THERMAL ANALYSIS FOR CHARACTERIZATION

DON BACKENSTOW
Carlisle SynTec Systems
Carlisle, Pa.

PETER FLUELER
Swiss Federal Laboratories for Materials Testing
Switzerland

Methods used to test the durability of new generation roofing membranes can be improved. For this paper new generation membranes means thermoplastic, thermoset and modified bituminous membranes. Manufacturers, designers and end users need to know if these membranes can be expected to perform under various climatic conditions.

To evaluate the durability of roofing membranes, laboratories use artificial weathering devices, which attempt to simulate the primary weathering agents, namely: solar radiation, temperature, ozone and moisture. Many laboratories also expose roofing membranes in the field to determine if their physical properties have changed with field weathering exposure.

After exposure to weathering, the physical properties of the product are usually compared with an unaged or "as manufactured" sample with the results stating, "Retains X percent of the original physical properties after aging."

Although this may be a valid method for evaluating a specific product, a problem arises when comparing different generic types of roofing materials that use different test methods. For example—imagine trying to test the tensile strength of a modified bitumen membrane before and after aging using the procedure in ASTM D412, Rubber Properties in Tension. The current myriad of test procedures used to evaluate a product depends more on its component base than on its application. This makes it difficult to compare a thermoplastic with a thermoset or a modified bitumen.

The RILEM/CIB Joint Committee on Elastomeric, Thermoplastic, and Modified Bituminous Roofing has evaluated various new test procedures that may allow all types of roofing membranes to be evaluated using the same test criteria. The test equipment used for the RILEM/CIB study requires very small samples, which minimizes the cost to age the samples in the laboratory and/or the size of the sample required to be taken from an existing roof. A 4-inch-by-6-inch sample is large enough to run a full evaluation.

It is the purpose of this paper to describe the features and advantages of using thermal analysis or thermo-analytical techniques to improve current analytical test procedure for all roofing membranes. At both the Carlisle Laboratories and the Swiss Federal Institute of Technology, many different types of membranes were measured before and after aging using three different thermo-analytical techniques; torsion pendulum (Swiss Laboratories), dynamic mechanical analysis (DMA Carlisle Laboratories) and thermogravimetric analysis (TGA Carlisle Laboratories).

WHAT IS THERMAL ANALYSIS?

Thermal analysis involves the measurement of a material's properties as a function of temperature. Depending on the equipment and test required, the temperatures can range from minus 150 C to 700 C (minus 238 F to 1,292 F). Although thermal analysis covers a wide range of techniques, we will discuss only those procedures and equipment used for this program.

TORSION PENDULUM

The torsion pendulum test measures the complete shear modulus of a material as a function of temperature. It can be applied as a method to detect changes after aging (artificial or natural). Changes due to formulation modifications may also be detectable.

The size of the samples to be tested are 60 millimeters (2.4 inches) by 70 millimeters (2.8 inches) by t (t = thickness) and are cut from the membrane with regard to the factory processing direction.

A rotating weighted pendulum is attached to the bottom of the sample and the shear modulus is recorded as the rotational cycle of the pendulum decreases. This is repeated numerous times as the temperature is increased from minus 100 C to 100 C (minus 148 F to 212 F) or higher if required.

The test has to be carried out with samples of both weathered and unweathered membranes. The difference in the data curves before and after aging is the data to be reported.

DYNAMIC MECHANICAL ANALYSIS

Dynamic mechanical analysis (DMA) is the measurement of a material's mechanical properties as they are deformed under periodic stress. These properties are measured as a function of temperature while the material is subjected to a controlled temperature program. In dynamic mechanical analysis, the sample is oscillated at its resonant frequency and an amount of energy equal to that lost by the sample is added on each cycle to keep the sample in oscillation at a constant amplitude. When setting up the DuPont 982 DMA, the sample is clamped between two arms, one of which is a passive support, while the other is driven by an electromechanical transducer. Rotation of the driven arm a few tenths of a millimeter puts the sample in flexure stress so that when the displacing force is released, the deflection energy stored in the sample causes it to go into resonant oscillation. The frequency and amplitude of this oscillation are detected by a linear voltage differential transformer (LVDT) positioned at the opposite end of the active arm. This LVDT signal is fed to a driver circuit, which then feeds back enough energy to the electromechanical transducer to keep the sample in oscillation at constant amplitude. The temperature range of the equipment is minus 150 C to 500 C (minus 238 F to 932 F) with the liquid nitrogen cooling accessory.

Mechanical properties measured by this technique include the modulus of the material as well as its damping charac-

teristics. Consequently, DMA provides a different approach to monitoring the extent or effects of aging and degradation. When cross-linking, embrittlement or chain scission occur in a polymeric network, one would expect corresponding changes in the modulus and damping characteristics of the system. These are readily detectable by dynamic mechanical analysis.

THERMOGRAVIMETRIC ANALYSIS

In thermogravimetric analysis (TGA) the change in mass of a sample as a function of temperature is measured. The DuPont Model 951 TGA Module consists of a furnace, sample holder, glass enclosure and recording balance mechanism. The technique involves placing a very small sample, e.g., 20 milligrams (0.0007 ounce), in the sample pan, which is on the recording balance. The glass enclosure is then used to surround the sample and balance so the environment can be controlled with a nitrogen or air purge gas. The TGA is operated in a percent weight loss mode. The temperature is increased at 20 degrees C per minute (36 degrees F per minute) for this study. The atmosphere is nitrogen until 600 C (1,112 F) is reached. This permits all of the organics to be volatilized. At 600 C (1,112 F) the atmosphere is switched to air, which will permit oxidation of the non-volatile carbonaceous matter such as carbon black. After the carbonaceous matter has been oxidized, all that remains are the inorganic fillers. This test quickly and accurately measures the volatile organic component, the non-volatile carbon component and the inorganic component of the membrane. As such, the test serves as a fingerprint to identify chemical changes that may have occurred in the product either due to manufacturing (formulation) or aging.

RILEM/CIB TEST RESULTS

It was decided at the Rilem/CIB meeting in Zurich, Switzerland, April 1986, to evaluate the various thermal analysis tests using materials from numerous sources. Three different programs were initiated:

Modified bituminous material exposed for five years on a roof in England were tested. The samples were taken from three different parts of the roof. Sample A was exposed on the roof for five years facing south at a 45 degree angle. Sample B was exposed on the same roof for five years horizontally. Sample C was exposed on the same roof horizontally, covered by 6 centimeters (2.4 inches) of gravel. Results from dynamic mechanical analysis and torsion pendulum tests could easily determine aging differences between samples A, B and C. Horizontally exposed samples B and C were virtually identical in their dynamic properties; however, sample A, which was exposed 45 degrees south for five years, had a significantly higher modulus, between minus 10 C and 60 C (14 F and 140 F).

Thermogravimetric analysis indicated no significant changes in the chemical composition of the three samples.

The second set of samples were received from Norway, where they had been exposed to laboratory aging procedures used by the Norwegian Building Research Institute. These tests exposed the samples to infrared heat, ambient heat, air cooling, ultraviolet light and water spray. Three modified bituminous samples, which were aged for 24 weeks, were tested. In all cases the aged samples could be easily discerned from the unaged samples using both the dynamic mechanical and torsion pendulum equipment. Sample 3 showed the largest change between original and aged results and, according to the source of the samples, was indicative of its lower quality level. Thermogravimetric analysis also showed significant chemical changes in all three samples after aging. Figures 1 and 2 show torsion pendulum curves (torsiogram) of the lower quality level modified bitumen sample before and after aging. The aged sample has increased in modulus due to aging, and the glass transition midpoint has increased from 8 C (46 F) to 28 C (82 F).

Two PVC samples that had been aged for 48 weeks were also sent in from Norway. Sample 1 had a significant increase in stiffness on both the dynamic mechanical and torsion pendulum equipment after aging. Sample 2 only had a small increase in stiffness after material aging. Again, according to the source, sample 1 was a lower quality PVC. Thermogravimetric analysis indicated only a small change in the chemical composition of the materials.

The third part of the test was to sample manufactured materials from both Europe and the United States (EPDM, modified bitumen, PVC and Hypalon). These various membranes were aged in a dark, dry oven for 56 days at 80 C (176 F). The oven-aged samples and new samples were tested using dynamic mechanical and torsion pendulum analysis as well as thermogravimetric analysis. The dynamic mechanical and torsion pendulum analysis could easily discern various manufacturers of the same generic materials (due to their different formulations). It was also easy to discern the magnitude of change in the samples before and after aging.

The correlation between the dynamic mechanical and torsion pendulum results was very good. However, future tests can probably be adjusted to improve the correlation. For example, the dynamic modulus analysis apparatus was set to increase temperature from minus 120 C to 80 C (minus 184 F to 176 F) at a rate of 5 degrees C (9 degrees F) per minute. The torsion pendulum equipment was set to increase the temperature at 1 degree C (1.8 degree F) per minute.

Thermogravimetric analysis indicated significant chemical changes before and after aging. Table 1 outlines the chemical composition changes as a result of aging for 56 days at 80 C (176 F) in a dry, dark oven.

Based on these encouraging preliminary test results, it has been decided that future work will be initiated by a new RILEM/CIB committee. The goal will be to refine the sample preparation methods, prescribe test procedures used to age samples, and optimize the test procedures for the dynamic mechanical and torsion pendulum equipment. This commitment to continue testing is based on a genuine belief by all involved that thermal analysis using sophisticated modern equipment can improve our ability to understand how materials change with aging. The reasons for these changes and whether the changes are beneficial or detrimental to the materials' performance on a roof would have to be evaluated using other methods.

As indicated in the previous paragraph, thermal analysis will only indicate that a physical and/or a chemical change has occurred. In most cases the magnitude of the change after aging is indicative of the membrane's stability. From the general point of view, we would prefer not to see a change (or only a minimal change) after aging. If a membrane is suitable for a roofing application in year one, then minimal changes in its physical and chemical properties after aging would be desirable in order to enhance the probability of performance in year 10, year 15 and beyond.

The net advantage of the RILEM/CIB work to date seems to be threefold. First, thermal analysis is extremely accurate and sensitive to changes in material properties. Second, very small samples can be used, which significantly reduces the effort required (cost) to age the sample in the laboratory and/or obtain samples from the field. Third, the testing procedures are very rapid so numerous samples can be analyzed on the equipment each day.

OTHER PUBLICATIONS

Concurrent with the RILEM/CIB work, a presentation was made on new laboratory procedures to evaluate the durability of roofing membranes in January 1987, to the Akron Rubber Group in Akron, Ohio. The paper was prepared and given by M.S. Farlling, copies of which can be obtained upon request. To quickly demonstrate what thermal analysis can do, we have extracted portions of that paper and graphs, which are attached. All of the aged samples quoted in this report were aged 60 days in a dry, dark oven at 70 C (158 F).

Figures 3 and 4 show dynamic mechanical analysis curves of an EPDM membrane before and after aging. The point in the curve where a large modulus change takes place is the glass transition. Plotting the damping along with the tensile storage modulus makes the onset and glass transition midpoint easily identifiable. In this case the onset of the glass transition (Tg) is minus 51 C (minus 60 F) and the midpoint is minus 32 C (minus 25.6 F) for the original sample. The aged sample has an onset of Tg at minus 47 C (minus 52.6 F) and a midpoint of minus 25 C (minus 13 F). The increase in Tg is probably due to increased crosslinking (vulcanization) during the dark oven aging.

Figures 5 and 6 show DMA curves of a PVC membrane. The original PVC membrane has an onset of Tg at minus 59 C (minus 74.2 F) and a minus 22.5 C (minus 8.5 F) midpoint. In the aged sample, the onset of Tg is minus 50.5 C (minus 58.9 F) and the midpoint is minus 5.5 C (22.1 F). The transition has also widened considerably. This probably is either related to the weight loss of plasticizer or to oxidative degradation.

Figures 7 and 8 are the DMA curves for the SBS-modified bitumen membrane. The original sample shows values of minus 35.0 C (minus 31 F) and 21.5 C (70.7 F) for the onset and midpoint of Tg. The aged sample shows a drop in the onset of Tg and two large damping peaks at minus 1.5 C (29.3 F) and 18.5 C (65.3 F). Generally speaking, a sharp damping peak is typical of a homogeneous material while a broad transition suggests somewhat less than a homogeneous blend. Totally incompatible materials would show two separate transitions signifying little attraction of one component with the other. This is probably the case in this curve where the modifier (polymer) has separated from the asphalt due to the aging. The reinforcement was removed from these samples prior to aging.

SUMMARY

In summary, thermal analysis is a technique that can contribute significantly to understanding material characteristics. It should be especially useful to users of polymeric products who need to know how finished products can be expected to change in normal use. Thermal analysis can also provide data on changes that have occurred in accelerated weathering tests or products that have been exposed on roofing systems.

For example, it is well known that thermosetting materials continue to cure slowly over long periods of time, with concomitant changes in mechanical properties. And thermoplastics or amorphous linear polymers also exhibit aging effects because of morphological and/or chemical changes such as oxidative degradation. The use of thermal analysis techniques can be a valuable tool for monitoring the structural and/or property changes that occur in a product, along with the factors that cause these changes.

We suggest that it is of fundamental importance to keep the end use and the properties associated with it in mind when assessing the durability of polymeric roofing membranes. The recommended approach would be to use thermogravimetric analysis to monitor chemical changes, and the dynamic mechanical or torsion pendulum analysis to monitor transition phenomena and specific physical property loss or changes.

The goal of this preliminary project was to demonstrate that new test equipment is now available to accurately evaluate changes in the properties of roofing materials. These materials can be aged either in the laboratory or in actual field application.

The next step is to refine and standardize the methods used to prepare the samples for testing, the aging criteria and the optimum operating parameters for the dynamic mechanical and torsion pendulum analysis equipment. These will be tasks for the new RILEM/CIB committee.

ACKNOWLEDGMENT

We would like to express our appreciation to the technicians at the Carlisle and Swiss Federal Laboratories for Material Testing for their patience, skills and valuable recommendations. We would also like to express our appreciation to the members of the RILEM/CIB Joint Committee on Elastomeric, Thermoplastic, and Modified Bituminous Roofing for their support. With special thanks to Jack May, Einar Paulsen, Walter Rossiter, Bob LaCosse and Bill Cullen, members of the joint committee that have provided both support and assistance.

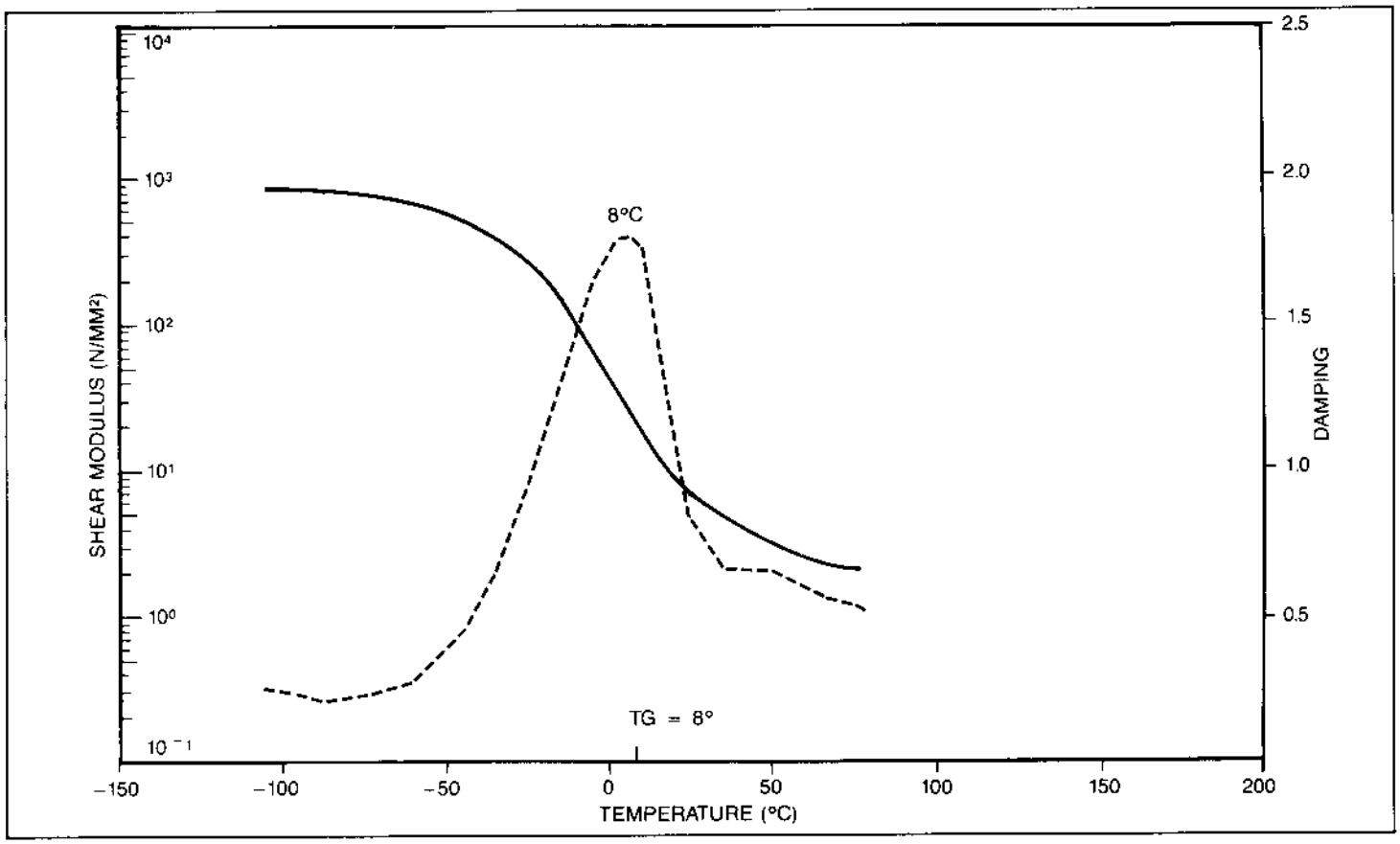

Figure 1 *SBS polymer bitumen new*

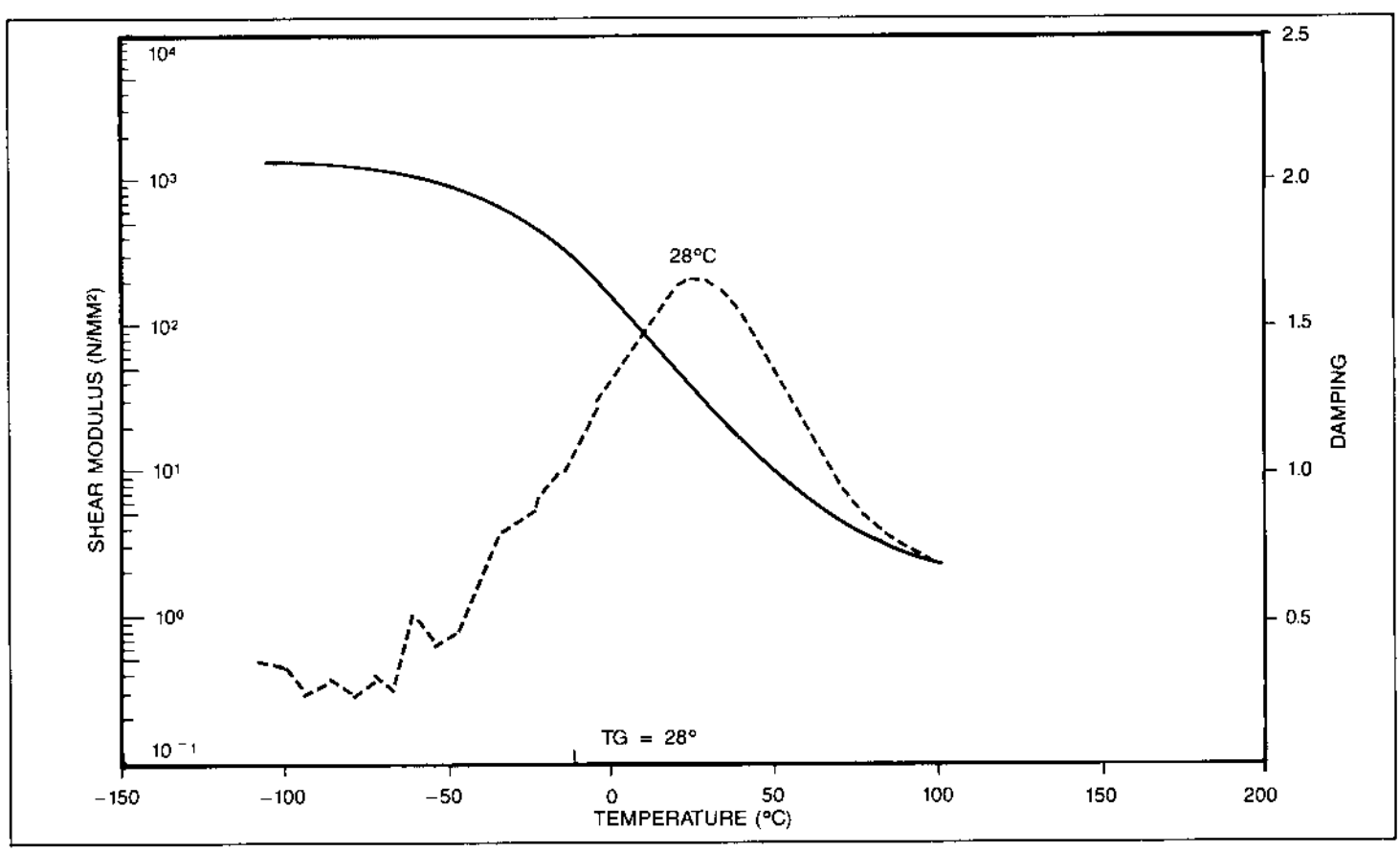

Figure 2 *SBS polymer bitumen aged six months, NBI 142/84 Procedure*

SAMPLE (Source)	Percent Organics		Percent Carbon	Percent Ash
EPDM (USA)	Original	56.91	32.37	10.72
	Aged	56.45	32.33	11.22
	Difference	−0.46	−0.04	+0.50
EPDM (Europe)	Original	51.94	28.71	19.35
	Aged	49.99	29.32	20.69
	Difference	−1.95	+0.61	+1.34
PVC G442 (Europe)	Original	79.59	9.74*	10.67
	Aged	78.91	10.02*	11.07
	Difference	−0.68	−0.28	+0.40
PVC 131 (Europe)	Original	79.52	10.59*	9.89
	Aged	79.09	10.76*	10.15
	Difference	−0.43	+0.17	+0.26
SBS MOD (Europe)	Original	68.22	15.95	15.83
	Aged	62.44	18.71	18.85
	Difference	−5.78	+2.76	+3.02
APP MOD (USA)	Original	67.24	18.07	14.69
	Aged	62.69	18.09	19.22
	Difference	−4.55	+0.02	+4.53
HYPALON (USA)	Original	52.12	-0-	47.88
	Aged	48.45	-0-	51.55
	Difference	−3.67		+3.67

*Char—a residue as seen in most halogenated compounds.

Table 1 *TGA results before and after aging 56 days in a dark oven at 80 C (176 F)*

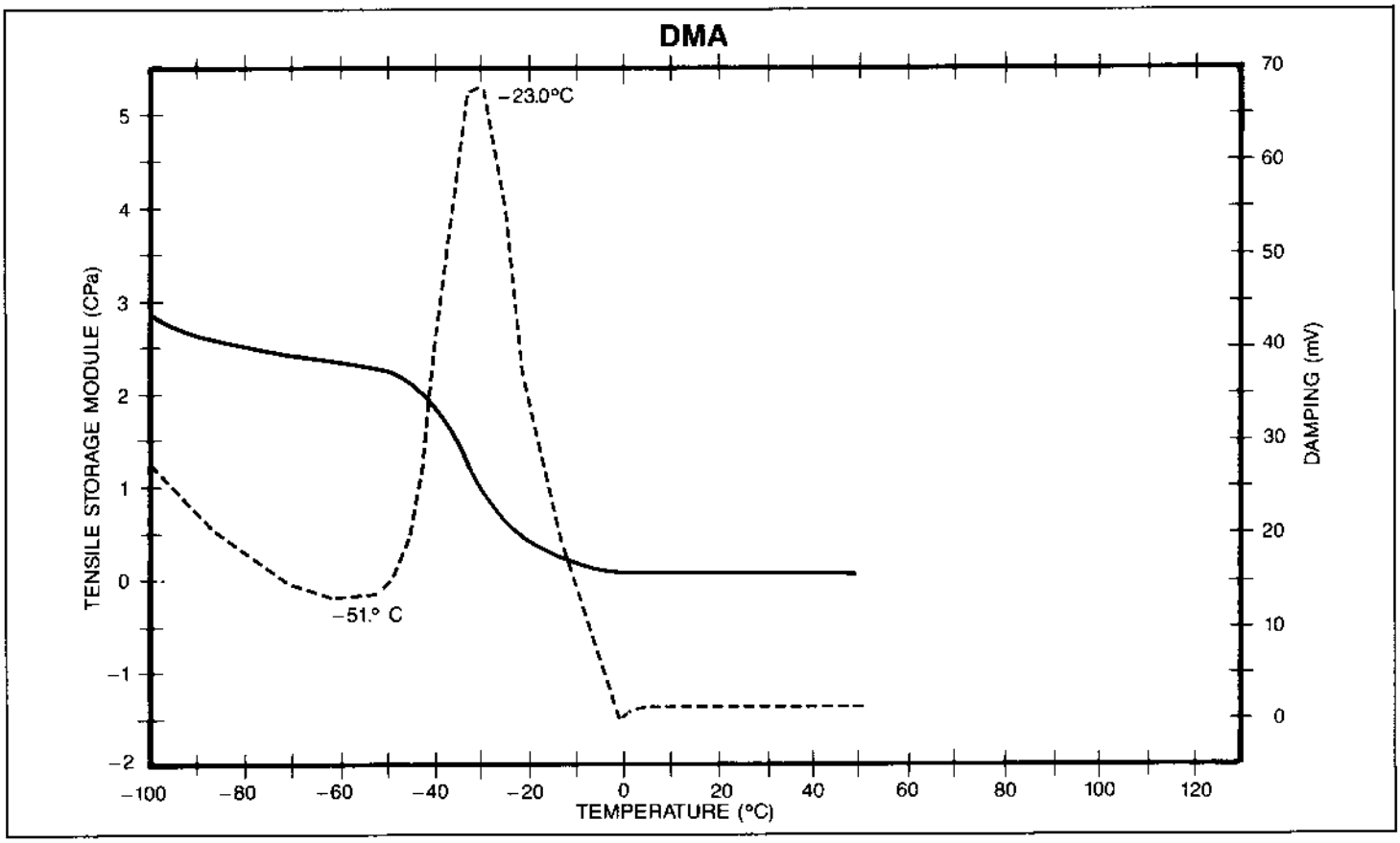

Figure 3 *EPDM unaged*

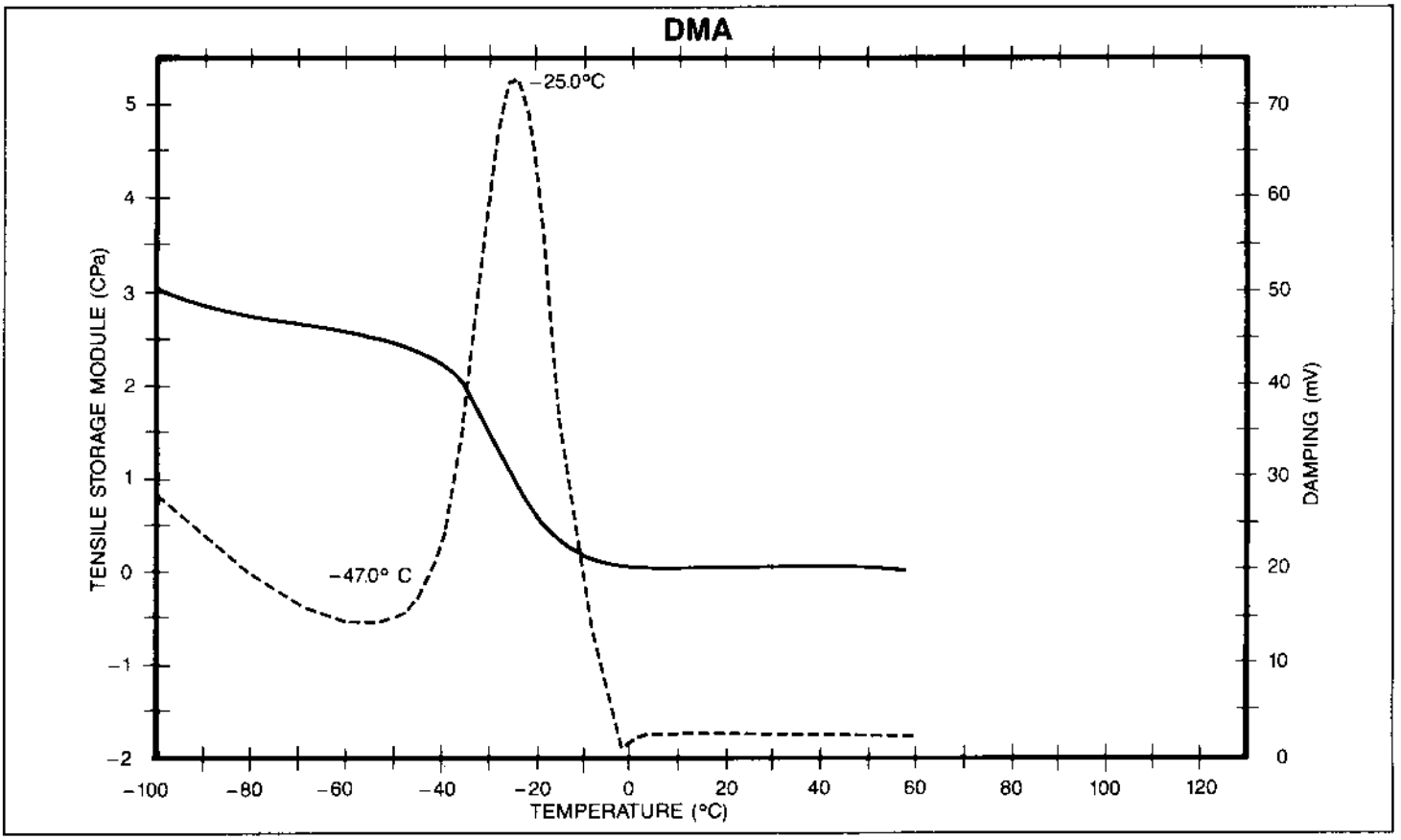

Figure 4 *EPDM aged*

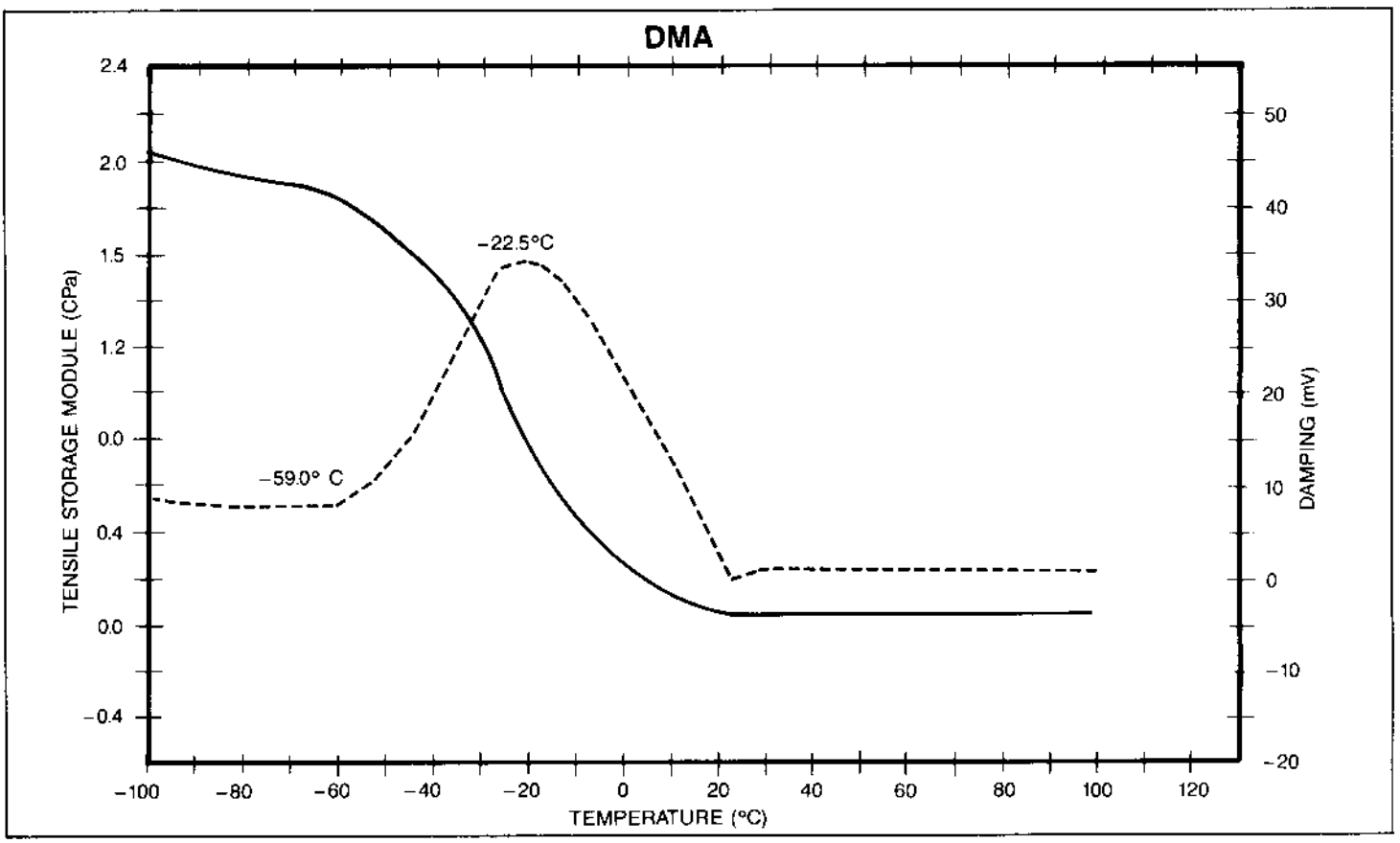

Figure 5 *PVC unaged*

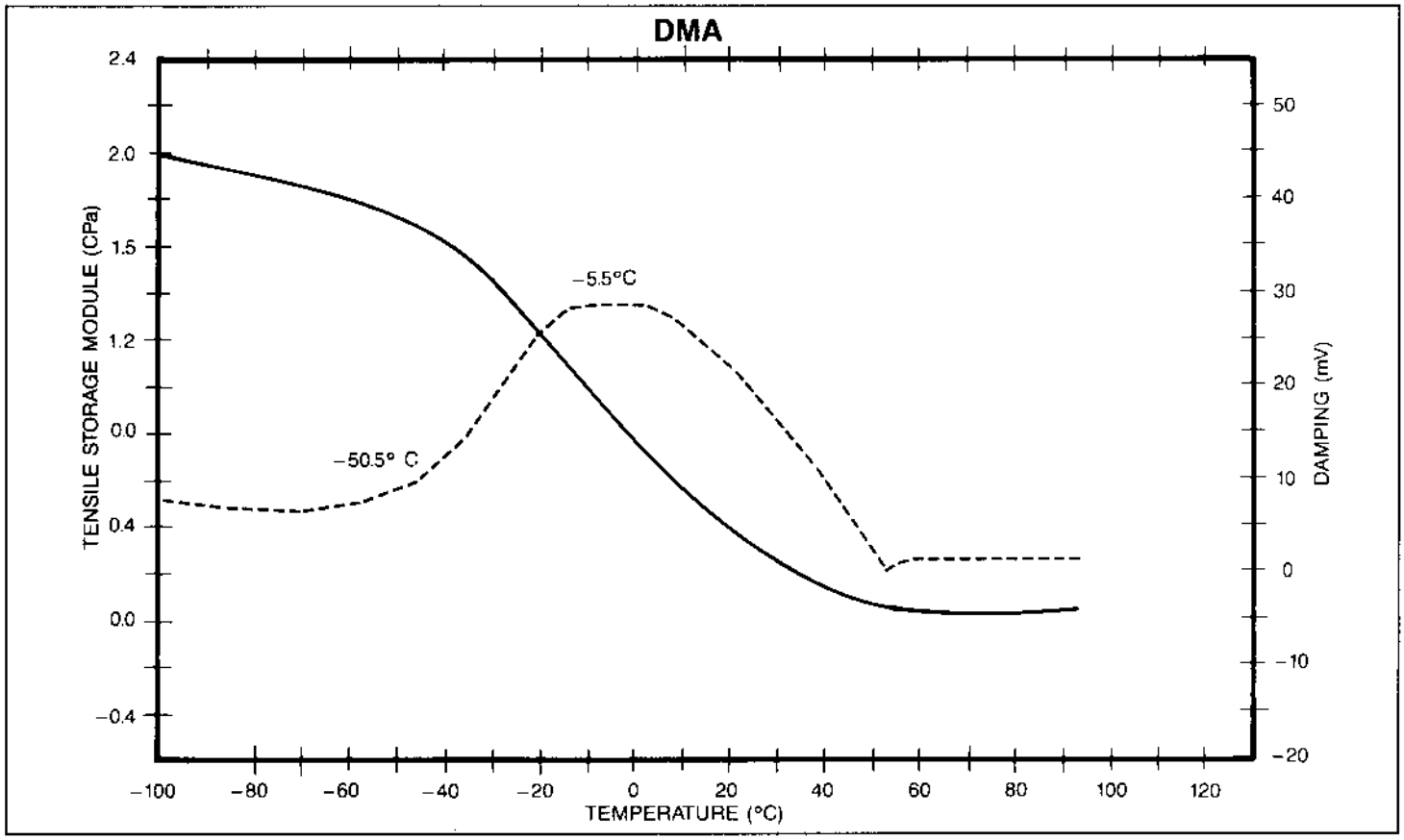

Figure 6 *PVC aged*

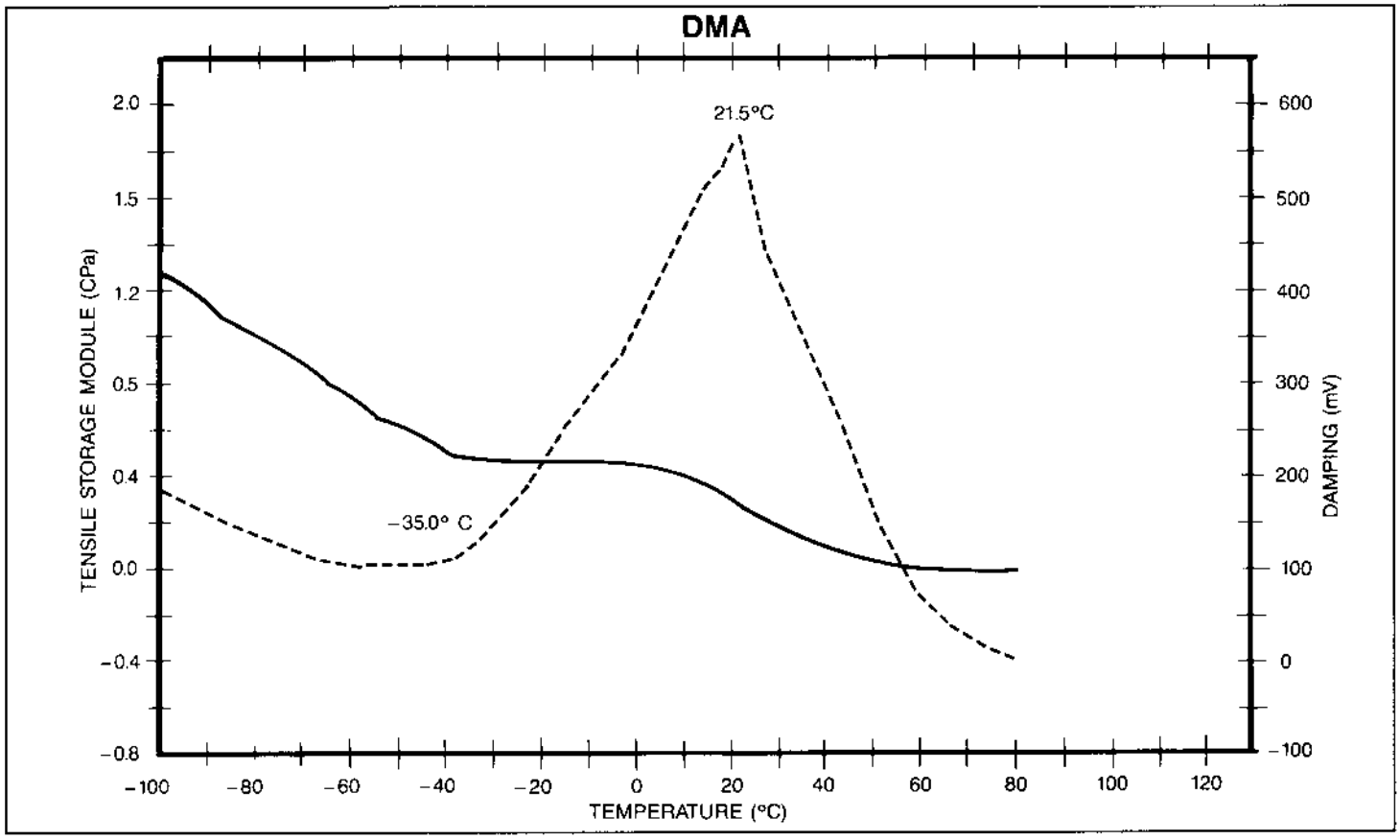

Figure 7 *SBS polymer bitumen unaged*

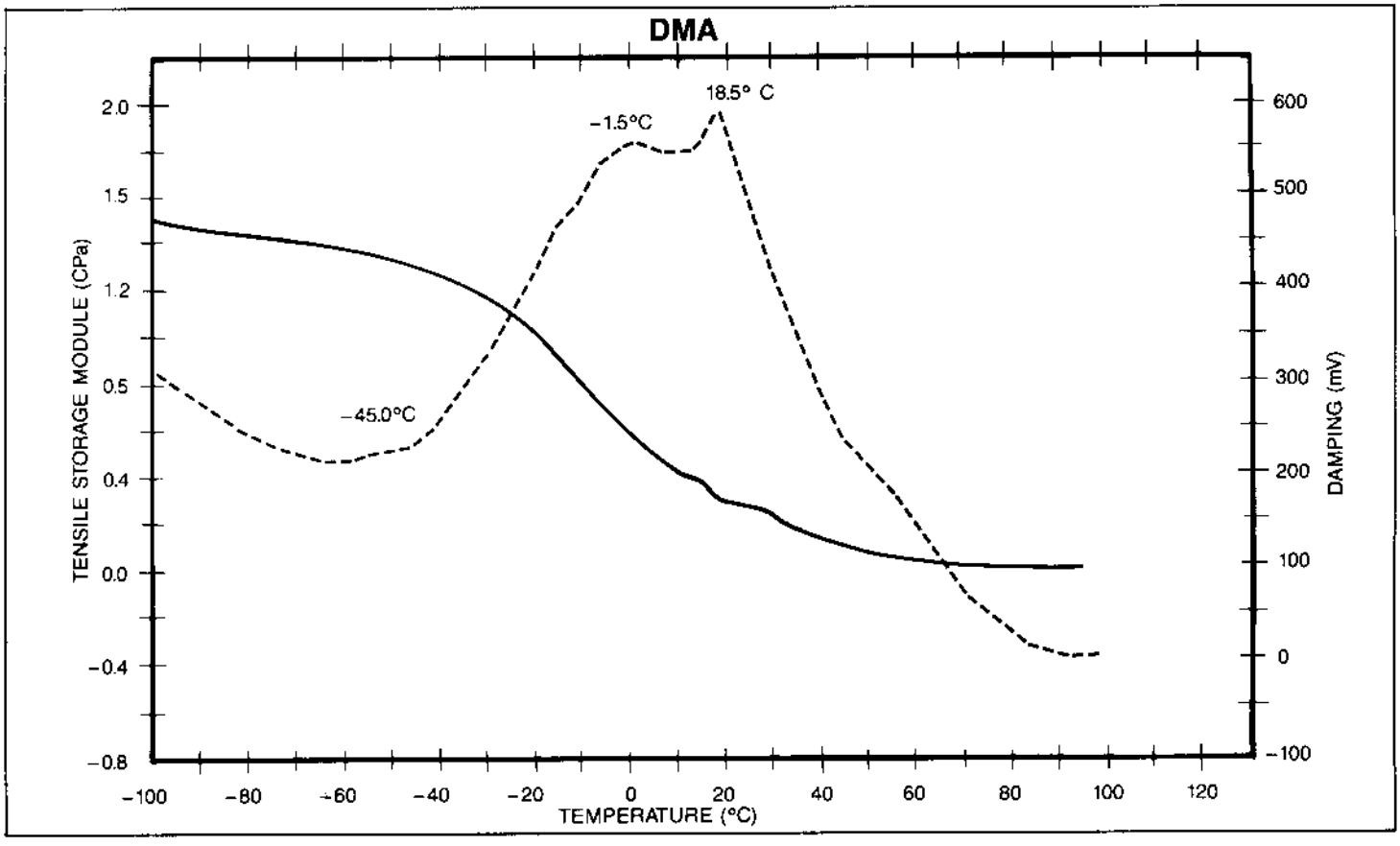

Figure 8 *SBS polymer bitumen aged*