

GLASS TRANSITIONS IN POLYMERIC ROOFING MEMBRANES—DETERMINATION BY DYNAMIC MECHANICAL ANALYSIS

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Three EPDM roofing membranes were studied before and after accelerated ageing using dynamic mechanical analysis and tensile testing. It was found that the glass transition temperature, T_g , can be used to explain the changes in mechanical properties of roofing membranes. Furthermore, the T_g values can easily be obtained using dynamic mechanical analysis. Lastly, it was shown that accelerating ageing at elevated temperatures can reduce the time required to evaluate the effect of heat on mechanical properties of polymer-based materials.

KEYWORDS

DMA, dynamic mechanical analysis, elastomers, EPDM, glass transition temperature (T_g), roofing membranes, thermal analysis.

INTRODUCTION

Polymeric roofing membranes are evaluated using various test methods developed for the assessment of durability. Mechanical properties of polymeric materials have two facets; one is related to the macroscopic behavior and the other, to the molecular behavior which includes chemical composition and physical structure. For engineering applications the description of mechanical behavior under the design conditions is generally all that is required. Accordingly, the information obtained from these tests does not explain why a material has failed and how it can be improved, unless the failure is related to structural strength. If the failure is related to molecular activity, additional information is necessary to comprehend the problem fully. Thermal analysis is a technique that can provide some insight as to why some roofing materials fail more prematurely than others. Dynamic mechanical analysis (DMA or DMTA) can be used routinely to determine various properties of a roofing membrane, for example, the glass transition temperature. DMA instruments usually employ forced vibration conditions to deform a sample and study its viscoelastic response. Since the instruments have the capability of not only varying the applied frequency but also the temperature, DMA falls under the broad terminology of thermal analysis.

THEORETICAL CONSIDERATIONS

In the work reported here, three ethylene-propylene-diene monomer (EPDM) based roofing membranes were studied, before and after accelerated ageing, using dynamic mechanical thermal analysis (DMA).

Glass Transition Temperature (T_g)¹⁻³

The glass transition temperature (T_g) is a property of a polymer and is defined as the temperature at which the polymer goes from a rubbery to a glassy state without any change in phase (i.e., local molecular motion is hindered). Below this temperature, polymeric materials undergo considerable changes in their physical properties, becoming stiff instead of flexible. Apart from hardness and brittleness, other properties that are affected by the T_g are thermal expansion coefficients, heat capacity and dielectric constants.

An amorphous (or non-crystalline) polymer has the following molecular motions, in order of decreasing activation energies, hence, requiring less thermal energy to occur:⁶

- (1) Translational motion of all the molecules which allows a polymer to flow.
- (2) Twisting, turning and jumping in unison of parts of a molecule up to 50 carbon atoms in length. This allows bending and coiling.
- (3) Motion of five or six atoms along the main chain or of the side groups.
- (4) Vibrations of atoms around their equilibrium position similar to that found in a crystal lattice. The difference between a crystal lattice and an amorphous polymer is that in the polymer the atomic centers are in an irregular arrangement.

It is believed that only motions (1) and (2) are either restrained or frozen below the T_g . The remaining energy in a molecule would then be motions (3) and (4) that would in turn become restrained at low temperatures as in non-polymeric materials.

The glass transition temperature depends on five factors:

- (1) **Free volume**—the volume of polymer mass not occupied by the molecules themselves. If the molecules are tightly packed and have little room to move, they need a lot of energy or a higher temperature to move.

- (2) **Attractive forces between molecules**—tightly bound molecules need more thermal energy to produce motion which in turn increases T_g .
- (3) **Rotation about bonds**—steric hindrance prevents motion, so that more energy is needed for rotation to occur, again resulting in a higher T_g .
- (4) **Stiffness of chain**—more or less similar to (3), in that if a chain of molecules needs more energy to bend or twist, a higher T_g is required for the motion to occur.
- (5) **Chain length**—the chain length of molecules affects their motion which affects the T_g . Plasticizers soften a polymer by interfering with the chain motions. Furthermore, the plasticizer forms secondary bonds with the polymer thereby reducing the bonding forces between the polymer chains.

A rough approximation of the relationship between the glass transition temperature, T_g , and the melting point, T_m , is as follows:

For polymers with a symmetrical repeating unit, e.g., PVC, $-\text{[CH}_2\text{-CCl}_2\text{]}_x-$, $T_g \approx 0.5T_m$, and with an unsymmetrical repeating unit, e.g., PP, $-\text{[CH}_2\text{-CHCH}_3\text{]}_x-$, $T_g \approx 0.67T_m$. In all cases, T_g is less than T_m .

All of the above applies to polymers that are not crosslinked or only slightly crosslinked. However, if there is a high degree of crosslinking, the alignment of the chains in a crystal lattice is prevented and crystallization does not occur. Crosslinking hinders chain mobility and thus increases the apparent T_g . If the crosslinks occur more frequently than every 40 main chain atoms, the type of motion necessary to reach the rubbery state will, in general, not be attained and the polymer decomposes prior to T_g . For example, splitting of PVC membrane could be attributed to this phenomenon.

Generally, the strength of polymeric materials above the glass transition temperature is inferior to the strength below T_g . Even in the glassy state, however, the strength of an amorphous polymeric material is less than that of oriented crystalline polymers.

There are various techniques that can be used to determine glass transition temperatures. The static techniques include differential scanning calorimetry (DSC), and differential thermal analysis (DTA), which are beyond the scope of this paper. The dynamic methods include torsional braid analysis (TBA) and dynamic mechanical analysis (DMA).

Description of DMA⁷⁻¹¹

The stress-strain relationship which is measured by DMA can be described by the following sinusoidal equations (see Figure 1):

$$\sigma = \sigma_0 \sin(\omega t + \delta) \quad (1)$$

$$\sigma = \sigma_0 \sin(\omega t) \cos \delta + \sigma_0 \cos(\omega t) \sin \delta \quad (1a)$$

where σ is the stress, ω is the angular frequency, t is the time and δ is the phase angle. The strain (ϵ) can be obtained by:

$$\epsilon = \epsilon_0 \sin(\omega t) \quad (2)$$

The stress and strain components can be either in-phase or 90° out-of-phase with each other. When stress is in-phase with strain, the component is labelled as "real" with an associated value of $\sigma_0 \cos \delta$. The "imaginary" component is 90° out-of-phase with strain and corresponds to $\sigma_0 \sin \delta$. By

resolving the stress and strain components, a real and imaginary component of modulus can be obtained:

$$\sigma = \epsilon_0 E' \sin(\omega t) + \epsilon_0 E'' \cos(\omega t) \quad (3)$$

where the real part of the modulus, E' , is defined as $E' = (\sigma_0/\epsilon_0) \cos \delta$ and is known as the storage modulus which is a measure of recoverable strain energy in a deformed body since it is related to the storage of energy in the form of potential energy. The imaginary component of the modulus E'' is defined as $E'' = (\sigma_0/\epsilon_0) \sin \delta$, where E'' is the loss modulus and is associated with the description of energy as heat due to the deformation of the material. Finally, 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.

The dynamic mechanical analysis curve shows E' and/or E'' and/or $\tan \delta$ plotted as a function of time or temperature. In general, the most intense peak observed for either E'' or $\tan \delta$ (and significant inflection for E') corresponds to the glass transition and is labelled as the α -transition. The α -transition is therefore associated with motion along the main chain of the polymer that has almost no movement below the glass transition temperature. As soon as a polymer is supplied with sufficient thermal energy, the various segments of the polymer begin to move, releasing heat. The intensity of the α -peak varies depending on the polymer type; amorphous polymers have a more intense α -peak than semi-crystalline polymers because the former have more freedom of movement than the latter. It is important to note that the T_g determined by DMA is not only heating-rate dependent but also frequency dependent. Therefore, T_g values obtained by DMA are generally different from that obtained by static techniques such as differential scanning calorimetry (DSC).

Other transitions can be observed below T_g . β -transitions arise from the motion of flexible side chains of polymers with short branches. γ -, δ -transitions, etc., are generally due to main chain motion of segments containing four carbons or less. The magnitude of β -, γ -, δ -, etc., transitions is less than that of α -transitions since they involve smaller segments of the polymer than with the α -transition.

The temperature of a polymer can also be increased by subjecting the material to high frequency and high amplitude oscillations. It is therefore of paramount importance that when studying dynamic mechanical properties, low frequencies and low strain amplitudes be used. Low strain amplitude is associated with the linear region of a stress-strain curve but if a large stress or strain amplitude is applied to a viscoelastic material, high internal heat due to molecular vibration is generated. This high internal heat yields a non-linear viscoelastic response that is quite complex to analyze. Furthermore, in non-linear viscoelastic regions the material is permanently modified, for example, microscopic crack formation or failure due to fatigue can result.

Various sources of errors do exist in DMA depending on the type of clamp used. It is for this reason that absolute modulus values are obtained with great difficulty using this technique. If care is taken, results within a given laboratory can be reproducible, hence comparison amongst various materials is feasible. Although DMA is weak with respect to the accuracy of absolute modulus, the transition temperatures can routinely be determined with great accuracy. It

is important to note, however, that the method used to obtain the temperature of transition affects the value. Thus, it is vital to specify whether the T_g was obtained using the loss modulus or the damping factor. As long as the same parameter is used throughout a study, the trend observed will be the same regardless of the parameter used.

EXPERIMENTAL

EPDM is one of the elastomers commonly used in prefabricated roofing membranes. A typical composition of the compound is given in Table 1. Three non-reinforced EPDM roofing membrane samples (R1, R2, R3) of commercially available products were obtained for testing as described in the following paragraphs.

Accelerated Ageing

Each sample was cut into seven pieces of about 150mm x 250mm of which one piece was used for control and three each were placed in air-circulating ovens preheated to 100°C and 130°C for heat-ageing. One piece of each sample was removed from the ovens at 1, 7 and 28 days. This scheme could provide the total of 105 specimens needed for tensile testing and thermal analyses.

Dynamic Mechanical Analysis

Polymer Laboratory dynamic mechanical thermal analyzer (PL-DMTA) Mark I (see Figure 2) was used with software version 4.0. The samples were run in the single cantilever mode using test frame L and clamp type C. In this 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. All the specimens were studied between -120 and 80°C using liquid nitrogen as a coolant. The fixed frequency used was 10 Hz with a heating rate of 2°C min.⁻¹

All roofing specimens were cut in the machine direction from the EPDM control and aged sheets. The rectangular specimens were 1mm thick, 5mm long and 12mm deep. The glass transition temperature (α -transition) values were obtained from the DMA curves and are reported as the maximum in the loss modulus (E'') vs. temperature curve.

Tensile Testing

The heat-aged samples were conditioned for a minimum of 24 hours. The specimens were cut from the control and aged samples using a dumbbell-shaped die in a hydraulic press. The tests were carried out at room temperature (22°C \pm 2°C) using an Instron tensile tester (model 1122) with a gauge length of 60mm and cross-head speed of 60mm 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 condition. The mean values of load at break and elongation are given in Table 3.

RESULTS AND DISCUSSION

A typical DMA curve showing the loss modulus as a function of temperature is shown in Figure 3. As illustrated, sample R1 undergoes very little change in glass transition temperature even after 28 days of heating at 100°C. This is also the case after heating at 130°C (Figure 4).

Unlike sample R1, sample R2 does sustain a significant change in T_g . Figure 5 shows the DMA curves for sample

R2 heated at 100°C for 0, 1, 7 and 28 days. It is apparent that T_g increases with the number of days, particularly 7 and 28 days, of heating. The glass transition temperature gradually increases from -61°C for no heating to -46°C for 28 days at 100°C. It is interesting to note, as can be seen from Figure 6, that after only 1 day at 130°C, the R2 sample raises its T_g from -61°C to -50°C. After this sudden jump, the T_g gradually increases to -43°C after 28 days of heat-ageing at 130°C. Sample R3 (Figures 7 and 8) shows little change in glass transition temperature after accelerated ageing. Consequently, the observed change in T_g for specimens R1 and R3 could be due to experimental error.

The glass transition temperature data for all three samples are summarized in Table 2. A plot of T_g as a function of days at 100°C and 130°C is shown in Figures 9 and 10, respectively. The figures indicate that R2 is greatly affected by the heat-ageing while R1 and R3 are only slightly affected. Although the T_g of R2 after 28 days of heat-ageing is similar to R1 and R3, the fact that it is shifting to higher temperatures indicates that it is becoming more crosslinked and its physical/mechanical properties are changing (Table 3). Moreover, the observed trend for change in T_g for specimen R2 is similar to the change in mechanical properties (Figure 11).

It is also interesting to note that although the maximum load at break follows the predicted trend, (i.e., the maximum loads for R1 and R3 are remaining somewhat similar while that for R2 is increasing with heat-ageing), the elongation-at-break is decreasing with heat-ageing for all samples. As shown in Table 3, this decrease in elongation is much more dramatic for R2 than for either R1 or R3. This decrease in elongation for all samples is occurring without a change in T_g for samples R1 and R3. This might be explained by the fact that processing oils are present in all formulations (see Table 1). It is possible that, even if the processing oils are not completely lost during heat-ageing, the quality of the oil is deteriorating and as such will not be lubricating efficiently. If this were the case, the elongation of the samples would decrease without seeing any change in T_g .

Another point of interest is with respect to the heat-ageing process itself. It would appear that 7 days of heat-ageing the materials at 130°C is equivalent to 28 days of heat-ageing at 100°C. The T_g value for R1 is -50°C after 28 days at 100°C and -49°C after 7 days at 130°C. In the case of R2, the glass transition temperature is -46°C after 28 days at 100°C and 7 days at 130°C indicating apparent equivalency. Finally, in the case of R3, the T_g values are -44°C and -45°C after 28 days at 100°C and 7 days at 130°C, respectively.

Since the above phenomena are of importance to the roofing industry, further investigation on other types of polymeric roofing membranes is needed.

CONCLUSIONS

- Glass transition temperature can be used to explain the change in mechanical properties of roofing membranes.
- Dynamic mechanical analysis is a valuable tool in characterizing polymer-based roofing materials, since one can easily obtain T_g data.
- Accelerated ageing by exposing membranes to elevated temperature may reduce the time required at the maximum service temperature to evaluate the effect of heat

on mechanical properties of polymer-based materials.

- Equivalency of responses of materials at different temperatures could help in establishing standard requirements.

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Ingredients*	% by Weight (Approx.)	Function
Synthetic rubber or blend	26	Imparts elastomeric properties
Carbon black	37	Reinforces elastomeric properties and absorbs UV, acts as filler
Extender oils	28	Aids processing and reduces cost
Curing agents	4	Necessary for proper cure
Antioxidants and antiozonants	3	Assist in resisting environmental factors
Processing aids	2	Anti-stick agent, promotes smooth surface in calendaring
Total	100	

*Based on technical notes and some related patent specifications.

Table 1 Typical composition of a generic EPDM roofing membrane compound.

Heat-ageing Schedule		T_g (°C) for Samples		
Temp., °C	Days	R1	R2	R3
—	0*	-49	-61	-46
100	1	-48	-58	-45
100	7	-49	-50	-42
100	28	-50	-46	-44
—	0*	-49	-61	-46
130	1	-48	-50	-46
130	7	-49	-46	-45
130	28	-48	-43	-44

*Unheated control material

Table 2 Glass transition temperatures of EPDM membranes.

Heat-ageing Schedule		Strength (kN m ⁻²)			Elongation (%)		
Temp., °C	Days	R1	R2	R3	R1	R2	R3
—	0*	10.6	8.7	11.4	522	285	307
100	1	20.9	8.8	10.8	433	266	314
100	7	11.6	9.5	11.3	396	211	297
100	28	10.7	10.5	10.6	324	132	270
—	0*	10.6	8.7	11.4	522	285	307
130	1	9.9	9.2	9.3	348	180	273
130	1	9.7	10.9	9.8	307	88	227
130	28	8.0	11.6	9.7	218	38	159

*Unheated control material

Table 3 Tensile strength and elongation values of EPDM membranes.

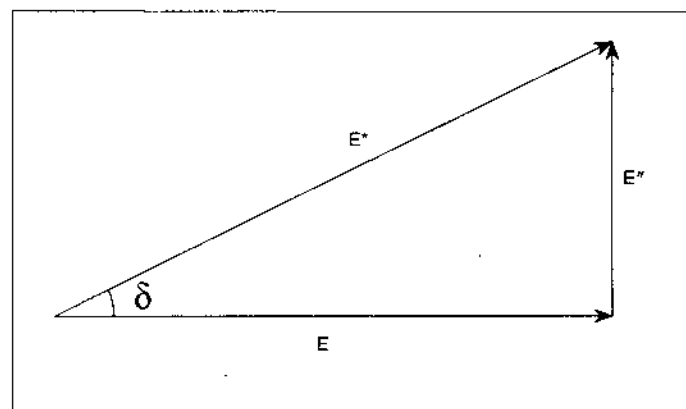


Figure 1a Relationship between the complex modulus (E^*), the storage modulus (E'), the loss modulus (E''), and the loss angle (δ).

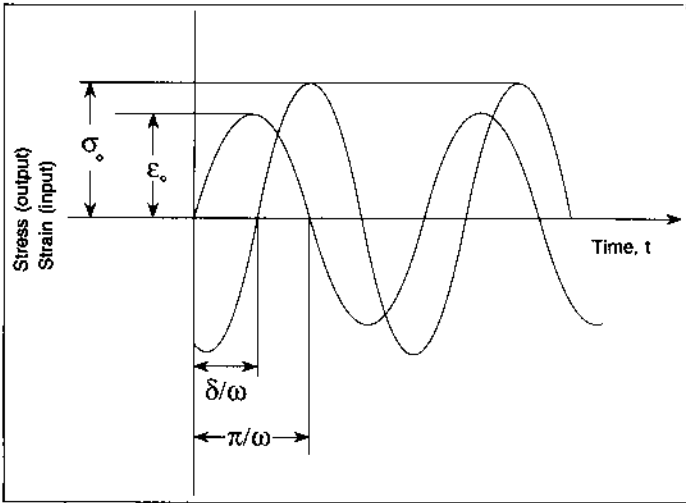


Figure 1b Graphical representation of the stress-strain relationship in DMA.

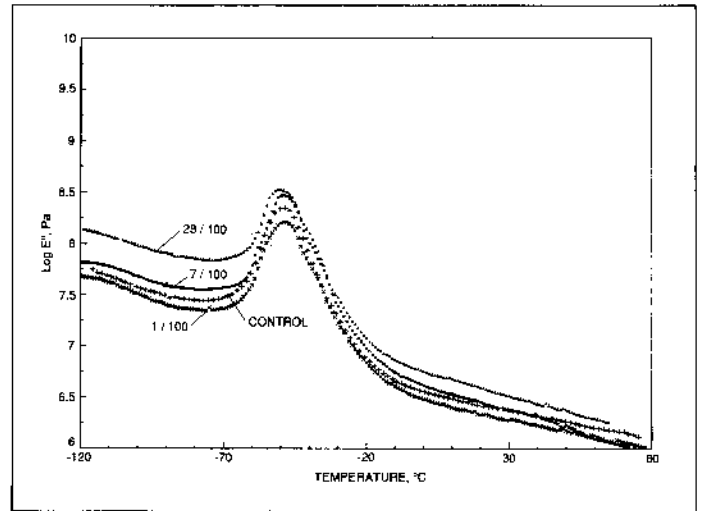


Figure 3 DMA curves for specimen R1 aged at 100°C for 0 days (control), 1 day (1/100), 7 days (7/100), and 28 days (28/100).

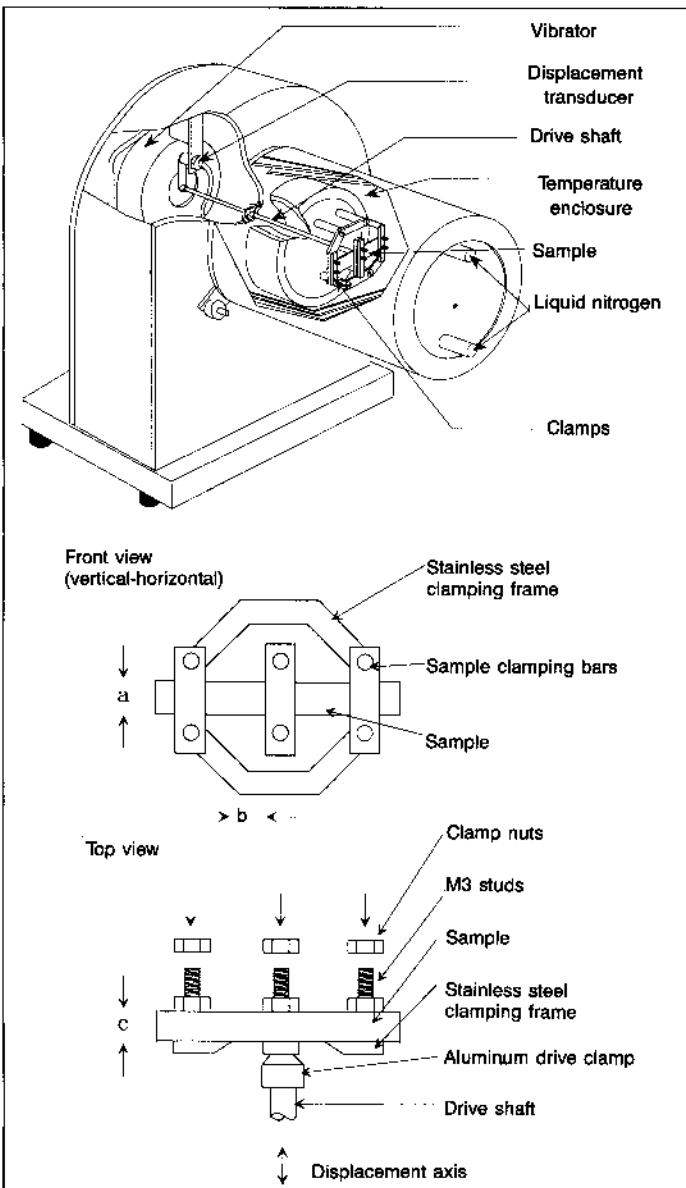


Figure 2 Polymer Laboratory dynamic mechanical thermal analyzer mechanical head and clamp.

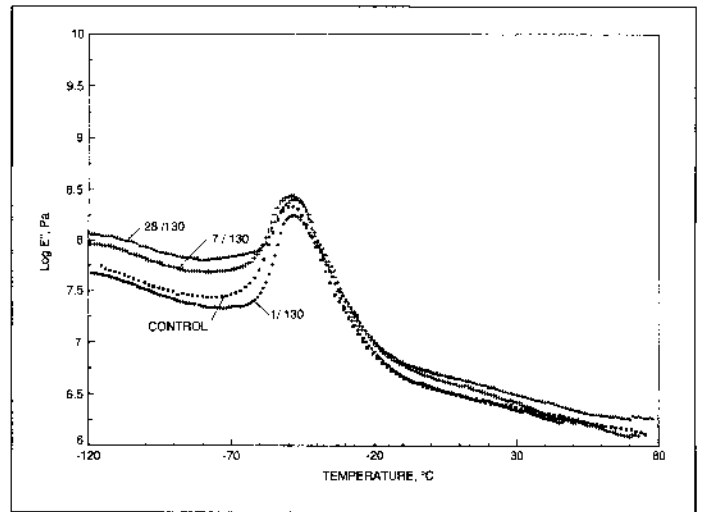


Figure 4 DMA curves for specimen R1 aged at 130°C for 0 days (control), 1 day (1/130), 7 days (7/130), and 28 days (28/130).

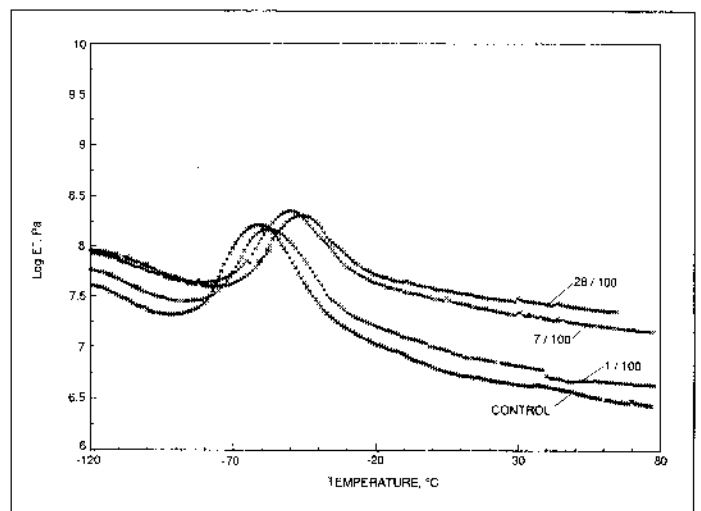


Figure 5 DMA curves for specimen R2 aged at 100°C for 0 days (control), 1 day (1/100), 7 days (7/100), and 28 days (28/100).

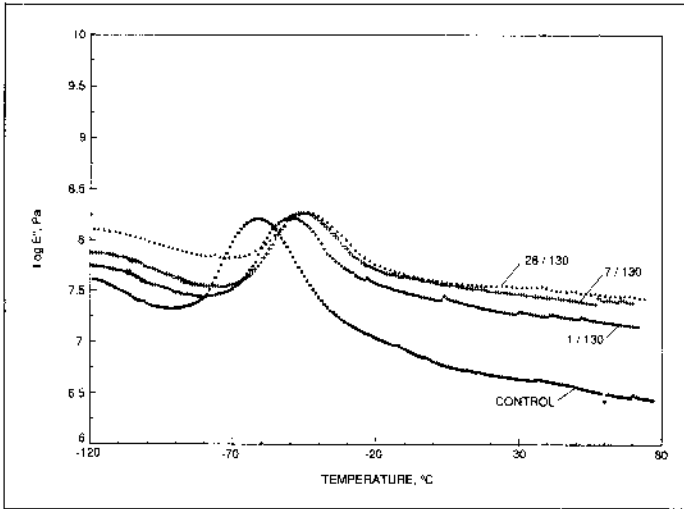


Figure 6 DMA curves for specimen R2 aged at 130°C for 0 days (control), 1 day (1/130), 7 days (7/130), and 28 days (28/130).

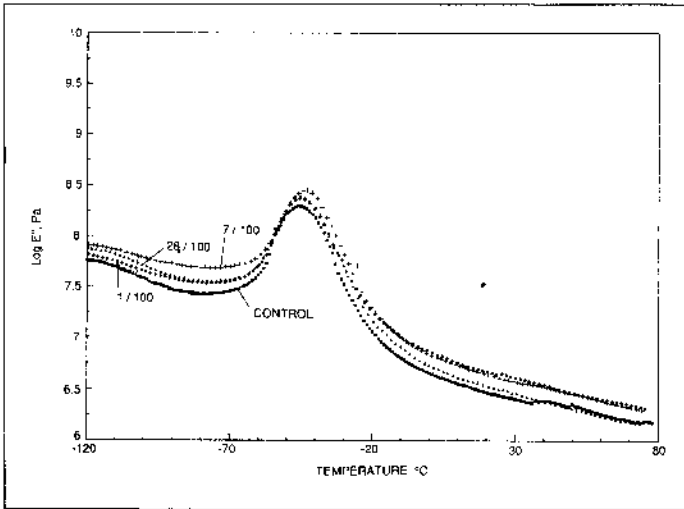


Figure 7 DMA curves for specimen R3 aged at 100°C for 0 days (control), 1 day (1/100), 7 days (7/100), and 28 days (28/100).

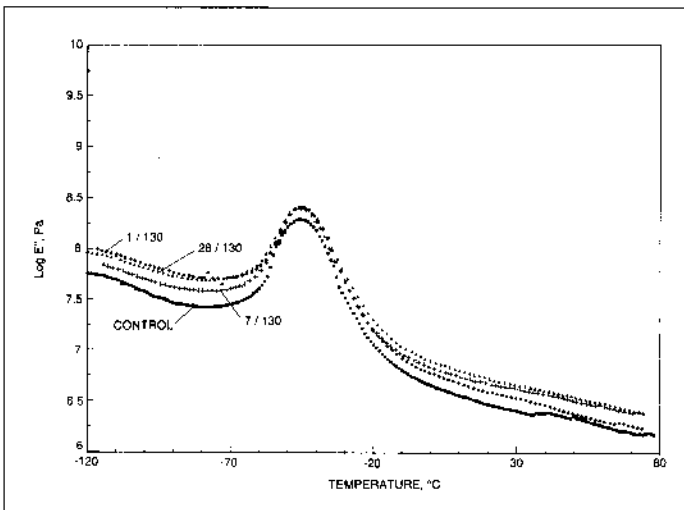


Figure 8 DMA curves for specimen R3 aged at 130°C for 0 days (control), 1 day (1/130), 7 days (7/130), and 28 days (28/130).

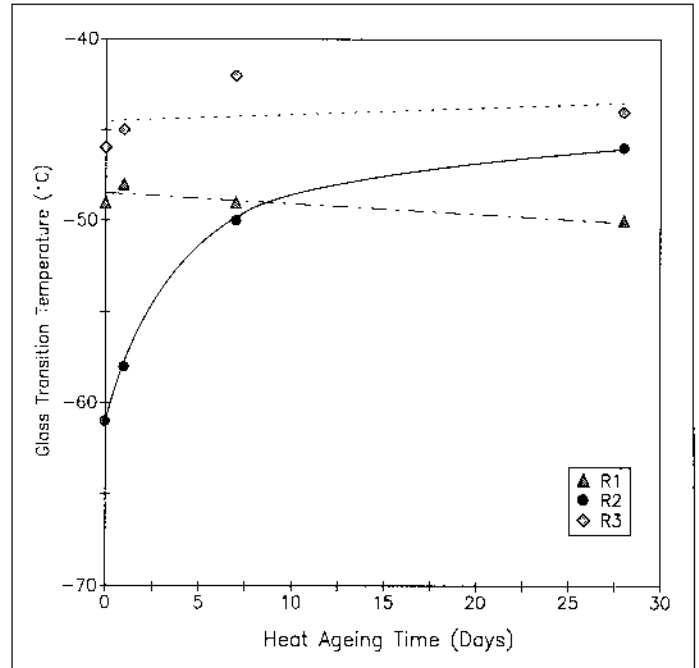


Figure 9 Variation of glass transition temperature as a function of heat ageing at 100°C for samples R1, R2, and R3.

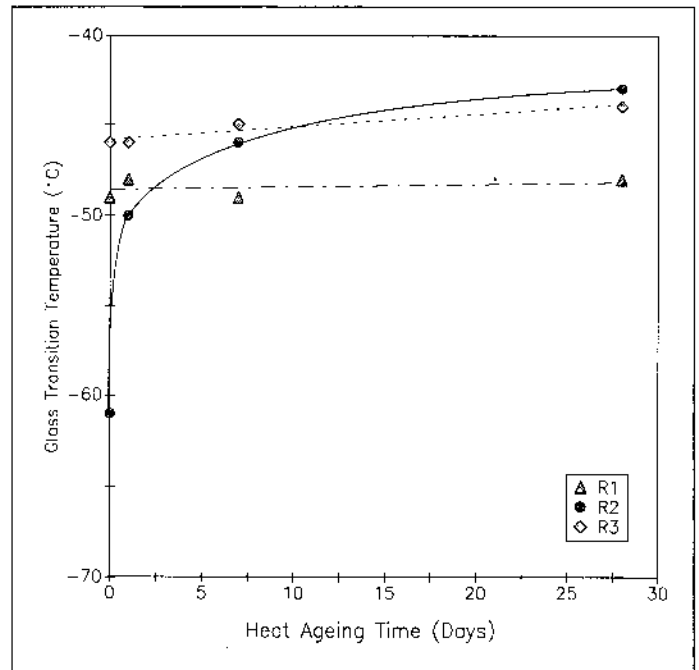


Figure 10 Variation of glass transition temperature as a function of heat ageing at 130°C for samples R1, R2, and R3.

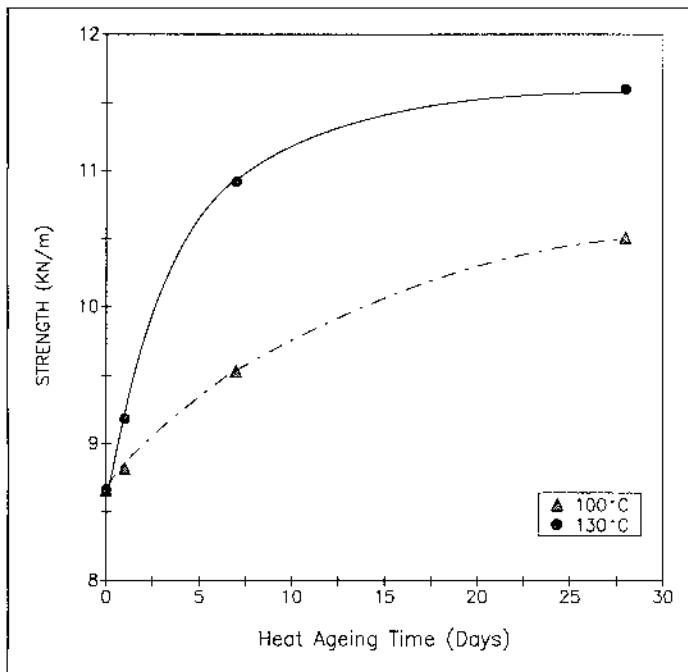


Figure II Variation of strength of R2 as a function of heat-aging at 100°C and 130°C.