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Measuring the Glass Transition Temperature of EPDM Roofing Materials: Comparison of DMA, TMA, and DSC Techniques

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ABSTRACT: Two ethylene-propylene-diene monomer (EPDM) roofing membranes were aged at 100°C for 7 and 28 days. The T_g of these membranes was then determined by dynamic mechanical analysis (DMA), thermomechanical analysis (TMA), and differential scanning calorimetry (DSC) and the results compared. It was found that: (1) T_g data can be obtained easily using the DMA and TMA techniques. The DSC method requires greater care due to the broad step change in the baseline which is associated with heavily plasticized materials. (2) The closest correspondence between techniques was for TMA and DSC (half-height). The latter, within experimental error, yielded the same glass transition temperature before and after heat-aging. (3) The peak maxima associated with $\tan\delta$ and E'' measurements should be cited with T_g values as significant differences can exist. (4) The $T_g(E'')$ values were closer to the T_g (TMA) and T_g (DSC) data than were the $T_g(\tan\delta)$ values. Data obtained at 1 Hz (or possibly less) should be used when making comparisons based on various techniques. An assessment of T_g values indicated that EPDM 112 roofing membrane is more stable than the EPDM 111 membrane. The T_g for EPDM 112 did not change significantly with heat-aging for 28 days at 130°C.

KEYWORDS: ethylene-propylene-diene monomer (EPDM), glass transition temperature (T_g), dynamic mechanical analysis (DMA), thermomechanical analysis (TMA), differential scanning calorimetry (DSC), elastomers, roofing membranes, thermal analysis

In the past, roofing membranes were mostly asphalt-based. Today, however, the choice of roofing materials is quite varied, ranging from asphalt-based or modified-asphalt to polymer-based materials such as polyvinyl chloride (PVC) and ethylene-propylene-diene monomer (EPDM). This variety has forced the international roofing industry to shift towards a multidisciplinary approach in solving roofing problems, i.e., both engineering and chemical principles are used. In 1988, a joint CIB/RILEM international roofing committee was established to investigate the applications of thermal analysis in the characterization of roofing membranes [1]. Thermal analysis, used extensively in characterizing polymeric materials, has not been widely used in the roofing industry [2-13]. Thermoanalytical techniques can be used to monitor a wide array of material characteristics. Some of the

applications include enthalpy, weight-loss, thermal stability, coefficient of thermal expansion, and the glass transition temperature.

Determination of chemical and mechanical characteristics of a material facilitate selection, application, and end-use. One important characteristic for the cold temperature performance of roofing membranes is its glass transition temperature (T_g). T_g is a property of an amorphous polymer and is defined as an assigned temperature at which the polymer changes from a rubbery to a glassy state without any change in phase, i.e., local molecular motion is hindered. Below T_g the material will be rigid and hard. Yet, above T_g the material will exhibit rubber-like characteristics such as pliability. Other properties that vary with T_g are thermal expansion coefficient, heat capacity, and dielectric constant [14-18]. Generally, the strength of polymeric materials above the glass transition temperature is lower than the strength below T_g .

Long-range translational motion of all the molecules is considered to be restrained or frozen below T_g [19]. In the case of noncrosslinked or slightly crosslinked polymers, the glass transition temperature depends on five factors: free volume, attractive forces between molecules, rotation about bonds, stiffness of chain, and chain length. Although different relationships exist between the glass-transition temperature and the melting point (T_m), T_g is always lower than T_m .

There are three thermoanalytical techniques that are commonly used to determine and monitor the changes in T_g . The traditional methods are static techniques such as differential scanning calorimetry (DSC). The drawback with DSC is that T_g is a pseudo-second-order transition and is detected by a step change in baseline (arising from a change in heat capacity). In the case of heavily plasticized materials (e.g., roofing samples) a broad transition is obtained and the step change is difficult to detect. The mechanical methods within thermal analysis include dynamic methods such as dynamic mechanical analysis (DMA) and static load techniques such as thermomechanical analysis (TMA). These techniques provide a greater change in signal arising from the T_g and therefore are easier to use for roofing materials. In this paper, a brief theory of these three thermoanalytical techniques is presented. In addition, the T_g data obtained by the various techniques on EPDM roofing materials are presented and compared.

Theory

DMA [20-24]

The DMA technique measures the stress-strain relationship for a viscoelastic material. A real and imaginary component of modulus can be obtained by resolving the stress-strain components

$$\sigma = \epsilon_0 E' \sin(\omega t) + \epsilon_0 E'' \cos(\omega t)$$

The storage modulus, E' , is defined as $E' = (\sigma_0/\epsilon_0) \cos \delta$ and is a measure of recoverable strain energy in a deformed body. The loss modulus, E'' , is associated with the dissipation of energy as heat due to the deformation of the material and is defined as $E'' = (\sigma_0/\epsilon_0) \sin \delta$. The ratio E''/E' yields the loss tangent or damping factor ($\tan\delta$) which is the ratio of energy lost per cycle to the maximum energy stored and therefore recovered, per cycle.

A typical dynamic mechanical analysis curve shows either E' , E'' , or $\tan\delta$ plotted as a function of time or temperature. In general, the most intense peak observed for either E'' or $\tan\delta$ in conjunction with a relatively pronounced drop in E' corresponds to the glass transition. However, to prove that this relaxation event is a T_g , a DMA multiplexing

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experiment to establish the activation energy would be required. Alternatively, other techniques such as nuclear magnetic resonance (NMR) could be used. Theoretically, the T_g is associated with large-scale molecular motion of the polymer. The T_g event may be affected by the crosslink density or degree of crystallinity and is directly related to the amorphous region within a polymer.

Care should be taken when reporting the glass transition temperature obtained by DMA. The transition temperature determined by DMA (or other dynamic techniques) is not only heating-rate dependent but also frequency dependent. In addition to heating rate and frequency, the mechanical/rheological property (E' , E'' , or $\tan\delta$) used to determine the T_g must also be specified. It has been found that the E'' peak maximum at 1 Hz corresponded closely with the T_g obtained from volume-temperature measurements [20].

TMA [21,25]

TMA is defined as a method for measuring the deformation of a material under a constant load as a function of temperature while the material is under a controlled temperature program (see ASTM E 473, Terminology Relating to Thermal Analysis). Essentially, the expansion or contraction of a sample with an applied force is measured as a function of time or temperature. The plot of this dimensional change versus temperature (or time) can then be used to obtain important sample parameters such as T_g , the coefficient of thermal expansion (CTE), softening temperature, and Young's modulus.

The measuring system consists of a linear voltage differential transformer (LVDT) connected to the appropriate probe. Any displacement of the probe generates a voltage which is then recorded. Various probes are available for the TMA and it is the measuring mode that generally dictates the probe to be used. The measurements can be done in either compression, expansion, penetration, flexural, or tensile mode. It is this variety of probes that allows for the measurement of a wide range of properties on samples of different configurations. The sample configuration ranges from films to fibers to powders to disks. Materials that can be studied by this technique include ceramics, polymers, and composites.

The change in linear dimension as a function of temperature can be described by the following

$$L_2 = L_1 \left(1 + \int_{T_1}^{T_2} \alpha_i dT \right)$$

where α_i is the coefficient of linear expansion, and L_1 and L_2 are the lengths of the specimen at temperatures (or time) T_1 and T_2 , respectively. If the difference between T_2 and T_1 is relatively small, then the equation can be represented by

$$L_2 - L_1 = L_1 \alpha_i (T_2 - T_1)$$

or it can be rewritten as

$$\alpha_i = \frac{1}{L_1} \frac{\Delta L}{\Delta T}$$

Therefore, the slope of the curve of length versus temperature yields $\alpha_i L_1$ and the coefficient of linear thermal expansion is obtained by dividing by L_1 .

There are several drawbacks with TMA. Proper calibration is required to obtain reliable and

reproducible data. Other sources of errors include slippage of the probe on the specimen and specimens undergoing creep in addition to length changes.

DSC

DSC is a simple and yet powerful thermoanalytical technique. It is widely used in providing valuable information on chemical and physical properties of materials. The DSC technique measures the amount of energy (or heat) absorbed or released as the material is heated, cooled, or held at an isothermal temperature. The plot obtained is known as a DSC thermal curve and shows the amount of heat evolved or absorbed as a function of temperature or time. This technique yields thermodynamic data such as enthalpy and specific heat, as well as kinetic data.

The shape and appearance of DSC curves can give a clue as to the type of transition taking place. Generally, distinct peaks are obtained by the DSC technique. These correspond to first-order transitions such as melting or solid-solid phase transformations. These peaks can be integrated and a value for enthalpy (ΔH) can be determined. In the case of second-order transitions such as the glass transition, a stepwise increase in heat capacity is observed. This is also detected in the DSC by a step change in baseline slope.

Calibration of a DSC instrument is needed to determine the T_g with accuracy. Normally, the melting points of pure standards are used. Generally, it is best to use a standard that will have a transition in the same temperature range as the samples being studied.

The glass transition temperature may be determined by taking the middle of the change in baseline (half-height method). This method requires establishing a tangent line. This step is facilitated by using the first derivative of the heat-flow signal. T_g values obtained by DSC are generally different from those obtained by dynamic techniques such as DMA since DSC is a static technique.

Experimental

Two commercially available, nonreinforced EPDM roofing membrane samples (111 and 112) were obtained. One specimen was used as a control. Another specimen was placed in an air-circulating oven preheated to 130°C and heat-aged for 7 and 28 days.

The Seiko DMS110 was used to characterize the rheological properties of the specimens. The instrument was operated in the 8 mm dual cantilever mode of deformation. The sample size was 30-mm-long by 3-mm-wide with a thickness of 1 mm. The temperature range was from -160°C to 100°C and a heating/cooling rate of 1°C per min was used. The parameters also included a constant amplitude of deformation of 30 μ m at frequencies of 1, 2, 5, 10, and 20 Hz.

A small specimen (1 mm by 7 mm by 7 mm) was placed upon a quartz platform inside a Seiko TMA/SS120C thermomechanical analyzer. The quartz expansion probe was positioned onto the sample under a compressive force of 1 g. The analysis was recorded from -100°C to 20°C at a rate of 2°C per min under static air environment. The temperature calibration of the TMA/SS was achieved by using the melting points of indium and mercury.

The DSC experiment (using a Seiko DSC210 module) was conducted by placing 15 to 20 mg of roofing material in an aluminum pan and a corresponding amount of inert material in a reference pan to counterbalance the specific heat capacity of the sample. The sample was tested between -150°C and 100°C at a cooling/heating rate of 20°C per min under a static air environment. The temperature calibration of the instrument was achieved by using the melting points of indium and tin.

Results and Discussion

Three rheological properties are recorded in a DMA experiment, storage modulus (E'), loss modulus (E''), and $\tan\delta$ (E''/E'). The glass transition temperature was determined using the E'' and $\tan\delta$ peak maxima. The two methods yield the same trend for both samples, i.e., the T_g shifts to higher temperatures with heat-aging. Furthermore, an increase of the E'' values above T_g in the rubber plateau region is also noted. The DMA data are summarized in Tables 1 to 4.

As expected, the T_g values shifted to higher temperatures as a function of heat-aging time and increased frequency. The EPDM 111 (as received) has a T_g (E'') at -64.6°C at 1 Hz while at 20 Hz it is shifted to -58.4°C . The T_g (E'') was found to be -48.2°C at 1 Hz and

TABLE 1— T_g determined by the DMA E'' peak maximum for EPDM 111.

	Frequency, Hz				
	1	2	5	10	20
As-received	-64.6	-63.3	-61.8	-60.7	-58.4
7 days	-50.5	-49.5	-47.3	-45.6	-44.5
28 days	-48.2	-46.4	-44.6	-42.8	-41.6

TABLE 2— T_g (in $^\circ\text{C}$) determined by the DMA E'' peak maximum for EPDM 112.

	Frequency, Hz				
	1	2	5	10	20
As-received	-43.7	-42.8	-41.3	-40.0	-38.3
7 days	-43.1	-41.5	-40.2	-38.9	-37.3
28 days	-42.9	-41.3	-39.9	-38.5	-36.9

TABLE 3— T_g (in $^\circ\text{C}$) determined by the DMA $\tan\delta$ peak maximum for EPDM 111.

	Frequency, Hz				
	1	2	5	10	20
As-received	-52.9	-50.2	-48.0	-47.6	-45.4
7 days	-42.7	-41.1	-40.0	-38.4	-36.8
28 days	-40.5	-39.5	-37.3	-36.2	-34.9

TABLE 4— T_g (in $^\circ\text{C}$) determined by the DMA $\tan\delta$ peak maximum for EPDM 112.

	Frequency, Hz				
	1	2	5	10	20
As-received	-34.9	-33.8	-32.2	-30.8	-29.2
7 days	-32.8	-31.0	-29.1	-27.2	-25.6
28 days	-32.6	-30.9	-28.9	-27.0	-25.3

-41.6°C at 20 Hz, after oven aging for 28 days at 130°C . This is a significant difference since the ΔT_g is $\sim 16^\circ\text{C}$. Sample EPDM 112 underwent much smaller changes (due to heat-aging) compared to EPDM 111. The T_g (E'') of the as-received specimen was -43.7°C at 1 Hz and -38.3°C at 20 Hz. The glass transition temperature increased to -42.9°C and -36.9°C for 1 Hz and 20 Hz, respectively, after 28 days at 130°C . It can be seen that EPDM 112 undergoes smaller changes than EPDM 111. Similar observations were noted for the T_g ($\tan\delta$) except that the peak maximum occurred at much higher temperatures. For example, the $\tan\delta$ glass transition temperature for the as-received specimen EPDM 111 was determined to be -52.9°C at 1 Hz and -45.4°C at 20 Hz. This is approximately 12°C higher than the equivalent T_g (E'').

The TMA results, summarized in Table 5, follow a similar trend. The T_g for the as-received specimen EPDM 111 was -66.2°C and -52.8°C after 28 days of heat-aging. In contrast, the glass transition temperature of EPDM 112 was -54.6°C and -52.4°C for the unaged and 28 day heat-aged specimens, respectively. These results were compared to the DMA data taken at 1 Hz and the following was observed. Firstly, the T_g for EPDM 111 shifts by 16.4°C (DMA E''), 12.4°C (DMA $\tan\delta$) and 13.4°C (TMA) after 28 days of heat-aging. Secondly, the T_g (E'') for EPDM 111 was much closer to the T_g determined by TMA than that determined by the DMA- $\tan\delta$ peak maximum. The results were -64.6°C (DMA E''), -52.9°C (DMA $\tan\delta$), and -66.2°C (TMA) for the as received specimens. After 28 days of aging, the difference in values obtained with the techniques was much greater -48.2°C (DMA E''), -40.5°C (DMA $\tan\delta$), and -52.8°C (TMA) but the T_g (TMA) is still closer to the DMA T_g (E'') than the DMA $\tan\delta$ glass transition temperature. Similar results were obtained for the EPDM 112 sample except difference in T_g values between the techniques was much greater (by as much as 20°C between the TMA and DMA- $\tan\delta$ T_g). The coefficient of linear thermal expansion (CTE) above the T_g decreased with increased aging. The T_g for EPDM 112 did not shift significantly with aging (the values also match those obtained by DSC); however, the CTE values did decrease with increased heat-aging.

The DSC results are summarized in Table 6. The average onset of the T_g of the as-received EPDM 111 specimen was -78.5°C ; the average T_g determined by the half-height

TABLE 5—TMA data.

	EPDM 111		EPDM 112	
	T_g ($^\circ\text{C}$)	CTE Above T_g ($\times 10^{-6}$ per $^\circ\text{C}$)	T_g ($^\circ\text{C}$)	CTE Above T_g ($\times 10^{-6}$ per $^\circ\text{C}$)
As-received	-66.2	342	-54.6	319
7 days	-59.2	235	-53.4	300
28 days	-52.8	202	-52.4	284

TABLE 6—DSC data.

	EPDM 111		EPDM 112	
	Onset of T_g ($^\circ\text{C}$)	T_g ($^\circ\text{C}$)	Onset of T_g ($^\circ\text{C}$)	T_g ($^\circ\text{C}$)
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

technique was -66.0°C . Heat-aging for 7 and 28 days at 130°C caused the T_g to shift to higher temperatures as was the case for the previous techniques. The DSC technique also confirmed that for the EPDM 112 sample the T_g remains relatively constant with heat-aging. It was observed that the T_g determined by TMA matched the T_g measured by DSC using the half-height technique. The average T_g (TMA) for the as-received EPDM 111 specimen was -66.2°C while the average T_g (DSC half-height method) was -66.0°C . A similar relationship was found for the EPDM 112 sample. Although the T_g (DSC) results matched those obtained by TMA, they were more difficult to determine. This was due to the broad step change in the baseline. This broad change is typical of heavily plasticized materials such as roofing membranes.

Conclusions

The following conclusions can be drawn from the results obtained by DMA, TMA, and DSC:

- The T_g data for the EPDM roofing materials used in this study were obtained more easily using the DMA and TMA techniques. In this case, due to the high amounts of plasticizer, the DSC method required greater care. The step change in baseline for the EPDM material was broad and weak (due to plasticizer) which created some difficulty in detecting the T_g .
- The peak maxima used to determine T_g must be reported since significant differences can exist between $\tan\delta$ and E'' peak maxima. Furthermore, if both peak maxima were recorded then they should be reported.
- The closest correspondence of T_g data was for TMA and DSC (half-height) techniques. Both techniques, within experimental error, yielded the same glass transition temperature before and after heat-aging.
- The $T_g(E'')$ values from DMA were closer to the T_g (TMA) and T_g (DSC) data than were the $T_g(\tan\delta)$ values. It is suggested that, where applicable, T_g data obtained from dynamic measurements be measured at 1 Hz (or possibly less), thus allowing the T_g to be compared more readily with T_g obtained from nondynamic techniques.
- T_g can be used to monitor changes in EPDM roofing membranes. In this case, EPDM 112 roofing membrane was more stable than the EPDM 111 membrane. The T_g for EPDM 112 did not change significantly with heat-aging for 28 days at 130°C .

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