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Delgado, A.H.; Howell, G.; Ober, R.; Oliveira, P.E.; Peterson, A.; Boon, R.; Paroli, R.M.

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Ana H. Delgado,¹ George Howell,² Randy Ober,³ Paul E. Oliveira,⁴ Arnold Peterson,⁵ Richard Boon,⁶ and Ralph M. Paroli¹

Investigation of the Effect of Heat on Specially Formulated Thermoplastic Polyolefin (TPO) Films by Thermogravimetry, Dynamic Mechanical Analysis, and Fourier Transform Infrared Spectroscopy

ABSTRACT: To explore the use of chemical methods of analysis in investigating the performance of thermoplastic polyolefins (TPO), the ASTM D08.18 Subcommittee undertook a study to evaluate TPO films of known composition. These specially formulated films with varying amounts of stabilizers were heat-aged for up to 56 days according to ASTM D 6878-03 and then analyzed using dynamic mechanical analysis (DMA), thermogravimetry (TG), and Fourier transform infrared (FTIR) spectroscopy. These techniques were found to be useful in characterizing the effect of heat on the TPO films under study and it is believed that they could be used to evaluate actual TPO membranes. Please note that these are *films* and not roof *membranes*. The formulations used for the films could be modified for use in actual membranes.

KEYWORDS: TPO, chemical properties, heat aging, dynamic mechanical analysis (DMA), Fourier transform infrared (FTIR) spectroscopy, thermogravimetry (TG), mass loss, derivative of TG (DTG)

Introduction

Thermoplastic olefin (TPO), in general, is a polymer blend of polypropylene (PP), ethylene propylene, rubber (EPR), polyethylene (PE), pigments, fillers, and additives [1]. Thermoplastic polyolefins are in the thermoplastic elastomer family and commonly referred as a TPO in the single-ply roofing industry. TPO roofing membranes are typically based on PP and EPR polymerized together using state-of-the-art polymer manufacturing technology [2]. The TPO resin is compounded with other components including heat, light and UV stabilizers, fire retardants, and pigments for color to provide stability against the elements associated with outdoor exposure [3]. For example, the effectiveness of a light stabilizer depends on factors such as solubility and concentration in the polymer matrix.

The physical loss of a stabilizer can occur by diffusion to the polymer surface during exposure [4], by photochemical reactions and degradation [5], and by evaporation and leaching from the polymer surfaces [6]. UV and FTIR analysis of low density polyethylene (LDPE) films before and after exposure to natural weathering and accelerated photo-oxidative conditions [7] suggested that the photostabilizer disappearance for HALS (hindered amine light stabilizer) content above 0.4 % (w/w) is most probably due to its physical loss for long photo-oxidation times under the conditions used. However, the photostabilizer disappearance at the initial stage was due to chain scission with a consequent volatilization and diffusion of these fragments on the surface. The most serious physical losses observed are from articles such as fibers, thin films, and coatings, which have a high surface to volume ratio.

Evaluation of the physical and chemical properties of polymeric roofing membranes before and after

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¹ National Research Council of Canada—Institute for Research in Construction, 1200 Montreal Road, Bldg. M20, Ottawa, ON K1A 0R6 Canada.

² UVTEC, Inc., 1121 108th Street, Arlington, TX 76011.

³ Carlisle Syntec, P.O. Box 7000, 1555 Ritner Highway, Carlisle, PA 17013.

⁴ Firestone Building Products, 525 Congressional Blvd., Carmel, IN 46032-5607.

⁵ Stevens Roofing, Route #2, Box 136, Westfield, NC 27053.

⁶ Consuper, 7901 S. Adams Way, Littleton, CO 80122.

TABLE 1—Composition of the TPO films.

Component	Sample (phr ^a)						
	A	B	C	D	E	F	G
Polypropylene	100	100	100	100	100	100	100
Low molecular weight NON hindered amine light stabilizer (NON HALS)	0.6	0.5	0.5	0.2	0.2	0.2	0
Hindered amine light stabilizer (HALS)	0.8	0.5	0.5	0.2	0.2	0	0
UV absorber	0.8	0.5	0.2	0.2	0	0	0

^aPart per hundred resin.

exposure to natural and accelerated laboratory exposure is of paramount importance to obtain information on the performance of the material. The minimum physical requirements of roofing membranes as specified in ASTM D 6878, “Specifications for Thermoplastic Polyolefin Based Sheet Roofing” [8] developed by the task group of the D08.18 Subcommittee involves accelerated laboratory aging and the use of physical and mechanical methods of analysis for membrane performance evaluation.

Based on previous work (see Refs [9–23]), it is known that chemical methods of analysis can be of assistance in understanding the causes of degradation of polymeric roof membranes such as EPDM, PVC, TPO, etc. Therefore, the ASTM D08.18 task group undertook the study of specially formulated TPO films to investigate the usefulness of chemical methods of analysis.

Seven specially formulated thermoplastic polyolefin (TPO) film samples (approximately 203 by 279 by 0.35 mm) (~8 by 11 by 0.01 in.) labeled A through G were prepared by a TPO manufacturer and sent to the National Research Council, Institute for Research in Construction (NRC—IRC) to evaluate the chemical properties before and after heating at 116°C for up to 56 days. A generic composition of the specially formulated films is given in Table 1 and graphically represented in Fig. 1. Dynamic mechanical analysis (DMA), thermogravimetric analysis (TG), and Fourier transform infrared (FTIR) spectroscopy were performed on the film samples before and after heating. The goal of this study is not to investigate in detail the degradation process but to evaluate the usefulness of these techniques for evaluating the performance of TPO roofing membranes when field failures occur.

Experimental

Sample Preparation and Exposure

Each of the received TPO films was labeled A–G and cut into strips to allow for ten different heating periods (exposure times). One of the strips was used as the control and was conditioned at 80°C for one hour in an air convection oven as per ASTM D 6878-03 [8] to provide a consistent thermal history while the other specimens were placed in an oven and heated at 116°C up to 56 days. The position of the film specimens on the oven racks was changed on a weekly basis. For example, if on the first week of exposure, the specimen occupied the left corner of one of the oven racks, the following week, it was moved to the

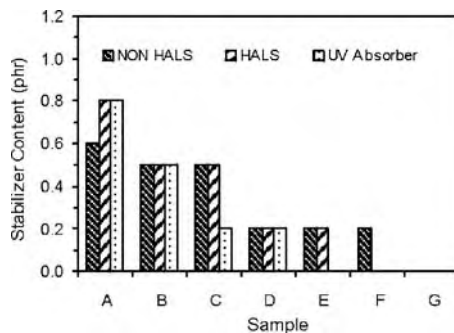


FIG. 1—Composition of TPO films.

TABLE 2—*Experimental parameters.*

Geometry:	Film
Sweep type:	Dynamic Temperature Ramp
Dimensions:	Thickness: 0.32–0.38 mm; Width: 1.23–1.44 mm Length: 19.23–22.65 mm
Frequency:	1 Hz (6.28 rad/s)
Temperature program:	–80°C to 50°C
Ramp Rate:	2°C
Soak Time:	1 minute
Time per Measure:	40 seconds
Strain:	0.1 %
Autotension Mode:	ON static force tracking dynamic force (25 %)
Autostrain Mode:	On
Strain Adjustment:	30–35 % of current strain

opposite corner, and so on, until the specimen occupied the four corners and center of the rack. Then, the specimen was moved to the next rack and the process was repeated. This was to ensure that all samples receive the same heat exposure.

A specimen was removed from the oven every seven days, labeled and stored in a desiccator until conducting the analysis. A specimen from each sample was also removed from the oven after ten days. For analysis purpose, the suffix “c” was added to the control film specimens and the heating period followed by the suffix “d” was added to the heated ones. For example, Sample Ac, was the control specimen for Sample A, while, A14d refers to the specimen that was heated for 14 days. This labeling system was used for all analyses.

Due to unexpected electrical power shutdown in the building on two weekends during heating periods, the 28, 35, 42, and 49-day periods were shortened by 17 hours.

Dynamic Mechanical Analysis (DMA)

Two Rheometric Scientific (now TA Instruments) Solid Analyzers (RSII and RSIII) equipped with an environmental controller and film geometry (tool) were used to measure the glass transition temperature (T_g) of the specimens in tension mode. Thin film specimens were carefully cut with a sharp utility knife (see Table 2 for dimensions) from each of the control and heat-aged samples. The film specimen was placed in the film tool (geometry) making sure it was properly loaded. The gap between the upper and lower parts of the tool was measured with a gage and the value used as the specimen length. The specimen was cooled to –80°C, the temperature was allowed to stabilize for five minutes and increased at 2°C/min to the final temperature program. The test was conducted as per ASTM D 5026-01 [24] under the experimental parameters in Table 2. All analyzed specimens were run at least in duplicate. If the T_g of the two runs differed by more than 2°C, a third specimen was analyzed.

Thermogravimetric Analysis (TG/DTG)

A Seiko Simultaneous Thermal Analyzer (STA) TG/DTA 320 was used to measure the thermal stability of the samples as per ASTM D 6382-99 [25]. A piece (5–20 mg) was taken from two different areas of the specimen, cut in smaller pieces, and heat aged at 20°C/min from 25 to 600°C under ultra high purity nitrogen and from 600 to 1000°C under ultra zero air. A flow rate of 150 mL/min was used for both gases. All samples were run at least in duplicates. If the difference in mass loss between the two runs of the same specimen was 3 % or greater, a third or fourth run was carried out. The sample labeling system used in the DMA analysis was also used for the TG analysis.

Fourier Transform Infrared (FTIR) Spectroscopy

A Nicolet Nexus 870 infrared spectrometer equipped with a DTGS detector and a Spectra Tech Thunderdome attenuated total reflectance (ATR) accessory with a germanium (Ge) crystal was used to collect the spectra of the samples. The specimen was placed on the Ge crystal of the Thunderdome accessory and scanned under the following collection parameters: 32 scans, 4 cm⁻¹ resolution, and 0.6329 cm/s mirror

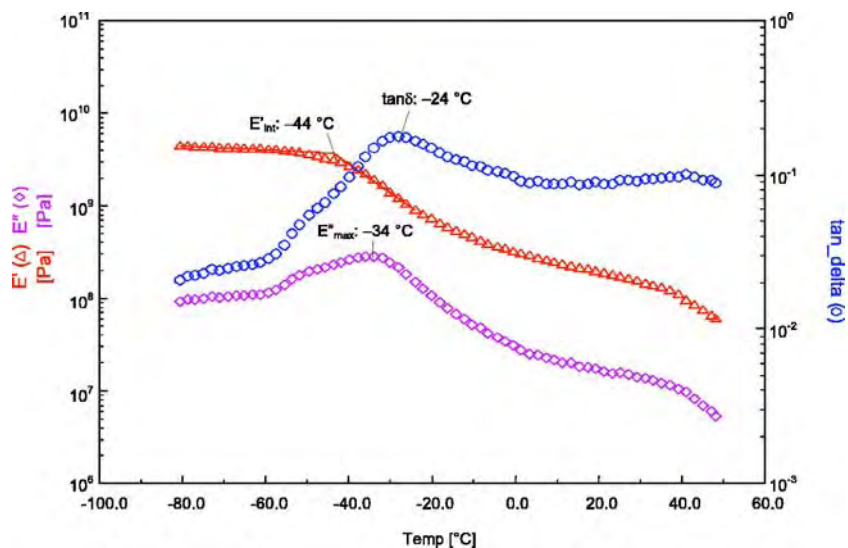


FIG. 2—Typical DMA plot showing how the T_g was obtained from E' and E'' curves.

velocity. The Ge crystal was cleaned between each specimen with a mixture of acetone-toluene (50 +50) using a cotton swab. The solvent was allowed to evaporate for 10 to 15 minutes before scanning the next specimen. The sample spectrum was ratioed against a background collected from the Ge crystal before each sample. The ATR, normalization scale, and automatic baseline correction routines from the Omnic software (Nicolet) were applied to all spectra before plotting.

Results and Discussion

Dynamic Mechanical Analysis (DMA)

Tables 3–8 summarize the average glass transition temperature (T_g) of the film samples (control and heated), the changes in the glass transition temperature (ΔT_g) and the storage modulus (E') values at 21 °C for each heating period. Each entry is the average and standard deviation of at least two individual measurements. The T_g was obtained from both the intersect of two tangents on the storage modulus (E'_{int}) and the maximum of the loss modulus (E''_{max}) curves as shown in Fig. 2.

The T_g obtained from the E'_{int} shows the same trend as that of E''_{max} ; hence, only the latter will be discussed. Note that due to an electrical power shut down, heating periods for 28 through 49 days were reduced by 17 hours (see Tables 3–8). However, the weekly period labeling system will be used hereafter for easy reference.

The glass transition temperature, T_g (E''_{max}), of film specimens for Sample A (Table 3) remained almost unchanged at -34°C regardless of the heating period. This sample contained all of the stabilizers. The

TABLE 3—Summary of average glass transition temperature of Sample A.

Sample ID	Exposure Type	T_g (E'_{int}) °C	ΔT_g (E'_{int})	T_g (E''_{max}) °C	ΔT_g (E''_{max})	$E' \times 10^8$, (Pa) at 21 °C	Comments
	0	-44 ± 0^a		-35 ± 1^a	0	2.0 ± 0.4^a	Control
	7d/116 °C	-43 ± 0	+1	-34 ± 0	+1	2.5 ± 0.1	
	10d/116 °C	-44 ± 0		-34 ± 0	+1	2.6 ± 0.0	
	14d/116 °C	-44 ± 0	0	-34 ± 0	+1	2.9 ± 0.1	
A	21d/116 °C	-43 ± 1	+1	-34 ± 0	+1	2.4 ± 0.5	
	28d/116 °C	NA		NA		NA	Not analyzed
	35d/116 °C	-43 ± 0	+1	-34 ± 0	+1	1.7 ± 0.1	
	42d/116 °C	-44 ± 1	0	-36 ± 0	-2	2.0 ± 0.0	
	49d/116 °C	-44 ± 0	0	-36 ± 0	-2	2.0 ± 0.0	
	56d/116 °C	-43 ± 0	+1	-34 ± 0	+1	1.9 ± 0.2	

^a \pm =Standard deviation.

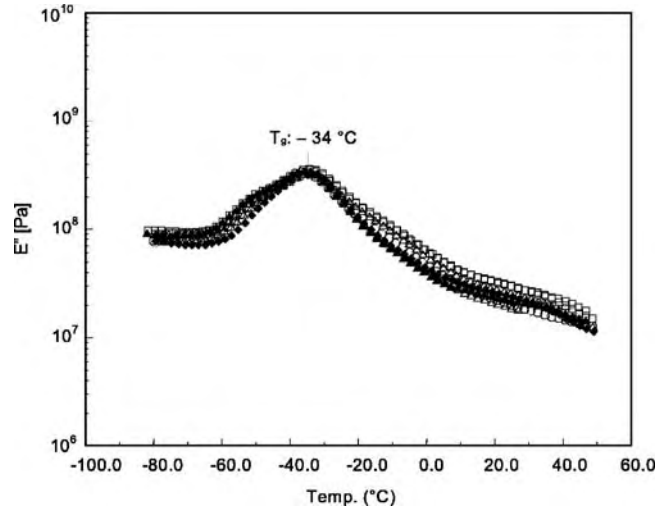


FIG. 3—Overlay of E'' curves of Sample A (control and heated).

overlay of the E'' curves in Fig. 3 shows that the maximum of the E'' curve is the same for the control and heated specimens. A similar trend was observed in the E'' curves for the analyzed specimens from the other six samples. Therefore, their E'' curves will not be shown due to space limitation.

The ΔT_g of -2°C observed for specimens exposed for 42 and 49 days is considered within the experimental error of the measurements of $\pm 2^\circ\text{C}$. Neither the T_g (E''_{\max}) nor the storage modulus (E') at 21°C showed significant changes after exposure. Note that for heating periods greater than 21 days, the E' values of the heated specimens decreases slightly and it is closer to that of the control specimen. However, this slight decrease may be due to experimental errors such as sample loading rather than to the heat treatment. Noise can also affect the E' values, which are read off the curve without any smoothing. If the heating is responsible for the decrease in the E' values, then the samples became slightly softer suggesting slightly compositional changes (e.g., degradation).

Table 4 summarizes the DMA results for Sample B. Results showed that for the analyzed specimens, heating up to 42 days did not have a major effect on their T_g and E' value at 21°C . Visual observations showed that specimens heated for 49 and 56 days underwent considerable degradation. They became very brittle and the slightest touch resulted in crumbling (this sample contained lower amounts of stabilizers than Sample A). Therefore, it was not possible to either prepare the specimen or to load it in the fixture because it broke into smaller fragments due to material degradation.

Sample C (Table 5) showed a similar trend as Sample B. For exposure times less than 42 days, there was no significant effect on T_g (E''_{\max}), which remained almost unchanged at -34°C and there was not much variation in the storage modulus (E'). Again, the specimens heated for 49 and 56 days were extremely brittle and it was not possible to analyze them by DMA.

The average T_g and E' values for Samples D and E are given in Tables 6 and 7. Again, no significant changes are observed in the T_g values of both analyzed samples. The D specimens heated for 14, 21, and

TABLE 4—Summary of average glass transition temperature of Sample B.

Sample ID	Exposure Type	T_g (E'_{int}) °C	ΔT_g (E'_{int})	T_g (E''_{\max}) °C	ΔT_g (E''_{\max})	$E' \times 10^8$, Pa at 21°C	Comments
	0	-44 ± 1^a	0	-34 ± 0^a	0	2.6 ± 0.2^a	Control
	7d/116°C	-43 ± 0	+1	-34 ± 0	0	2.5 ± 0.2	
	10d/116°C	-44 ± 0	0	-34 ± 0	0	2.1 ± 0.1	
	14d/116°C	-45 ± 1	-1	-34 ± 0	0	2.5 ± 0.7	
B	21d/116°C	-44 ± 1	0	-34 ± 0	0	2.5 ± 0.1	
	28d/116°C	NA	...	NA		NA	Not analyzed
	35d/116°C	-45 ± 1	-1	-35 ± 1	-1	2.9 ± 0.1	
	42d/116°C	-42 ± 0	+1	-34 ± 0	0	2.4 ± 0.3	
	49–56d/116°C	NA		NA		NA	Not analyzed. Too brittle

^a \pm =Standard deviation.

TABLE 5—Summary of average glass transition temperature of Sample C.

Sample ID	Exposure Type	$T_g (E'_{int})$ °C	$\Delta T_g (E'_{int})$	$T_g (E''_{max})$ °C	$\Delta T_g (E''_{max})$	$E' \times 10^8$, Pa at 21 °C	Comments
C	0	-44 ± 1^a	0	-34 ± 0^a	0	2.5 ± 0.1^a	Control
	7d/116 °C	-43 ± 0	+1	-34 ± 0	0	2.2 ± 0.7	
	10d/116 °C	-44 ± 0	0	-34 ± 0	0	2.9 ± 0.0	
	14d/116 °C	-46 ± 1	-2	-34 ± 0	0	2.5 ± 0.3	
	21d/116 °C	-43 ± 1	+1	-34 ± 0	0	2.2 ± 0.3	
	28d/116 °C	NA		NA		NA	Not analyzed
	35d/116 °C	-45 ± 1	-1	-34 ± 0	0	2.8 ± 0.1	
	42d/116 °C	-42 ± 0	+2	-34 ± 0	0	2.2 ± 0.5	
	49–56d/116 °C	NA		NA		NA	Not analyzed. Too brittle

^a±=Standard deviation.

28 days showed a slight increase in the modulus (E') values. It was not possible to analyze the 35-day specimen because it became very brittle and crumbled on cutting. After 28 days of heating, E specimens also became very brittle.

Samples F and G were both greatly affected by the heating treatment (Table 8). Sample F showed considerable degradation after 14 days of heating to the point of crumbling. Sample G showed a similar degradation at ten days of exposure (Fig. 4). For the analyzed specimens from F and G samples, the glass transition temperatures as well as the measured moduli values were similar to those of the other analyzed samples.

Modulated Differential Scanning Calorimetry (MDSC™)

Since it was not possible to measure the T_g of some of the heated specimens from Samples B–G by DMA, preliminary analysis using modulated differential scanning calorimetry (MDSC™) was carried out on some of the heated film specimens. The control and 56 days of Sample A, as well as Samples D (35 days), F (21 days), and G (14 days) were analyzed by MDSC™. The T_g of Sample A (control and heated) was measured by DMA; therefore, this will allow establishing a comparison between the T_g trend observed by

TABLE 6—Summary of average glass transition temperature of Sample D.

Sample ID	Exposure Type	$T_g (E'_{int})$ °C	$\Delta T_g (E'_{int})$	$T_g (E''_{max})$ °C	$\Delta T_g (E''_{max})$	$E \times 10^8$, Pa at 21 °C	Comments
D	0	-42 ± 0^a	0	-34 ± 0^a	0	2.2 ± 0.1^a	Control
	7d/116 °C	-42 ± 1	+1	-34 ± 1	0	2.0 ± 0.0	
	10d/116 °C	-44 ± 0	-2	-34 ± 0	0	2.1 ± 0.0	
	14d/116 °C	-44 ± 0	2	-34 ± 0	0	2.9 ± 0.0	
	21d/116 °C	-43 ± 0	-1	-34 ± 0	0	2.5 ± 0.1	
	28d/116 °C	-42 ± 0	0	-34 ± 0	0	2.6 ± 0.1	
	35–56d/116 °C	NA		NA		NA	Not analyzed. Too brittle

^a±=Standard deviation.

TABLE 7—Summary of average glass transition temperature of Sample E.

Sample ID	Exposure Type	$T_g (E'_{int})$ °C	$\Delta T_g (E'_{int})$	$T_g (E''_{max})$ °C	$\Delta T_g (E''_{max})$	$E' \times 10^8$, Pa at 21 °C	Comments
E	0	-43 ± 0^a	0	-34 ± 0^a	0	1.9 ± 0.2^a	Control
	7d/116 °C	-42 ± 0	+1	-34 ± 0	0	2.0 ± 0.1	
	10d/116 °C	-44 ± 0	-1	-34 ± 0	0	2.2 ± 0.1	
	14d/116 °C	-44 ± 1	1	-34 ± 0	0	3.2 ± 0.1	
	21d/116 °C	-42 ± 0	+1	-33 ± 1	+1	2.4 ± 0.0	
	28–56d/116 °C	NA		NA		NA	Not analyzed. Breaks on cutting

^a±=Standard deviation.

TABLE 8—Summary of average glass transition temperature of Sample F and G.

Sample ID	Exposure Type	$T_g (E'_{int})$ °C	$\Delta T_g (E'_{int})$	$T_g (E''_{max})$ °C	$\Delta T_g (E''_{max})$	$E' \times 10^8$, Pa at 21 °C	Comments
F	0	-44 ± 1^a	0	-34 ± 0^a	0	2.4 ± 0.1^a	Control
	7d/116 °C	-43 ± 1	+1	-34 ± 0	0	2.0 ± 0.0	
	10d/116 °C	-44 ± 0	0	-34 ± 0	0	2.3 ± 0.1	
	14d/116 °C	-42 ± 0	+2	-33 ± 1	+1	2.9 ± 0.1	
	21–56d/116 °C	NA		NA		NA	Not analyzed. Too brittle
G	0	-43 ± 0^a		-34 ± 0^a		2.7 ± 0.2^a	Control
	7d/116 °C	-44 ± 1	-1	-34 ± 0	0	2.0 ± 0.3	
	10d/116 °C	-42 ± 1	+1	-31 ± 1	+3	3.0 ± 0.4	Signs of degradation at 10 days
	14d/116 °C	NA		NA		NA	Not analyzed—Sample crumble

^a \pm =Standard deviation.

DMA and DSC. The analysis was performed from -80 to -100 °C at 2 °C/min, an amplitude ± 0.318 °C and a 60-second period. The T_g of the film samples summarized in Table 9 was obtained from the derivative of the reverse heat capacity (C_p) curves, which will not be shown.

Preliminary MDSCTM results (Table 9) suggests that Sample A has a T_g at -37 °C and another at 44 °C. Sample D only shows a T_g at -28 °C. The reverse heat capacity curves (not shown) for Sample F has a peak at -25 °C and a shoulder at -15 °C. The curve for Sample G, on the other hand, displays T_g s at -19 , -10 , and $+68$ °C. The multiple T_g observed in the film samples may result from the PE polymer or poor miscibility of the components in the polymer matrix. Glass transitions ranging from -25 to -120 °C have been reported for PE [26]. The lack of agreement among research is related to the fact that PE is not commonly accessible in the amorphous state (below its melting temperature) due to its extremely high crystallization rate originated from the perfect chain structure [27].

The T_g (-37 °C) of the control and 56-day specimens of Sample A is ~ 3 °C lower than those measured by DMA (Table 3). Although the T_g of these two samples measured by MDSCTM is lower than that measured by DMA; it follows the same trend indicating that heating of Sample A up to 56 days did not have a significant effect on its T_g . Previous work on measurements of T_g of roofing materials by DMA, TMA, and DSC [28] showed that the T_g of unheated and heated EPDM roofing samples obtained from the maximum of the loss modulus curve (E''_{max}) as measured by DMA is slightly warmer than that measured by

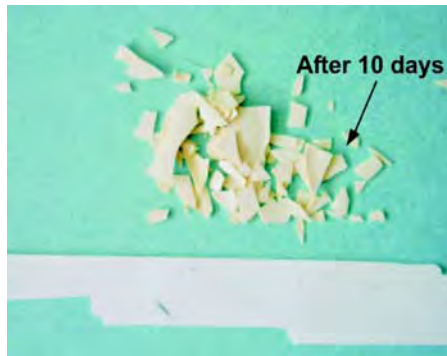


FIG. 4—Sample G after ten days at 116 °C.

 TABLE 9—Summary of average glass transition temperature measured by MDSCTM.

Sample ID	Exposure Type	T_g (MDSC TM) °C
A	0	$-37 / +44$
	56d/116 °C	$-37 / +44$
D	35d/116 °C	-28
F	21d/116 °C	$-25 / -15 / +43$
G	14d/116 °C	$-19 / -10 / +68$

TABLE 10—Summary of average mass loss of TPO Sample A.

Sample ID	Exposure Type	Mass Loss (%)		Residue %	Comments
		Nitrogen 25–590°C	Air 590–1000°C		
	0	71.2±0.2 ^a	0.9±0.1 ^a	27.9±0.2 ^a	Control
A	7d/116°C	71.1±0.3	0.8±0.1	28.1±0.2	
	14d/116°C	71.1±0.2	0.9±0.1	28.1±0.1	
	21d/116°C	71.3±0.1	0.8±0.0	28.0±0.1	
	35d/116°C ^a	71.2±0.2	0.8±0.1	27.9±0.1	
	49d/116°C	70.8±0.3	0.9±0.1	28.4±0.2	
	56d/116°C	71.0±0.1	1.0±0.1	28.1±0.1	

^a±=Standard deviation.

DSC. Hence, it is reasonable to say that the T_g of the specimens from Sample D (35 days), F (21 days), and G (21 days) can be considered as an indication of increases in their T_g of the analyzed film specimens due to heating.

Thermogravimetric Analysis (TG/DTA)

The average mass losses between 25 and 1000°C for the specially formulated TPO film samples are summarized in Tables 10–16. Each entry is the average and standard deviation of at least two individual measurements. Under the experimental conditions used, the control film specimens can be considered thermally stable up to approximately 250°C and start to decompose near 350°C. The analyzed heated specimens, however, appear to be slightly less thermally stable than the control specimens. Both heated and control specimens analyzed display 60–71 % mass loss from 25–590°C under a nitrogen atmosphere due to the decomposition of organic components, approximately 1 % between 590 and 1000°C under air (inorganic), except Samples F and G which show 2–4 % mass loss in this region after 14 days of heating. All analyzed specimen display a 27–33 % residue.

Overlays of the derivative of the mass loss (DTG) curves for all samples are shown in Figs. 5–11. The DTG curves for the analyzed control specimens showed an unresolved DTG peak between 350 and 550°C with a maximum rate of decomposition in the range of 468–481°C and a shoulder near 450°C. The higher temperature mass loss corresponds to decomposition of the polymer matrix, whereas the shoulder may be due to additives (e.g., stabilizers, flame retardants, etc.). Due to the large amount of data only the DTG curves displaying differences will be shown.

Some of the overlays do not have DTG curves for all heating periods. After exposure, it was not possible to measure the mass loss of some specimens using a 20-mg sample size because large spikes in the signals between 300 and 450°C were observed. The sample mass was then reduced by at least half (see Tables 11–15) but the signal problem persisted for some of the heated specimens. To further investigate the signal problem, Samples C, D, E, which still showed the problem were reanalyzed by TG using a 5 mg mass. No signal problem was observed for this mass size. Please note that only the heating period where the signal problem persisted was investigated. It is not known if samples heated for longer periods (e.g., 42–56 days) will show the same problem when using the latter mass size.

The signal problem encountered during the TG analysis may be due to either some material flying out of the measuring pan or exothermic reactions occurring during heating. The causes are not fully understood, but a possible explanation is that heating may have affected significantly the chemical composition of the specimen and as a result either the combustion rates changed or its density decreased so the gas flow removed material from the pan. It is also possible that the heat exposure may have decreased the effectiveness of the flame retardant. Sample A has the highest content of NON HALS such as flame retardant, whereas G does not have any. It is interesting to note that the specimens where such a problem was encountered corresponded to those that became very brittle with heating and DMA testing was not possible.

The control and heated specimens from Sample A show a similar mass loss (Table 10). The major DTG peak at 468°C in Fig. 5 corresponding to the decomposition of the polymer matrix and the shoulder at 423°C remains unchanged for all specimens from this sample. This is an indication that heating up to

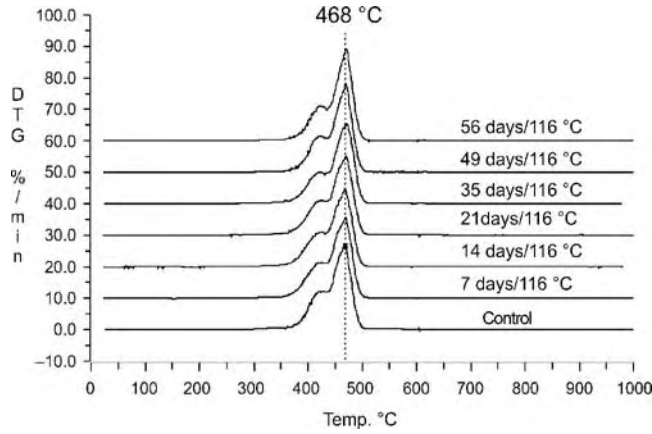


FIG. 5—DTG overlay for Sample A.

56 days did not affect significantly its chemical composition. This sample has the highest content of all stabilizers used (Table 1); hence, it would be expected that heating up to 56 days might have a lesser effect on this film than on the others.

Control and heated specimens from Sample B (Table 11) showed mass losses similar to Sample A. For heating periods above 35 days, the shoulder observed in the DTG curves (Fig. 6) at approximately 425 °C became more resolved, noisier, and its maximum shifted to near 375 °C. This is an indication that heating periods greater than 35 days affected the thermal stability of the sample. Another indication of degradation is the fact that it was necessary to reduce the mass size by half for the 56-day specimen due to signal problem. These results are consistent with the observations when attempting to prepare the specimens

TABLE 11—Summary of average weight loss of TPO Sample B.

Sample ID	Exposure Type	Mass Loss (%)			Residue %	Comments
		Nitrogen		Air		
		25–300 °C	25–590 °C	590–1000 °C		
	0		71.2±0.4 ^a	0.8±0.1 ^a	28.0±0.4 ^a	Control
	7d/116 °C		70.8±0.3	0.9±0.1	28.3±0.2	
	14d/116 °C		71.4±0.14	0.8±0.0	27.8±0.1	
B	21d/116 °C		71.0±0.2	0.8±0.1	28.3±0.1	
	35d/116 °C		71.0±0.07	0.8±0.1	28.2±0.1	
	42d/116 °C		71.3±0.2	0.9±0.1	27.9±0.1	
	49d/116 °C ^a	2.9±0.0	70.1±0.0	0.8±0.0	28.5±0.0	
	56d/116 °C	2.8±0.2	69.6±0.0	1.0±0.1	29.4±0.1	Reduced mass (10 mg)

^a±=Standard deviation.

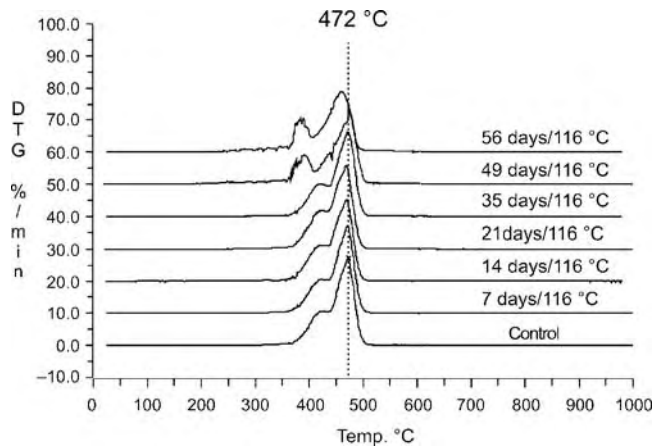


FIG. 6—DTG overlay for Sample B.

TABLE 12—Summary of average mass loss of TPO Sample C.

Sample ID	Exposure Type	Mass Loss (%)				Residue %	Comments
		Nitrogen			Air		
		25–300 °C	25–402 °C	25–590 °C	590–1000 °C		
C	0			71.0±0.2 ^a	0.9±0.0 ^a	28.1±0.2 ^a	Control
	7d/116 °C			70.7±0.1	0.9±0.0	28.4±0.1	
	14d/116 °C			71.0±0.1	0.8±0.0	28.2±0.1	
	21d/116 °C			71.9±1.2	0.9±0.1	27.3±1.1	
	35d/116 °C			71.0±0.0	0.9±0.0	28.1±0.0	
	42d/116 °C			70.7±0.1	0.9±0.0	28.4±0.1	
	49d/116 °C	2.2±2.2		70.8±0.6	1.0±0.1	28.2±0.4	Reduced mass (10 mg)
	56d/116 °C	3.7±0.6	21.9±1	69.6±0.1	0.8±0.5	29.7±0.4	Reduced mass (5 mg)

^a±=Standard deviation.

heated for 49 and 56 days for DMA analysis. They became brittle and it was not possible to measure their T_g . This TPO film has equal parts per hundred resins (phr) of stabilizers (Table 1) but lower than Sample A. The signal problem observed for the sample heated for 56 days may be an indication that such heat exposure may have diminished the effect of one of the stabilizers.

The average mass losses for Sample C are given in Table 12. The mass loss for the analyzed specimens heated up to 42 days remained almost unchanged. The sample showed similar behavior to that of Sample B for 49 days of heating for which half of the original mass was used, but for 56 days, signals problem continued. Therefore, the mass size was further reduced. From the DTG curves (Fig. 7), it can be seen that the shoulder maximum at 425 °C shifted to near 385 °C for 56 days at which point it was almost fully resolved, which explains the 22 % mass loss (Table 12) in the temperature range of 25–402 °C. The mass loss up to 300 °C is higher than for 49 days. A slight shift to lower temperature is observed in maximum of the DTG peak for the 49 and 56-day specimens. This suggests material degradation as a result of heating. It can be observed that the signal problem for this sample appears at an earlier heating period than in Sample B. The difference in the chemical composition of Sample C and B is the UV absorber content which is lower in the former. Therefore, the signal problem may be attributed to effect of heat on one of the stabilizers.

Specimens from Sample D showed a similar mass loss pattern through the first 28 days of heat exposure (Table 13 and Fig. 8). No major changes were observed until 28 days of heating. The 35-day specimens degraded and it was necessary to reduce the original mass by at least half to analyze them by TG. The DTG curves showed a shoulder on the DTG peak up to 28 days. This shoulder is fully resolved for the 35-day specimen, which explains the loss ~23 % up to 402 °C (Table 13). No mass loss data are available for specimens heated for periods longer than 35 days because signs of degradation started to appear at this heating period. Only the heating periods at which the signal problem was first encountered were analyzed. Again, it was observed that the signal problem corresponded to specimens that were too

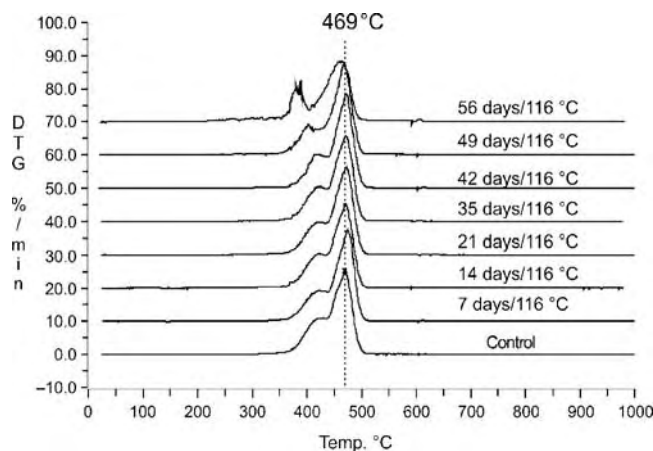


FIG. 7—DTG overlay for Sample C.

TABLE 13—Summary of average mass loss of TPO Sample D.

Sample ID	Exposure Type	Mass Loss (%)				Residue %	Comments
		Nitrogen			Air		
		25–300 °C	25–402 °C	25–590 °C	590–1000 °C		
D	0			70.8±0.2 ^a	1.0±0.1 ^a	28.3±0.1 ^a	Control
	7d/116 °C			70.7±0.3	1.0±0.1	28.4±0.4	
	14d/116 °C			70.8±0.21	0.8±0.0	28.4±0.21	
	21d/116 °C			71.2±0.3	0.8±0.1	28.1±0.2	
	28d/116 °C ^a			70.1±0.5	0.4±0.1	29.4±0.5	
	35d/116 °C	4.9±0.1	22.8±0.1	68.0±0.8	1.5±0.1	30.6±0.8	Reduced mass (5 mg)
	42–56d/116 °C ^a	NA	NA	NA	NA	NA	Not analyzed

^a±=Standard deviation.

brittle for DMA testing, indicating degradation of the material due to heat aging. The signal behavior for this sample is consistent with the observations made for Sample C regarding the effect of heating periods on one of the stabilizers. Although Sample D has equal phr (0.2) of each stabilizer (Table 1), the phr content of NON HALS and HALS is lower than Sample C.

If the behavior of the film samples with increasing heating periods is due to the heat effect on a specific stabilizer, it is reasonable to expect that samples will show a similar behavior as stabilizer content decreases. For example, Sample B has the same components but lower phr than A. Sample C has only lower phr of UV absorber than B. In fact, the TG results showed that signs of degradation for Sample C are observed at earlier heating periods (49 days) than in B (56 days). Therefore, it may be tempting to attribute the signal problem (degradation) to the UV absorber. However, this is not the case for Sample D, which has the same phr of UV absorber than C but lower phr of NON HALS and HALS stabilizers. This suggests that although each stabilizer is used for a specific purpose, their stabilizing effect on the final product may be a combined one rather than individual. From the film composition, it is difficult to attribute degradation of the films to a specific stabilizer because the phr of more than one stabilizer was varied in the same sample.

The average mass losses in Table 14 for Sample E show no major changes in the mass loss values for control and heated specimens up to 28 days. The TG analysis of the specimens heated for 35 days also required smaller mass than the 28-day specimens. No weight data are available for specimens heated above 35 days at which signs of degradation were first observed. The DTG curves for this sample are similar to those of Sample D and will not be included. The specimen heated for 21 and 35 days became brittle, which is a sign of degradation. This sample has the same phr of NON HALS and HALS but it has no UV absorber. Therefore, the behavior observed in the samples with increasing heating periods may not be related to UV stabilizer content.

The DTG curves in Fig. 9 for Sample F (control and heated) showed a considerable shifting in the maximum of the peak at 477 °C at 35 and 56 days of heating and the shoulder, somehow noisy, starts to resolve at 14 days and above. The mass loss for this sample summarized in Table 15 showed a slightly

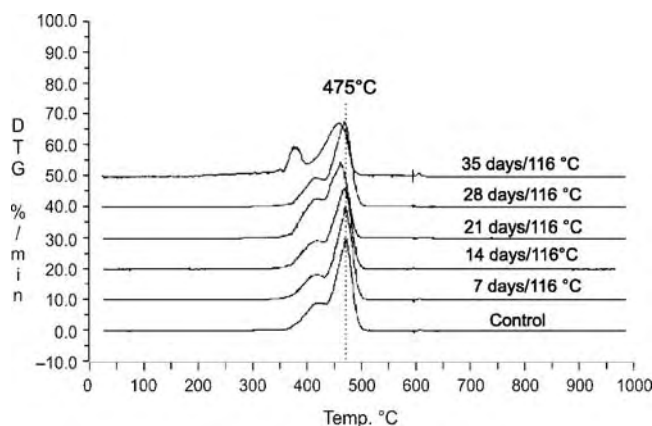


FIG. 8—DTG overlay for Sample D.

TABLE 14—Summary of average mass loss of TPO Sample E.

Sample ID	Exposure Type	Mass Loss (%)					Residue %	Comments
		Nitrogen			Air			
		25–300 °C	25–402 °C	25–590 °C	25–590 °C	590–1000 °C		
E	0			70.9±0.4 ^a	0.9±0.0 ^a	28.3±0.4 ^a	Control	
	7d/116 °C			70.9±0.1	0.9±0.0	28.2±0.1		
	14d/116 °C			70.9±0.1	0.9±0.0	28.2±0.1		
	21d/116 °C			71.1±0.0	0.9±0.0	28.0±0.0		
	28d/116 °C			71.0±0.2	0.8±0.1	28.2±0.2		
	35d/116 °C	4.9±0.1	21.6±0.2	68.0±0.8	1.5±0.1	30.6±0.8	Reduced mass (5 mg)	
	(42–49)d/116 °C	NA	NA	NA	NA	NA	Not analyzed	
	56d/116 °C	NA	NA	NA	NA	NA	Not analyzed	

^a±=Standard deviation.

different pattern for the specimen heated above ten days. They display 3–6 % mass loss in the 25–325 °C range. It was not possible to quantify the mass loss from the DTG curve in this temperature range for specimens heated up to 14 days because the shoulder on the DTG peak was not fully resolved. For specimens heated above 14 days, the shoulder is fully resolved, which allows reading the mass loss of the curve.

The change in mass loss between the control and heated specimen (21 days and more) of the F sample in the temperature range of 25–590 °C is about 5 %, which is above the CIB/RILEM recommended limit of 3 % [29]. This indicates that heating has a detrimental effect on the chemical composition of the sample.

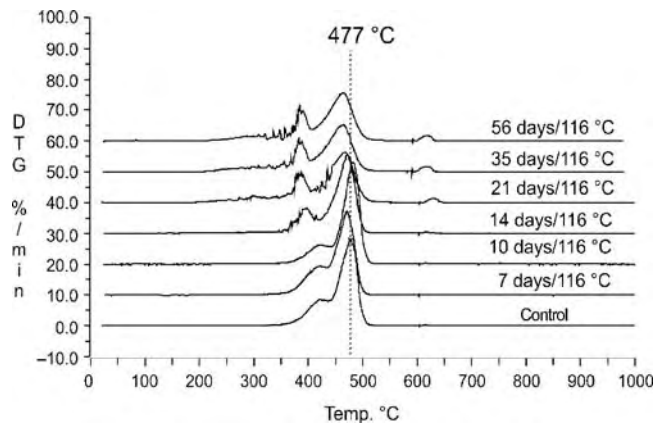


FIG. 9—DTG overlay for Sample F.

TABLE 15—Summary of average mass loss of TPO Sample F.

Sample ID	Exposure Type	Mass Loss (%)					Residue %	Comments
		Nitrogen			Air			
		25–300 °C	300–325 °C	325–590 °C	25–590 °C	590–1000 °C		
F	0	0.4±0.1 ^a	0.2±0.0 ^a	70.5±0.2 ^a	71.0±0.1 ^a	0.9±0.1 ^a	28.2±0.1 ^a	
	7d/116 °C	0.2±0.1	0.2±0.1	70.4±0.0	70.8±0.0	0.8±0.0	28.4±0.0	
	10d/116 °C	0.2±0.0	0.2±0.1	70.5±0.1	70.9±0.1	1.0±0.1	28.2±0.1	
	14d/116 °C	2.1±0.4	0.7±0.3	67.7±0.6	70.4±0.1	1.0±0.1	28.5±0.1	
	21d/116 °C	4.4±0.3	1.8±0.2	60.8±0.1	67.1±0.4	2.0±0.1	30.9±0.3	
	28d/116 °C	4.8±0.1	1.6±0.3	61.4±0.4	67.8±0.1	2.0±0.2	30.3±0.1	
	35d/116 °C	4.4±0.1	1.6±0.1	59.8±0.1	66.0±0.01	2.7±0.0	31.4±0.1	Reduced mass (10 mg)
	(42–49)d/116 °C	NA	NA	NA	NA	NA	NA	Not analyzed
56d/116 °C	4.2±0.2	1.8±0.1	59.8±0.1	65.8±0.4	2.8±0.2	31.4±0.1	Reduced mass (10 mg)	

^a±=Standard deviation.

TABLE 16—Summary of average mass loss of TPO Sample G.

Sample ID	Exposure Type	Mass Loss (%)					Residue %	Comments
		Nitrogen			Air			
		25–300 °C	300–325 °C	325–590 °C	25–590 °C	590–1000 °C		
G	0	0.4±0.1 ^a	0.2±0.1 ^a	70.7±0.7 ^a	71.2±0.7 ^a	0.9±0.1 ^a	27.9±0.8 ^a	Control
	7d/116 °C	0.2±0.1	0.1±0.0	70.7±0.0	71.0±0.1	0.8±0.1	28.1±0.1	
	10d/116 °C	4.7±1.1	0.8±0.1	65.7±0.0	71.1±0.7	1.4±0.1	27.6±0.8	
	14d/116 °C	7.2±0.2	2.1±0.1	56.4±0.1	65.7±0.4	3.2±0.2	31.2±0.6	
	21d/116 °C	7.4±0.1	2.4±0.0	53.1±0.3	62.8±0.2	4.3±0.01	32.8±0.1	
	(28–56)d/116 °C	NA	NA	NA	NA	NA	NA	Not analyzed— Sample removed from oven at 21 days (crumbled)

^a±=Standard deviation.

It is possible that the effectiveness of some of the additives (e.g., stabilizers) decreased with heating and the sample became more susceptible to heating. In fact, this film has only NON HALS stabilizers.

Sample G showed mass losses below 300 °C, ranging from 4 % at 10 days to 7 % at 21 days of heat exposure (Table 16). At ten days the shoulder originally at 425 °C became more resolved at 395 °C (Fig. 10). The major peak at 481 °C also became broader as exposure time increased and shifted slightly to a lower temperature (~460 °C), indicating a deterioration of the material due to the heat. Moreover, a small peak at approximately 600 °C also became more pronounced with exposure time. It was not possible to heat age the specimens from Sample G beyond 21 days since the specimen crumbled to the touch. DMA results showed a change in the material's T_g (+3 °C) after ten days which is consistent with the mass loss data.

Fourier Transform Infrared (FTIR) Spectroscopy

The spectra of some of the TPO films (control and heated) are displayed in Figs. 11–15. Only spectra showing changes in their absorption bands after heating will be shown due to the large number of spectra. The purpose of the FTIR analysis was to ensure correlation between the three analysis techniques used in this study.

In general, the IR spectra of the films show an intense band at 3690 cm^{-1} that may result from OH in compounds such as $\text{Mg}(\text{OH})_2$ or other organoclays that are used in TPOs. $\text{Mg}(\text{OH})_2$ has been reported to be an effective nonhalogen flame retardant and smoke suppressant [30]. Bands in the 3000–2800 cm^{-1} region are due to the stretching vibrations of the CH_3 and CH_2 groups. The band at 1460 cm^{-1} is attributed to the CH_3 asymmetric bending and that at 1376 cm^{-1} results from the CH_3 symmetric bending plus the CH_2 wag and the C–C chain stretching. The spectrum of control and heated specimens from Sample A (Fig. 11) showed slight differences in the absorption bands up 56 days of heating. The relative intensity of

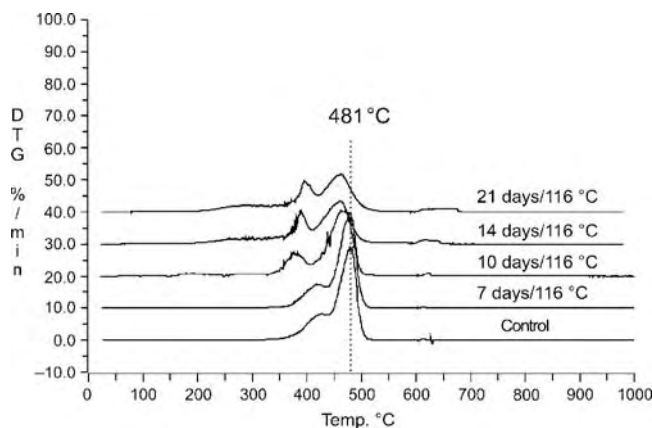


FIG. 10—DTG overlay for Sample G.

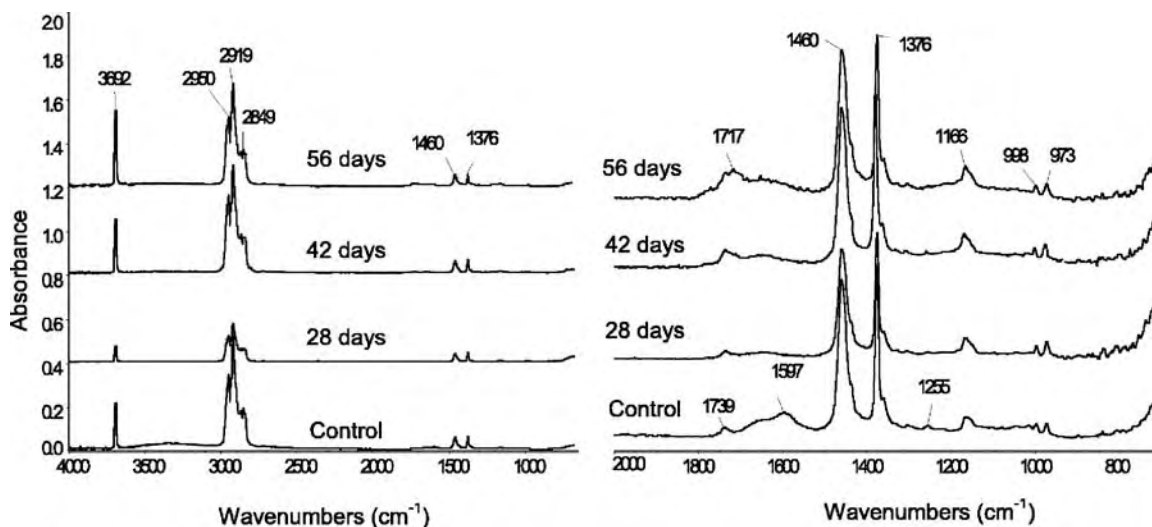


FIG. 11—Sample A—Spectra of control and heated specimens.

the band near 1600 cm^{-1} in the control specimens appears to decrease whereas its shoulder ($\sim 1650\text{ cm}^{-1}$) becomes more defined with increasing heating periods but is still a weak absorption band. The band and the shoulder may be due to the olefinic ($\text{C}=\text{C}$) group vibrations. Amines also show bands near 1600 cm^{-1} . Due to the intensity of the CH_3 and CH_2 bands in the $3000\text{--}2800\text{ cm}^{-1}$ region, it is difficult to see the shoulder; therefore, this region was expanded.

Specimens from Sample B (Fig. 12) heated for 49 and 56 days show some additional bands at 1715 and 1598 cm^{-1} , which may result from carbonyl ($\text{C}=\text{O}$) and olefinic ($\text{C}=\text{C}$) groups, respectively. The presence of the carbonyl band is indicative of oxidation. Similar bands are observed in the same range for all heated samples depending on the heating period (Figs. 13–15) for the same exposure time. The FTIR results confirm the DMA and TGA results. The latter show differences in the DTG curves of Sample B at 49 and 56 days and problems with brittleness were encountered with the same specimens during the DMA analysis.

Sample E did not show significant differences between the absorption bands of the control and heated specimens up to 28 days of heat exposure (Fig. 13). However, there are additional bands at 1714 and 1596 cm^{-1} already observed in the spectrum of Sample B (Fig. 12). A shoulder is also observed on the 1770 cm^{-1} band near 1780 cm^{-1} as well as another band at 1165 cm^{-1} characteristic of CH_3 that has been attributed to crystalline PP [31]. The $2000\text{--}800\text{ cm}^{-1}$ region was expanded in Fig. 13 for 35 days of heating to show the additional bands.

The spectra for Samples F and G are given in Figs. 14 and 15. The spectra of Sample F (Fig. 14)

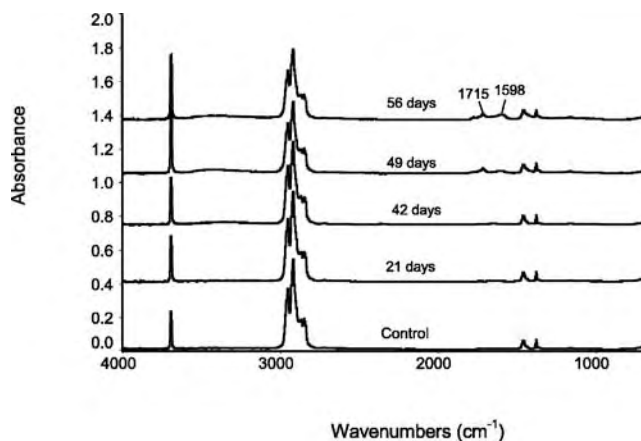


FIG. 12—Sample B—Spectra of control and heated specimens.

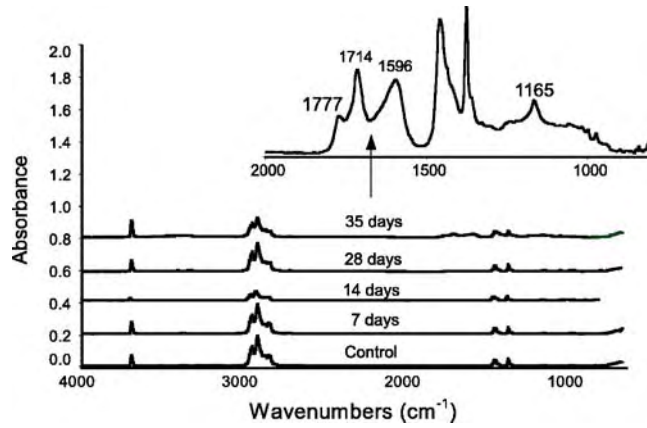


FIG. 13—Sample E—Spectra of control and heated specimens.

indicate differences between the control and heated material at 21 days of heating whereas for G they are slightly visible at 10 days. Again, the 2000–800 cm^{-1} region was expanded in Fig. 15 to show the disappearance or decrease in the band at 1598 cm^{-1} with heating.

ATR analysis on the surface oxidation of thermoplastic olefin elastomer under ozone exposure [32] indicated that after ozone exposure new IR bands were observed near 1746 cm^{-1} and 1714 cm^{-1} characteristic of carboxyl and carbonyl groups. The ozone attack on rubbery materials can form unstable ozonides and polymeric peroxide, and then cleave to generate oxygenated products, such as acids, esters, ketones, and aldehydes. The study also showed that unsaturated double bonds are a common product from saturated polymers under ozone attack. As a result a broad band near 1630 cm^{-1} is attributed to the double bond formation ($\text{C}=\text{C}$). Although the type of exposure used on the TPO film samples is different from ozone exposure, it is possible that low phr of stabilizer combined with the long exposure resulted in a similar degradation. The bands characteristic of oxidation (1780, 1714, and 1165 cm^{-1}) observed in the ATR analysis of the TPO subject to ozone exposure [32] were observed in the TPO film.

Results from the ATR-FTIR analysis have shown that this technique can be used to follow the changes in the samples due to heating. For example, the spectra of the control Samples B-F did not show absorption bands near 1600 and 1165 cm^{-1} or the concentration of the component responsible for such a band is too low to be detected by the ATR technique, which is primarily a surface technique. However, at 35 days of heating, a weak broad band centered near 1650 cm^{-1} is observed as well as the two new bands at 1598 and 1717 cm^{-1} at 49 and 56 days of heating. These two bands are observed in all heated samples and its

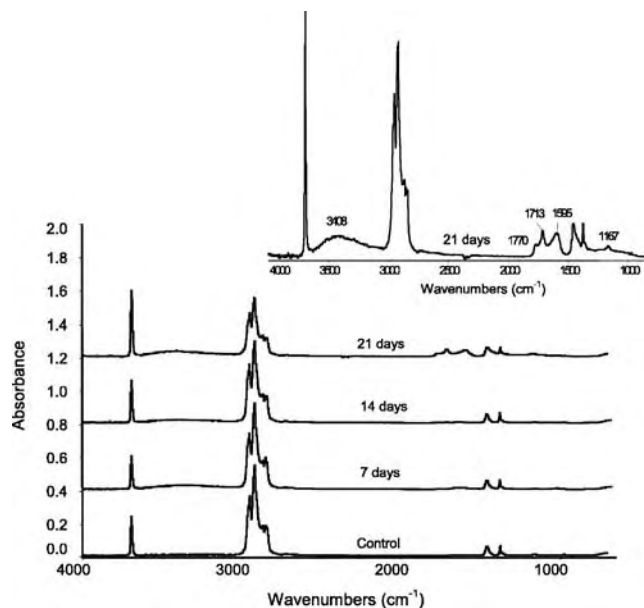


FIG. 14—Sample F—Spectra of control and heated specimens.

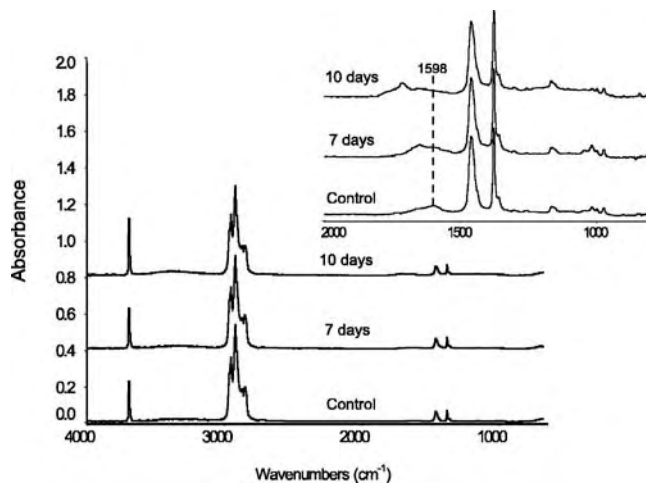


FIG. 15—Sample G—Spectra of control and heated specimens.

relative intensity appears to increase as the heating period increases suggesting the formation of carbonyl (due to oxidation) and olefinic groups. The decrease and increase, or both, in the relative intensity of the IR bands as well as appearance of new ones are indicative of compositional or structural changes in the sample.

An FTIR surface sampling technique such as photoacoustic spectroscopy (PAS) depth profiling, which has been reported to provide information on the stratification of components in TPO [1,31], may help to gain more information on the heating of the samples under study.

Conclusions

1. With the exception of Sample A, all samples were susceptible to the heating schedule used in this study. Some of the samples underwent significant degradation after certain exposure periods. Some of them became brittle after 10 or 21 days whereas others degraded after 42 days.
2. No significant changes in the glass transition temperature measured by DMA of the analyzed samples were observed, except Sample G that showed a ΔT_g of $+3^\circ\text{C}$ after ten days of heating. However, one must remember that some specimens were too embrittled to be analyzed by DMA.
3. The degradation of the TPO film samples was confirmed by thermogravimetric analysis. The DTG overlay curves provided some evidence of the onset of degradation temperatures as significant changes in the DTG peaks were observed as a function of heating periods.
4. Certain specimens were not analyzed by TG due to signal problems (spikes) encountered during the TG analysis. In these cases, the sample size was reduced by at least half and the test repeated for the heating period at which the problem was first encountered. It is possible that the remaining heating periods could be analyzed by further reducing the sample mass. Such problems were usually encountered with samples that showed physical degradation due to heat aging and corresponded to the exposure periods at which they had become brittle.
5. The FTIR analysis confirmed the DMA and TG results as well as the visual observations of the film samples. The spectra of the film samples showed that the changes observed in DMA and TG data are consistent with the spectra of each sample after exposure. For example, DMA, TG, and FTIR did not show significant changes for Sample A even after being heated for 56 days. However, Sample G became gummy and broke easily after ten days of heating. This sample showed a $+3^\circ\text{C}$ increase in the T_g . The shoulder observed in the DTG curve of the control specimen heated for ten days became more resolved in the DTG curve showing an $\sim 5\%$ mass loss between 25 and 300°C (Table 16), which is not observed in the control sample.
6. The appearance of new IR bands on the heated film with heat exposure suggests that oxidation due to heat exposure may be the cause degradation since the bands observed by other researchers on oxidation of TPO has also been observed on the heated film specimens.
7. The study has demonstrated that DMA, TG, and FTIR are valuable analysis tools for evaluating TPO films:

- Sample degradation or failure was observed earlier with decreasing concentration of the stabilizer used. This can be correlated with the failure of the sample with increasing heating;
- Based on the FTIR results, the main absorption bands to follow for the degradation are: 1596 and 1700 cm^{-1} ;
- In TG, the mass loss and DTG peak resolution associated with the increased heat aging correlated well with the about IR absorption bands; and
- Modulated DSC (MDSC™) showed some potential as a analysis tool to measure the T_g of samples that could not be analyzed by DMA due to failure (e.g., brittle).

Acknowledgments

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