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Publisher's version / Version de l'éditeur:

Journal of Materials in Civil Engineering, 5, 1, pp. 83-95, 1993-02

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RANKING PVC ROOFING MEMBRANES USING THERMAL ANALYSIS

By R. M. Paroli,¹ O. Dutt,² A. H. Delgado³ and H. K. Stenman⁴

ABSTRACT: The effects of accelerated heat aging on three polyvinyl chloride (PVC) roofing membranes was determined using thermogravimetry (TG), dynamic mechanical thermal analysis (DMA), and tensile testing. The heat aging was done at 100°C and 130°C. In general, it was found that the degradation of the reinforced PVC roofing membranes was proportional to the aging temperature and exposure time. Furthermore, it was found that these thermoanalytical techniques can be used to not only record the changes incurred by the samples due to heat aging, but also to provide a ranking of the heat stability of the various materials. The order of stability, using these techniques, was determined to be $V1 < V3 < V2$, which corresponded with the observed order of stability from actual records obtained on roofs. The results obtained demonstrate that TG and DMA, in conjunction with tensile testing, provide a viable, routine method of evaluating the quality of single-ply PVC-based roofing membranes.

INTRODUCTION

Polyvinyl chloride (PVC) has been studied for many years, and its mechanical and chemical properties are quite well known (Abbas and Sorvik 1975; Turi 1981; Titow 1984; Wypych 1985, 1986; Feldman 1989). Although thermal analysis techniques have been used quite extensively in the chemical characterization of PVC, they have rarely been applied to the study of PVC-based roofing materials. The roofing industry has generally relied on mechanical testing as an indicator of quality and performance. Since roofing materials range in composition from polymer-modified bitumen to PVC and ethylene-propylene-diene monomer (EPDM) rubber with a variety of reinforcement, it is difficult to predict their long-term behavior solely on the basis of results from mechanical tests. 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 in the artificial weathering systems are more intense than the average values under general exposure conditions. Following the heat-aging process, the materials were tested and the results were compared with those obtained using well-known standards. It is very difficult, and perhaps even unjustified, to compare the mechanical properties of a range of materials from bitumen-based to polymer-based, without taking into account the micro and chemical processes involved. The behavior of these materials is related to macroscopic

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Note. Discussion open until July 1, 1993. To extend the closing date one month, a written request must be filed with the ASCE Manager of Journals. The manuscript for this paper was submitted for review and possible publication on January 28, 1992. This paper is part of the *Journal of Materials in Civil Engineering*, Vol. 5, No. 1, February, 1993. ©ASCE, ISSN 0899-1561/93/0001-0083/\$1.00 + \$.15 per page. Paper No. 1844.

behavior, and to the chemical composition and molecular arrangement. Although simulation is helpful in predicting the performance of materials, it is of paramount importance that the behavior of the material be understood. It is for this reason that the Conseil International du Batiment pour la Recherche, l'Etude et la Documentation/Réunion Internationale des Laboratoires d'Essai et de Recherche sur les Matériaux et les Constructions (CIB/RILEM) Joint Committee on Membrane Roofing Systems (that includes elastomeric, thermoplastic, and modified-bituminous roofing) has initiated investigation on the applicability of thermal analysis or thermoanalytical techniques. Our previous work has demonstrated that thermogravimetry (TG) and dynamic mechanical analysis (DMA) can be used to predict the relative durabilities of EPDM-based roofing membranes (Dutt et al. 1990; Paroli et al. 1990).

Thermogravimetry (TG) can be used to determine how the chemical composition has been altered by heat aging, and DMA can provide information on changes in glass transition temperatures (T_g), the storage modulus (a measure of hardness), and the loss moduli (associated with energy absorption, e.g., degradation of macromolecules). The objective of this study is to examine how thermal techniques can be used to characterize and rank PVC-based roofing membranes in conjunction with conventional mechanical tests when attempting to solve problems related to roofing materials.

EXPERIMENTAL

Sample Preparation

Three commercially available PVC roofing membranes were obtained and labeled as V1, V2, and V3. A typical composition for the PVC roofing samples used in the thermal analyses, as well as the mechanical tests, is given in Table 1. Each material was cut into seven pieces of about 150 mm × 250 mm. One piece was used as a control, three were placed in an air-circulating oven preheated at 100°C, and the remaining three were placed in an air-circulating oven set at 130°C for heat aging. One piece of each material was removed from the oven, in turn, after one, seven, and 28 days, and specimens were then cut out for tensile testing and thermal analyses.

TABLE 1. Typical Composition of Generic PVC Roofing Membrane

Ingredients (1)	Percent by weight (approximately) (2)	Function (3)
PVC resin	55	Basic material (powder or granular)
Plasticizers	28	Impart flexibility
Fillers	7	Increase dimensional stability, and reduce cost
Pigments	5	Provide color to the PVC compound
Processing oils and biocides	3	Improve processing and reduce cost
Stabilizers	2	Provide resistance to heat and light during manufacture

Dynamic Mechanical Analysis

The PVC control and aged samples were cut (~1 mm thick, 5 mm long, 12 mm deep) and tested in a Polymer Laboratory dynamic mechanical thermal analyzer (PL-DMTA Mark I) using software version 4.0. The experimental profile was as follows: a fixed frequency of 10 Hz; a heating rate of $2^{\circ}\text{C min}^{-1}$; and a temperature range between -120° and 80°C . The DMA was operated in the single cantilever mode using test frame L and clamp type C. In the Polymer Laboratory system, a sinusoidal stress is applied to a vibrator unit using a sinusoidal current. The stress imposed upon the specimen is therefore directly related to the amount of current delivered to the vibrator. The sample is subjected to strain via the induced displacement. A more detailed description is presented in Dutt et al. (1990).

The glass transition temperatures (α -transition) values were obtained from the maximum in the loss modulus (E'') versus temperature curve. The glass transition temperature data for all three samples are summarized in Table 2.

Thermogravimetric Analysis

A DuPont Instruments model 951 thermogravimetric analyzer interfaced to a model 9900 and 1090 computer was used to record the weight loss of each PVC roofing sample. Approximately 25–40 mg of sample was cut using a hole puncher to ensure a uniform shape and a better contact with the sample pan. The analyses were carried out at temperatures between 20°C and 800°C using a nitrogen gas flow of 100 mL/min^{-1} , and a scanning rate of $20^{\circ}\text{C/min}^{-1}$. Although both the weight loss (TG) and the computer calculated first derivative weight loss (DTG) curves were recorded, only the DTG curve was used because it provided the desired quantitative data. The data obtained from the DTG curves are tabulated in Table 3 as a function of heat-aging temperature and exposure time.

Tensile Testing

The heat-aged material was conditioned at room temperature ($22^{\circ}\text{C} \pm 2^{\circ}\text{C}$) for a minimum of 24 h prior to testing. The control and aged specimens were cut using a dumbbell-shaped die in a hydraulic press (overall dimensions were 149.16 mm long and 37.5 mm wide). The tests were carried out

TABLE 2. Glass Transition Temperatures of PVC Membranes

Heat-Aging Schedule		T ($^{\circ}\text{C}$) for Samples		
Temperature ($^{\circ}\text{C}$) (1)	Days (2)	V1 (3)	V2 (4)	V3 (5)
22 ^a	0	-28	-33	-29
100	1	-27	-34	-25
100	7	-26	-34	-27
100	28	-16	-33	-20
130	1	-21	-34	-25
130	7	-18	-23	-19
130	28	-5	-25	-14

^aUnheated control material.

TABLE 3. Thermogravimetry Data for HCl, Plasticizer, and Other Components Content in PVC Samples Prior to and after Heat Aging at 100°C and 130°C

Heat Aging Schedule		HCl and Plasticizer Loss ^b (%)			Others ^c (%)		
Temperature (°C) (1)	Days (2)	V1 (3)	V2 (4)	V3 (5)	V1 (6)	V2 (7)	V3 (8)
22 ^a	0	69.4	65.8	71.2	15.5	13.3	14.6
100	1	68.9	67.3	70.3	15.9	13.5	15.3
100	7	68.6	66.7	69.8	15.0	14.9	14.3
100	28	65.4	65.7	70.4	16.4	13.8	16.7
130	1	65.8	67.3	72.1	15.7	14.2	16.6
130	7	62.9	65.6	66.0	15.6	14.2	16.5
130	28	63.7	64.9	66.8	15.4	16.3	15.8

^aUnheated control sample.^bBased on the integrated area of peak between 200°C and 400°C.^cBased on the integrated area of peak between 400°C and 600°C.**TABLE 4. Tensile Strength and Elongation Values of PVC Membranes**

Heat Aging Schedule		Strength (kN m ⁻¹)			Elongation (%)		
Temperature (°C) (1)	Days (2)	V1 (3)	V2 (4)	V3 (5)	V1 (6)	V2 (7)	V3 (8)
22 ^a	0	31.1	28.9	29.7	124	65	229
100	1	27.5	28.8	29.1	149	47	153
100	7	31.9	23.4	33.0	124	54	175
100	28	33.6	27.5	33.7	51	47	158
130	1	28.9	24.7	30.7	139	89	201
130	7	35.2	25.2	34.0	47	54	165
130	28	32.6	25.4	29.8	45	22	183

^aUnheated control material.

at room temperature using an Instron tensile tester (model 1122) with a gauge length of 60 mm and a cross-head speed of 60 mm/min⁻¹. The load and elongation curves were recorded on the machine chart recorder, as well as stored in the computer. Five specimens were tested for each heat conditioning, and the mean values of load and elongation-at-break were recorded (Table 4).

RESULTS AND ANALYSIS

Dynamic Mechanical Analysis

The DMA curves for samples V1, V2, and V3 heat aged at 100°C and 130°C are plotted in Figs. 1–3, respectively. The glass transition temperatures (T_g) for all three PVC samples increased after heat aging. The sample that appeared to be the most stable of the three was V2. As can be seen from Fig. 2 and Table 2, the T_g for this sample did not vary much, even after 28 days of heat aging at 100°C. The T_g did show a change of ~10°C when subjected to the more severe temperature of 130°C for seven and 28 days. The T_g for sample V1 went from -28°C (control) up to -16°C after

28 days at 100°C. The most substantial change occurred when V1 was exposed to 130°C for 28 days; the T_g after this heat aging was -5°C . PVC sample V3 appears to be more stable than V1, as its T_g changed from -29°C (control) to -20°C after being heat aged for 28 days at 100°C and -14°C after being heat aged for 28 days at 130°C.

The changes observed in the glass transition temperatures of the PVC

FIG. 1. DMA Curves for Specimen V1 Aged at: (a) 100°C for 0 Days (Control), 1 Day (1/100), 7 Days (7/100), and 28 Days (28/100); and (b) 130°C for 0 Days (Control), 1 Day (1/130), 7 Days (7/130), and 28 Days (28/130)

FIG. 2. DMA Curves for Specimen V2 Aged at (a): 100°C for 0 Days (Control), 1 Day (1/100), 7 Days (7/100), and 28 Days (28/100); and (b) 130°C for 0 Days (Control), 1 Day (1/130), 7 Days (7/130), and 28 Days (28/130)

samples can be attributed to the loss of plasticizer from the specimens, and also to the loss of HCl. The loss of HCl is also the cause of the discoloration that is commonly observed after the samples have been heat aged. The zip-like thermal degradation mechanism of PVC is believed to be as follows

(Wypych 1985, 1986):

The observed discoloration is due to the formation of conjugated double bonds. This autocatalyzed reaction increases the T_g . The degradation process can eventually lead to the deterioration of the backbone of the polymer. At higher temperatures, the thermal degradation of PVC involves both pyrolysis and combustion. Lattimer and Kroenke have proposed that as PVC thermally degrades, aromatic compounds such as benzene are formed (Lattimer and Kroenke 1988).

Thermogravimetric Analysis

The TG curves for the V1 PVC (control and heated samples) are shown in Fig. 4. As can be seen, under a nitrogen atmosphere approximately 80% of the weight loss occurs between 200° and 600°C. In this range, there are two weight-loss regions; the larger loss occurs in the 200–400°C region, and the other loss occurs in the 400–600°C region. As previously mentioned, thermal degradation of PVC is characterized by two types of processes. The primary process, known as dehydrohalogenation, forms polyenes (double-bonds), and the secondary processes involve reactions associated with the newly formed polyenes (Turi 1981). Examples of secondary processes include cross-linking, gel formation, cyclization, chain scission, benzene formation, oxidation, and Diels-Alder reaction with additives (Turi 1981). PVC degrades via the elimination of HCl, and does not involve main chain scission. It has been reported that practically all HCl (60 wt%) is released by the time the sample has reached 220°C (Turi 1981). Thermogravimetric-mass spectrometric (TG-MS) studies have shown that the degradation products of PVC were composed of HCl, aromatics, and other hydrocarbons such as ethylene, ethane, propylene, xylene, and methane (Stromberg et al. 1959; Mardosky 1964). The first weight loss observed in Fig. 4 (200–400°C) can be attributed to the elimination of HCl and plasticizers, and the weight loss at (400–550°C) may result from the volatilization of any of the other components that have been reported above 400°C (Stromberg et al. 1959; Mardosky 1964).

Stabilizers are added to PVC to neutralize the effect of HCl, thus offsetting the catalytic effect of HCl with respect to the degradation of PVC (Wypych 1986). Commercial formulations usually contain a large number of compounding ingredients such as plasticizers, impact modifiers, and mold lubricants, in addition to stabilizers (see Table 1). The shoulder occurring between 250°–320°C (Fig. 4) is probably due to the volatilization of the stabilizer.

Unmodified PVC is one of the least stable polymers used commercially. It is very sensitive to mild heating, with the first sign of discoloration appearing after several hours at temperatures in the range of 100°–140°C (Turi 1981). As can be seen for sample V1 (Fig. 4a), the weight loss in the 200°–400°C region does not vary significantly, even after 28 days of heating at 100°C. Almost no decrease is observed when the sample is heat aged for one day at 100°C. A similar trend is observed when the samples were heated for the same number of days at 130°C [Fig. 4(b)]. The percent weight loss in the region of 400°–550°C also remains unchanged. The weight loss in the

FIG. 3. DMA Curves for Specimen V3 Aged at (a) 100°C for 0 Days (Control), 1 Day (1/100), 7 Days (7/100), and 28 Days (28/100); and (b) 130°C for 0 Days (Control), 1 Day (1/130), 7 Days (7/130), and 28 Days (28/130)

200°–400°C for the control sample was 69.4%, after 28 days at 100°C the detected loss was 65.4%, and 63.7% after 28 days at 130°C. This slight decrease in weight loss (after heat aging) implies that some HCl had been released during heat aging.

It is well known that dehydrochlorination occurs mainly at the surface, and causes a color change in PVC due to the formation of polyenes (Turi

FIG. 4. Derivative TG (DTG) Curve for the V1 PVC Sample Heat Aged for 0 (Unheated), 1, 7 and 28 Days at: (a) 100°C; and (b) 130°C

1981; Wypych 1985). A visual inspection of the V1 PVC samples heated at 100°C did not reveal any significant sign of discoloration or loss in flexibility until 28 days, whereas the samples heated at 130°C for seven and 28 days became brown and brittle. The loss in flexibility may indicate that the PVC at 130°C has cross-linked and/or lost some of its plasticizer.

Thermogravimetry (TG) curves for the V2 PVC are shown in Fig. 5, and

FIG. 5. Derivative TG (DTG) Curve for the V2 PVC Sample Heat Aged for 0 (Unheated), 1, 7 and 28 Days at: (a) 100°C; and (b) 130°C

those for the V3 PVC are displayed in Fig. 6. The thermograms of the V3 sample show a similar trend to that observed in the V1 PVC samples, i.e., a slight decrease in the percent weight loss in the 200°–400°C region. No decrease is observed for the V2 samples in the same region. This may indicate that the V2 PVC has a greater thermal stability at 100° and 130°C than the V1 PVC. Visual inspection of the V2 samples heated at 100°C showed neither sign of discoloration nor loss in initial flexibility, which

FIG. 6. Derivative TG (DTG) Curve for V3 PVC Sample Heat Aged for 0 (Unheated), 1, 7 and 28 Days at: (a) 100°C; and (b) 130°C

indicates that heat-aging did not have a significant effect on the sample. However, the V2 PVC heated at 130°C showed some discoloration after seven days, and a major discoloration and loss of flexibility after 28 days. The V3 PVC showed slight decrease in flexibility and some visual discoloration after seven days when heated at 100° and 130°C, thus indicating probable loss of HCl and/or plasticizer. Although all the PVC roofing sam-

ples are reinforced with some scrim, the thermal stability of samples V1 and V3 appears to be lower than that of the V2 PVC material. The lower thermal stability of the V1 and V3 materials may result from the type of stabilizer used and/or the compounding process. The thermogravimetric results indicate that the order of thermal stability of the PVC samples is $V1 < V3 < V2$.

Tensile Testing

The tensile strengths and elongation values for the three PVC specimens are listed in Table 4. As can be seen, there is no clear trend in the values for mechanical strength for any of the samples. In the case of percent elongation, a significant change is only observed after 28 days of heating at 100°C for samples V1 and V3; sample V2 does not exhibit any significant difference after being subjected to the same aging process. The V2 PVC was also quite stable at 130°C after one and seven days of heating. The sample did, however, change dramatically after 28 days of aging. The V1 and V3 samples show changes in their elongation values after seven days of heat treating at 130°C.

Although no substantial change was observed in the mechanical tests, the thermal analyses did record differences in the samples that were subjected to heat aging. Since the PVC samples are reinforced, it is possible that the mechanical data cannot reflect the changes incurred by the matrix material through heat aging. In this case, thermogravimetry and dynamic mechanical analysis can be used to record the behavior of the material, regardless of whether or not it is reinforced. This finding shows the importance of using both mechanical testing and chemical characterization in diagnosing roofing problems. Additionally, predictions of the behavior of the materials using TG and DMA are confirmed by field observations. Roofs made with V1 material developed more problems than those made with V3 roofing material. It was also found that roofs made from V2 material had the least amount of recorded problems.

CONCLUSIONS

Thermal analysis is a useful tool for the characterization of PVC roofing materials. Mechanical analysis was unable to clearly demonstrate that the material properties had been modified by heat aging. TG and DMA were able to not only record the changes incurred by the samples due to heat aging, but also to provide a ranking of the heat stability of the various materials. Furthermore, the order of stability $V1 < V3 < V2$ corresponded to the observed order of stability from actual records obtained on roofs.

Thermoanalytical techniques are important prognostic tools for predicting the behavior of single-ply roofing membranes. These techniques may also be used for developing new formulations of roofing materials.

ACKNOWLEDGMENTS

The writers wish to thank V. S. Ramachandran and N. P. Mailvaganam for their very useful comments, and D. Charron for her assistance in preparing this manuscript. This joint research project is funded by Canada Post Corporation, Department of National Defense, the Department of Public Works Canada, and the National Research Council of Canada.

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