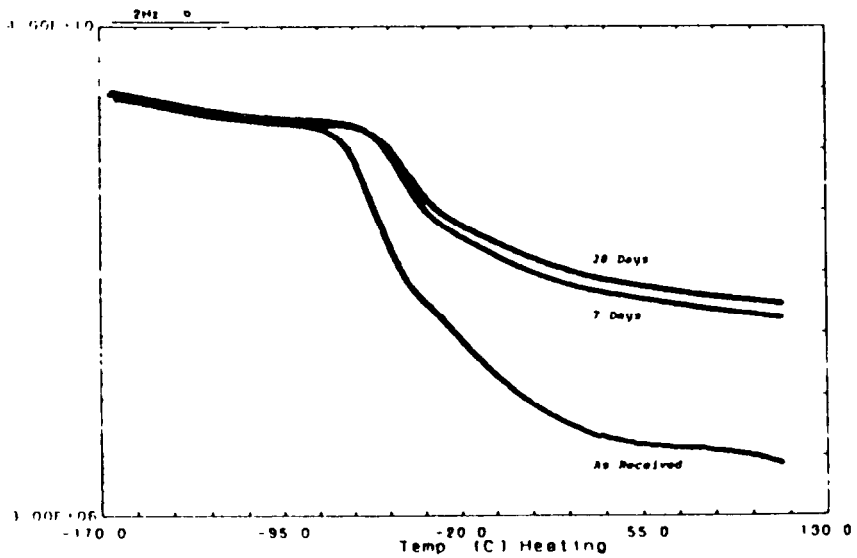

Fig. 3. Storage modulus (E') curves for EPDM 111: as-received; 7 days at 130°C; and 28 days at 130°C.

TABLE 5
DMA data at 2 Hz

	EPDM 111		EPDM 112	
	Peak temp./°C E''	Peak temp./°C tan δ	Peak temp./°C E''	Peak temp./°C tan δ
As-received	−63.3	−50.7	−45.1	−34.5
7 Days	−49.5	−41.1	−44.8	−34.0
28 Days	−46.4	−39.5	−42.8	−31.8

appreciable change below the T_g, i.e. in the glassy state. However, above T_g (the rubber plateau region), E' increases with increased aging. The loss modulus, the ability of the material to dissipate mechanical energy by converting it to heat through molecular motion, does not undergo any significant change as far as the modulus below T_g is concerned. However, when the T_g values based on the E'' peaks are compared, a shift to higher temperatures is noted. Furthermore, an increase in the E'' values above T_g in the rubber plateau region is also noticed. The tan δ data indicate a similar trend of increasing values of the peaks with heat aging. The DMA data is summarized in Table 5. Once again, it can be seen that EPDM 112 undergoes smaller changes than EPDM 111.

CONCLUSIONS

Thermal analysis was found to be useful in comparing the heat stability of two EPDM roofing materials. Heat aging was found to induce a significant change in glass transition temperature, CTE, storage modulus and chemical composition for sample EPDM 111. It is important to understand the significance of these changes because they can affect field performance. These changes were not observed for EPDM 112. Based on the thermoanalytical data, the EPDM 112 roofing membrane is more thermally stable than the EPDM 111 membrane.

ACKNOWLEDGMENTS

The authors are grateful to Ms. Ana H. Delgado, Mr. Ryoichi Kinoshita and Mr. Nobuaki Okubo for experimental assistance.

REFERENCES

1 E.A. Turi, Thermal Characterization of Polymeric Materials, Academic Press, San Diego, CA, 1981.
2 J.D. Ferry, Viscoelastic Properties of Polymers, John Wiley, New York, 1980.
3 F.W. Billmeyer, Jr., Textbook of Polymer Science, John Wiley, New York, 1984.

4 R.M. Paroli, O. Dutt, A.H. Delgado and M.Mech, Characterization of EPDM roofing membranes using thermogravimetry and dynamic mechanical analysis, Thermochim. Acta, 182 (1991) 325–333.
5 W.J. Sichina, Thermal Aging Behaviour of Polycarbonate: Studies using Dynamic Mechanical Analysis, Seiko Instruments USA, Inc., Application Brief, Torrance, CA, 1992.