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Aging study of neoprene FB uncured rubber in support of an obsolescence issue for EPDM rubber insulation used in the Reusable Solid Rocket Motor of the Space Shuttle

Charles D. Wingard

NASA/MSFC, Mail Code ED34, Marshall Space Flight Center, Alabama, AL 35812, USA

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Abstract

Thiokol/Wasatch (TC/W) in Utah is the manufacturer of the Reusable Solid Rocket Motor (RSRM) for the Space Shuttle, and filled EPDM and NBR rubber insulators are used on RSRM for erosion resistance. Since DuPont/Dow is closing production lines for Neoprene FB and two Nordel EPDM polymers used in three EPDM insulators for RSRM, TC/W will stockpile 6–7 years of Neoprene FB and Nordel to support RSRM production until reformulated EPDMs can be developed and recertified. NASA/MSFC used several thermal analysis techniques to study the effect of aging on a lot of uncured Neoprene FB kept in cold storage at 40°F (4.4°C) for more than 11 years ('old'). A lot of uncured Neoprene FB kept in cold storage for 8 months ('new') was used for comparison in the study. In processing of uncured calendered sheets by the Shuttle vendor that are later cured near 150°C as RSRM insulation by TC/W, Neoprene FB is mixed into the EPDM formulation at 105°C. Uncured Neoprene FB is a solid at room temperature with a texture similar to that of cheese, but was shown by DSC to have a peak melting endotherm at 50°C, becoming a low viscosity liquid until it begins to cross-link at higher temperatures. From a DMA study on the uncured 'old' and 'new' lots of Neoprene FB at cure temperatures of 95, 105 and 115°C, a linear Arrhenius relationship of the logarithm of the time to gelation versus reciprocal absolute temperature yielded activation energies for the two lots of rubber. When this linear relationship was extrapolated down to the cold storage temperature of 4.4°C, gel times of the 'old' and 'new' rubber lots were predicted to be 12.7 and 72.6 years, respectively. This data shows that the 'old' lot of Neoprene FB still has a considerably useful shelf life in cold storage.

Keywords: Neoprene FB; EPDM rubber insulation; Nordel polymers

1. Introduction

DuPont/Dow, the producer of Neoprene and Nordel products, has data showing that the ambient shelf life of Nordel polymers is excellent over at least a 7-year period. Data has also shown that uncured Neoprene FB has as much as a 2-year ambient shelf life, with possibly a longer life if stored at 40°F, the normal storage temperature at TC/W. Due to the earlier closing date of the Neoprene FB plant and the apparent shorter shelf life of Neoprene FB, initial shelf life/aging studies and stockpiling efforts focused mainly on Neoprene FB instead of Nordel polymers [1].

DuPont/Dow literature recommends storing Neoprene FB at a temperature of 65°F for a shelf life of 2 years. They conducted a recent aging study on

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E-mail address: doug.wingard@msfc.nasa.gov (C.D. Wingard)

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Neoprene FB that does nothing to alter this recommendation. The study utilized a cone-and-plate rheometer to measure the viscosity of samples of uncured Neoprene FB with ages ranging from 0.8 to 2.4 years (DuPont/Dow samples) and 10 to 13 years (TC/W and Alliant samples). Viscosity measurements were made after the samples were aged at 38 and 50°C for up to 14 days, with measurements made on each sample at 50, 60 and 80°C. The data showed the following rises in viscosity (millions of centipoise (cps)/day over 100 days) of Neoprene FB for several storage temperatures: (a) 0.00026 at ambient (20–23°C); (b) 0.008 at 38°C; and (c) 0.02 at 50°C. From this data, it was reasonable to predict that at a cold storage temperature such as 32–40°F, the Neoprene FB would be exceedingly stable to viscosity increase [2].

A study performed in 1973 on Neoprene WRT showed that storage of the uncured rubber at 40°C for 8–16 weeks had a very adverse effect on its curability as compared to storage at ambient conditions (23°C/65% RH) for 6–12 months. Viscometer scorch times (a measure of incipient vulcanization) were so accelerated after 40°C/8-week storage that they could not be measured. The gel content of the Neoprene WRT, as measured by Soxhlet extraction with benzene, dramatically increased to 92% (for the 40°C/8-week storage) above the 41–53% reported for the ambient storage [3].

The thermal analysis techniques of dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were used at NASA/MSFC in the aging study of samples of the ‘old’ and ‘new’ lots of Neoprene FB supplied by Thiokol/Wasatch. Block samples of the ‘old’ and ‘new’ lots of Neoprene FB used in the thermal analysis testing are shown in Fig. 1.

2. Experimental methods

2.1. DSC testing

The TA Instruments DSC 2920 Differential Scanning Calorimeter was used in the standard mode for each Neoprene FB sample. Temperature scans were made from −60 to 280°C at a linear heating rate of 10°C/min. Isothermal tests at 110°C for 180 min were also made on samples. Each Neoprene FB sample (weighing from 46 to 62 mg) was crimped in a hermetic stainless steel DSC pan with a rubber O-ring seal, and was tested in the DSC sample chamber under an argon gas purge. For the isothermal tests, the actual test temperature was 109.2°C for a set point temperature of 110°C. For isothermal testing, the sample chamber was preheated at the set point cure temperature, the sample pan was placed in the chamber, and each test was started when the actual temperature was within 4°C of the set point temperature.

2.2. TGA testing

The TA Instruments TGA 2950 Thermogravimetric Analyzer was used in the standard mode for each Neoprene FB sample. Temperature scans were made from 30 to 800°C at a linear heating rate of 10°C/min with an argon gas sample purge. Samples weighing about 13–16 mg were placed in an open platinum pan for testing.

2.3. DMA testing

2.3.1. Cure study

The DuPont (now TA) Instruments DMA 983 Dynamic Mechanical Analyzer was used in the fixed frequency mode for Neoprene FB samples. A cure study on samples of ‘old’ and ‘new’ Neoprene FB was performed at isothermal temperatures of 95, 105 and 115°C. DMA temperature control was within 0.2°C above each isothermal set point temperature. Rubber samples weighing 45–55 mg were cut from near the rubber block surface, then mounted on a glass cloth support (12.6 mm wide×0.75 mm thick). Each rubber/glass cloth sample was mounted in the horizontal DMA testing configuration, with a cloth sample length of 20 mm. Other DMA parameters used were: (a) frequency=1 Hz; (b) oscillation amplitude=0.1 mm; (c) sample torque=4–5 in. lb; (d) no inert gas purge used.

2.3.2. Temperature/frequency sweep

Two rectangular samples of ‘new’ Neoprene FB were cut from the uncured rubber block and mounted in the vertical DMA testing configuration. The following DMA parameters were used: (a) temperature ranges: from −40 to 28°C (−40 to 82°F) and from −100 to −20°C; (b) temperature increments=3.0 and 2.0°C; (c) frequencies at each temperature=0.25, 0.5,

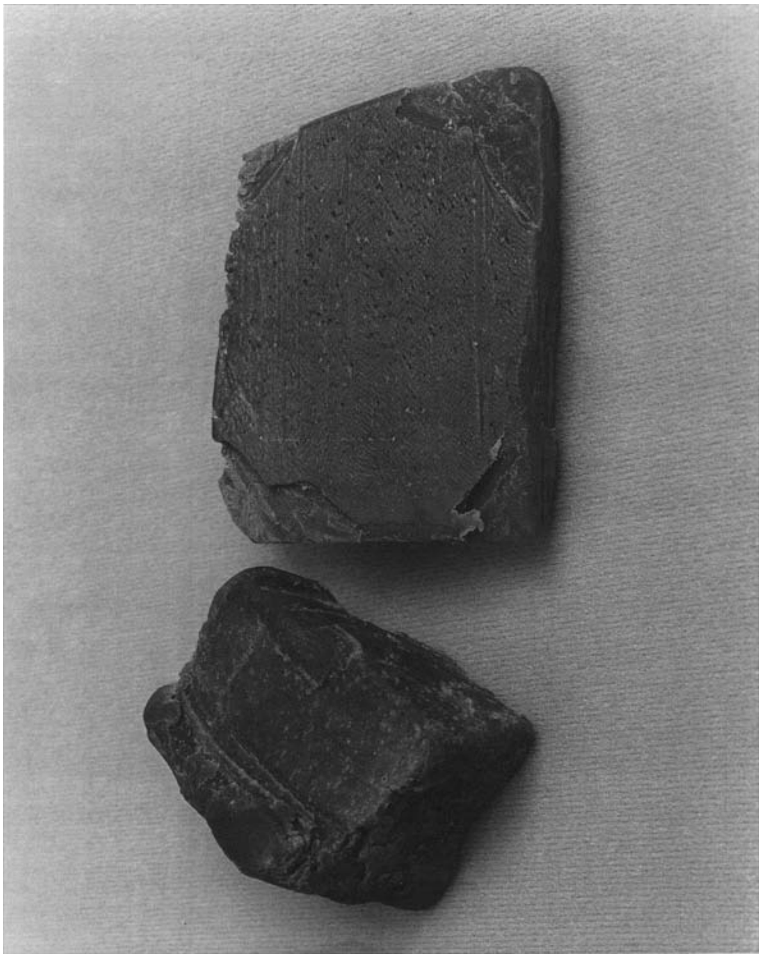

Fig. 1. Block samples of Neoprene FB uncured rubber used in the NASA/MSFC thermal analysis testing: (a) 'new' material kept in cold storage at 40°F for 8 months (left); and (b) 'old' material kept in cold storage for more than 11 years (right).

1.0 and 2.0 Hz; (d) oscillation amplitude=0.3 mm; (e) sample length/thickness ratio=1.5; (f) sample torque=3 in. lb cold (finger-tight at room temperature); (g) no inert gas purge used.

2.4. Hardness testing

The Exacta Hardness Tester, a vertical digital benchtop tester, was used to measure Shore A hardness on the cured samples of Neoprene FB on the glass cloth support from DMA testing. Five to seven hardness measurements were made on each rubber sample. Each hardness measurement was recorded at the end of a three-second period in which the blunt Shore A tip was applied with constant pressure to the sample. A printer attached to the tester records each hardness measurement, and average hardness and standard deviation can be calculated for the total number of measurements.

3. Results and discussion

3.1. DSC data

3.1.1. Dynamic (temperature scanning) data

For DSC testing, Neoprene FB samples were cut from both the rubber block surface and block interior.

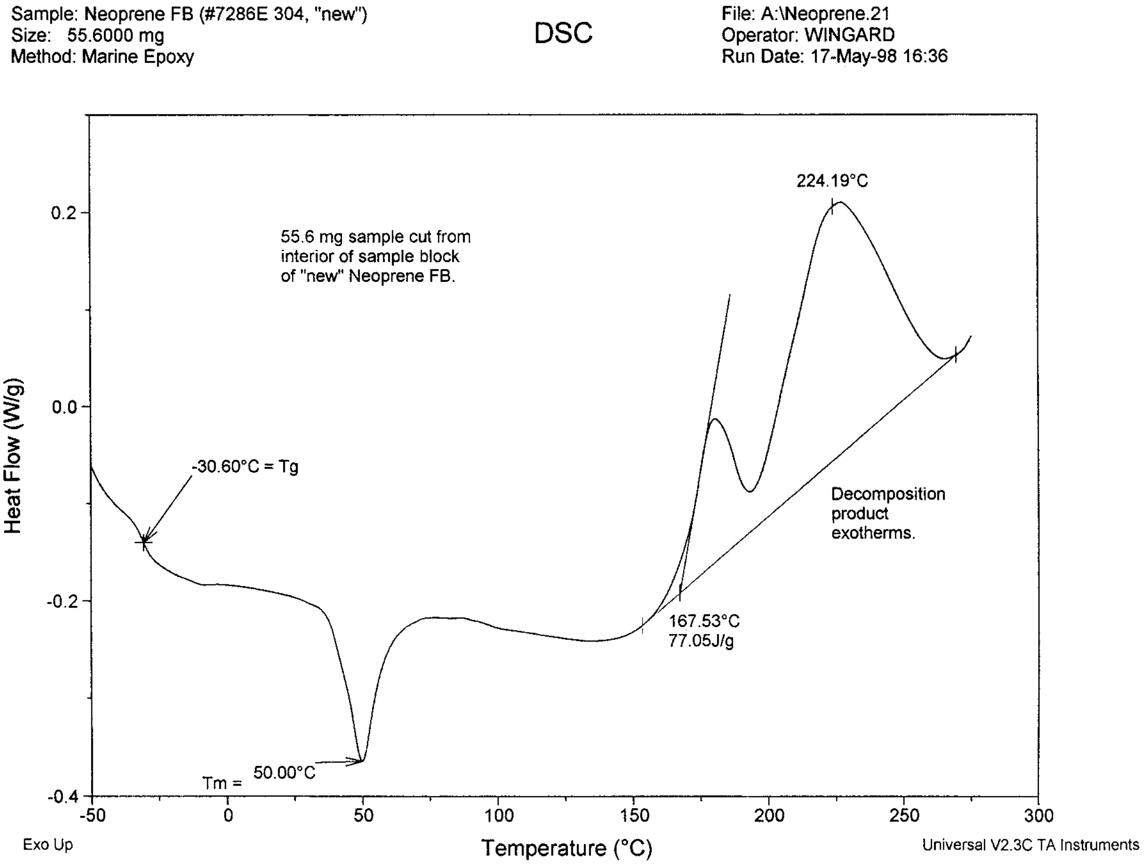

Fig. 2. DSC heating scan at 10°C/min on a sample of 'new' Neoprene FB.

A temperature scan at 10°C/min of heat flow versus temperature for one of these samples taken from the 'new' Neoprene FB lot is shown in Fig. 2. The glass transition temperature (T_g) of this sample was determined to be −30.6°C as the midpoint of the half-extrapolated tangents method. In comparing the two sample types for T_g, the T_g of the 'old' material was 3.4°C higher than that of the 'new' material, indicating slightly greater cure advancement for the 'old' material in cold storage. The peak melting temperature (T_m) is clearly shown at 50°C in Fig. 2, and was the same for both sample types of Neoprene FB. This melting transition is more accurately defined by a dramatic decline in polymer viscosity due to the cleavage of sulfur–sulfur linkages in the polymer backbone by thiuram disulfide and other curatives, although some crystallites may be melted as well [2]. The two exotherm peaks near 175 and 225°C were found to correspond to two weight loss processes in a TGA heating scan on both Neoprene FB sample types, as shown in Fig. 3 for TGA derivative weight (%/°C) versus temperature (°C). The total heat of decomposition for these two DSC exotherms averaged 74.8 J/g for two samples of the 'new' Neoprene FB and 86.9 J/g for two samples of the 'old' lot of rubber, a difference of about 16%. Even these low-temperature DSC exotherms are accompanied by material weight loss in an open pan (TGA testing), but the hermetic stainless steel DSC pan successfully contained mass (no weight loss) during heating to 280°C.

3.2. Isothermal data

Isothermal DSC data was also obtained on one sample each of the two Neoprene FB sample types by

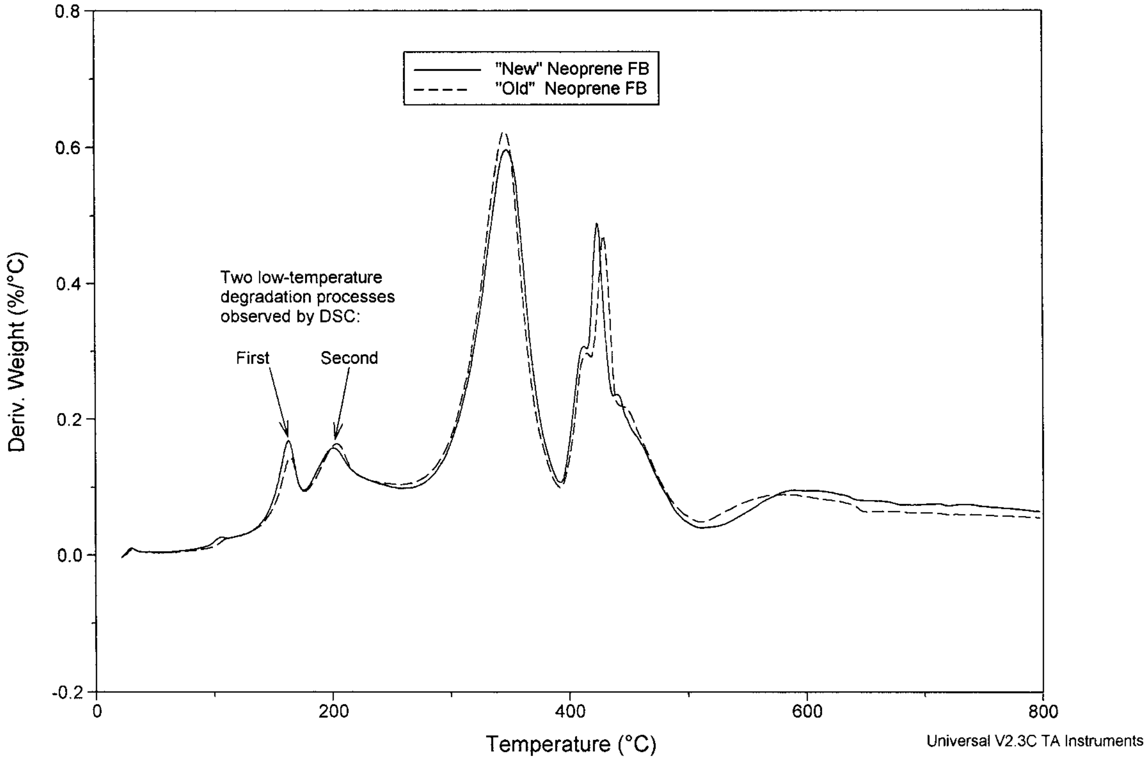

Fig. 3. TGA heating scan at 10°C/min on samples of 'new' and 'old' Neoprene FB for the derivative of weight with respect to temperature (%/°C) vs. temperature (°C).

curing at 110°C for 180 min. For this cure, the total isothermal exothermic heat was 7.1 J/g for the 'new' material and 3.2 J/g for the 'old' material (Fig. 4), also indicating slightly more cure advancement in cold storage for the 'old' material. Evaluation of cure kinetics for the two sample types by DSC was not pursued since the values of isothermal heat were so small.

3.3. TGA data

TGA heating scans of weight percent versus temperature on the 'old' and 'new' material yielded almost identical results, as evidenced by the derivative curves in Fig. 3.

3.4. DMA data

3.4.1. Cure study

For DMA testing, Neoprene FB samples of 'old' and 'new' material were mounted on a glass cloth support and tested at cure conditions of 95°C/360 min, 105°C/180 min and 115°C/120 min. Fig. 5 shows several DMA samples of 'new' and 'old' Neoprene FB on glass cloth support after cure at several cure conditions. One of these DMA cures is shown in Fig. 6 as a plot of flexural storage modulus (E') versus time. This plot shows that the Neoprene FB is in a liquid state when the isothermal temperature is reached, the E'-time curve goes through a minimum value, then E' begins to increase with cure time as the rubber cross-linking occurs. The maximum in tan δ (E''/E') shows an approximate 'gel time' for the rubber. An Arrhenius plot of ln(gel time) versus reciprocal absolute cure temperature for the 'old' and 'new' rubber yielded a straight line from which the activation energy (E_a) of cure was determined, as shown in Fig. 7. Values of E_a were determined to be 22.9 and 26.6 kcal/mole for the 'old' and 'new' Neoprene FB, respectively. From the Arrhenius equation, the following linear relationships were determined:

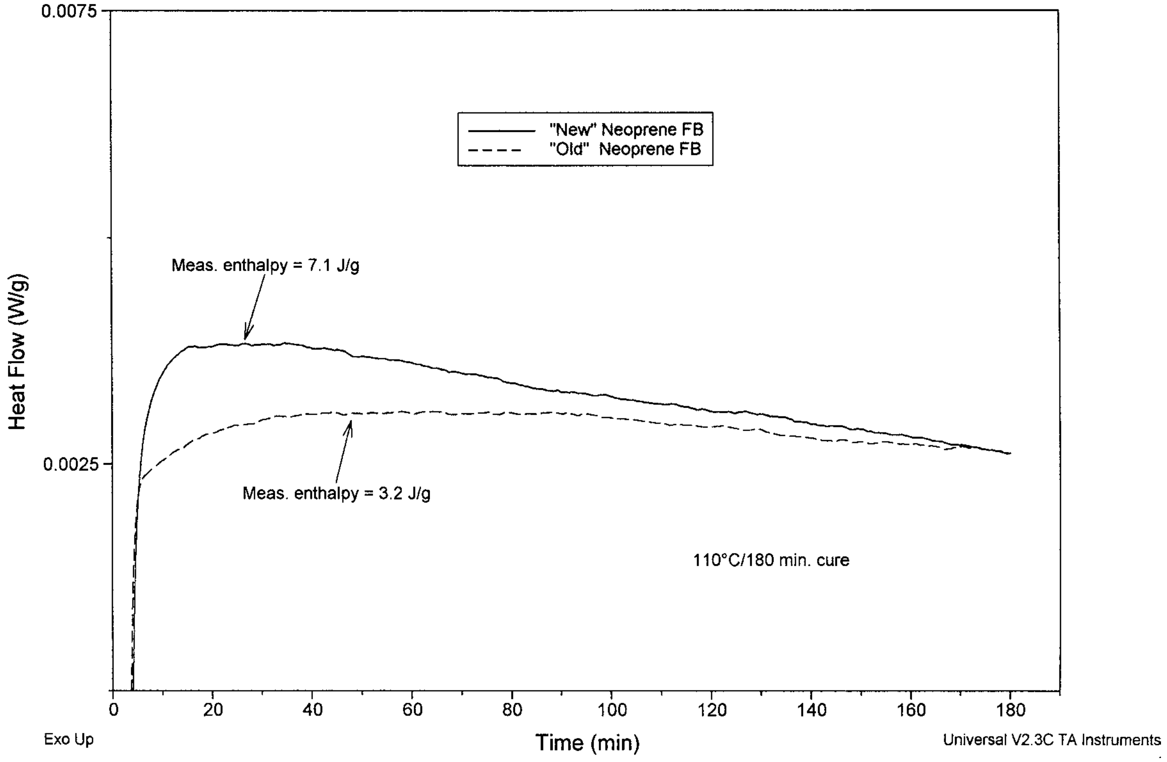

Fig. 4. DSC isothermal cure of 'new' and 'old' Neoprene FB for 180 min at a set point temperature of 110°C.

$$\text{'old' Neoprene FB}: \quad \ln(t_{\text{gel}}) = -25.79 + 11522\left(\frac{1}{T}\right)$$

$$\text{'new' Neoprene FB}: \quad \ln(t_{\text{gel}}) = -30.82 + 13403\left(\frac{1}{T}\right)$$

For a linear extrapolation of the Arrhenius equation down to a rubber storage temperature of 40°F (277.6 K), the following gel times were determined:

$$\text{'old' Neoprene FB}: \quad t_{\text{gel}} = 12.7\,\text{years}$$

$$\text{'new' Neoprene FB}: \quad t_{\text{gel}} = 72.6\,\text{years}$$

The above calculations predict that even the 'old' Neoprene FB material would not begin gelation (i.e., initiation of an infinite network of molecular weight with cross-linked molecular chains) for almost another 13 years in cold storage.

Deuri and Bhowmick [4] determined the gel content of uncured EPDM rubber by a 16 h soak in cyclohexane at 35°C. The gel content was determined for aging of the uncured rubber in air at temperatures of 70–150°C for up to 75 h, with the different slopes of the gel content versus aging time plot yielding rate constants for gelation. An Arrhenius plot was generated, yielding an activation energy for gelation of 23.4 kcal/mol. This activation energy is in good agreement with the values of 22.9 and 26.6 kcal/mol determined in our work for uncured Neoprene FB by DMA gelation times.

The DMA data also yielded the increase in E' during cure (E' of the rubber relative to the glass cloth support) from the minimum in E' versus time to the end of cure, as determined for each cure condition for the 'old' and 'new' Neoprene FB. It was found that E' was 14% higher for the 'new' material than for the 'old' material at a cure condition of 105°C/180 min, with slightly lower percentages for the 'new'/'old' ratio at the other two cure conditions. Shore A hardness data obtained from the cured Neoprene FB samples on glass cloth by DMA showed that the average hardness of the 'new' material was 4–5% higher than that of the 'old' material for each cure

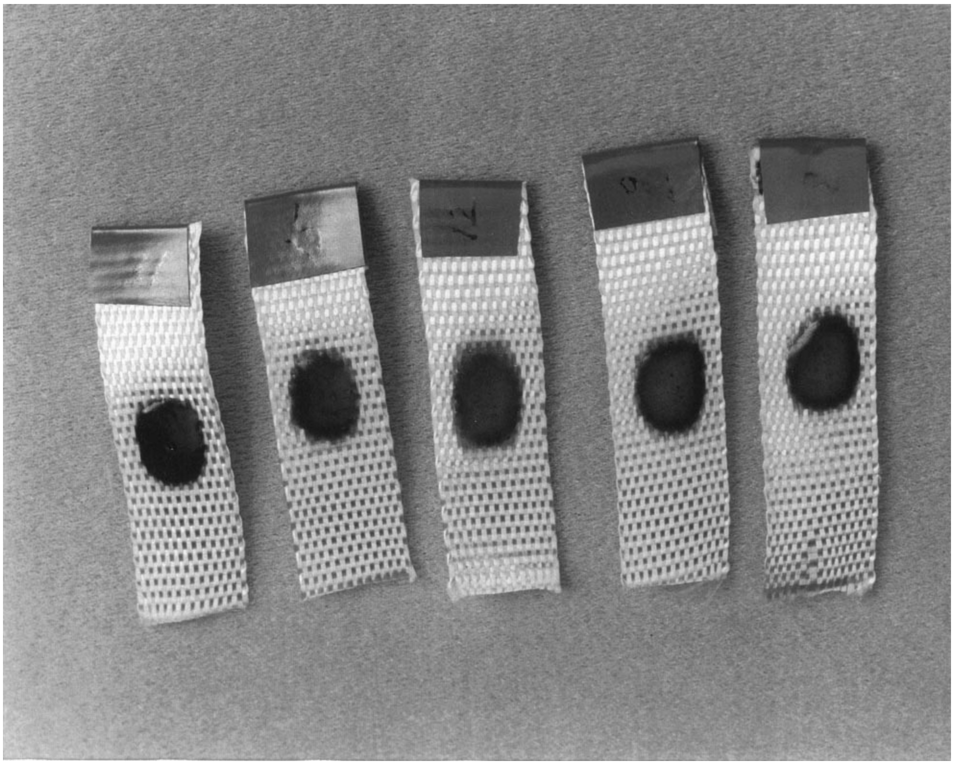

Fig. 5. DMA samples of 'new' and 'old' Neoprene FB on glass cloth support after cure at several isothermal temperatures and times.

condition, which is consistent with the E' data by DMA. The post-cure data summary for DMA Neoprene FB samples on glass cloth for the ratio of 'new' to 'old' material is as follows:

Measured parameter	'New'/'old' ratio
E' of rubber (psi, end of cure — minimum)	1.14
Shore A hardness	1.04–1.05

3.4.2. Temperature/frequency sweep data

To help verify the validity of the Arrhenius linear extrapolation down to 40°F, a rectangular sample of 'new' Neoprene FB uncured rubber was tested with a DMA temperature sweep from -40 to 28°C at four frequencies with a temperature increment of 3°C between frequency measurements. This temperature range starts near the T_g, ends before the onset of melting, and brackets the normal storage temperature of 40°F (4.4°C) for the uncured Neoprene FB. Fig. 8 shows the DMA data for this sample as log E' versus log(frequency^{-1} (hour)) for the different temperatures and frequencies. This plot is the result of time–temperature superposition (TTS), in which a reference, mid-range temperature (at -7.9°C) allows 'shift factors' to move the curve segments horizontally (and vertically, if necessary) to superimpose them onto the reference segment, creating the best possible single, continuous curve. The TTS software from TA Instruments uses a cubic spline to fit such a 'master curve' to the continuous curve, and also allows the shifted segments to be fitted to the Arrhenius equation [5]. The calculated activation energy (E_a) of 96.86 kJ/mol (23.1 kcal/mol) for the temperature range from -40 to 28°C is similar to the value of E_a calculated previously for the temperature range of 95–115°C, showing that extrapolation of the DMA cure data for Neoprene FB down to 40°F is probably valid.

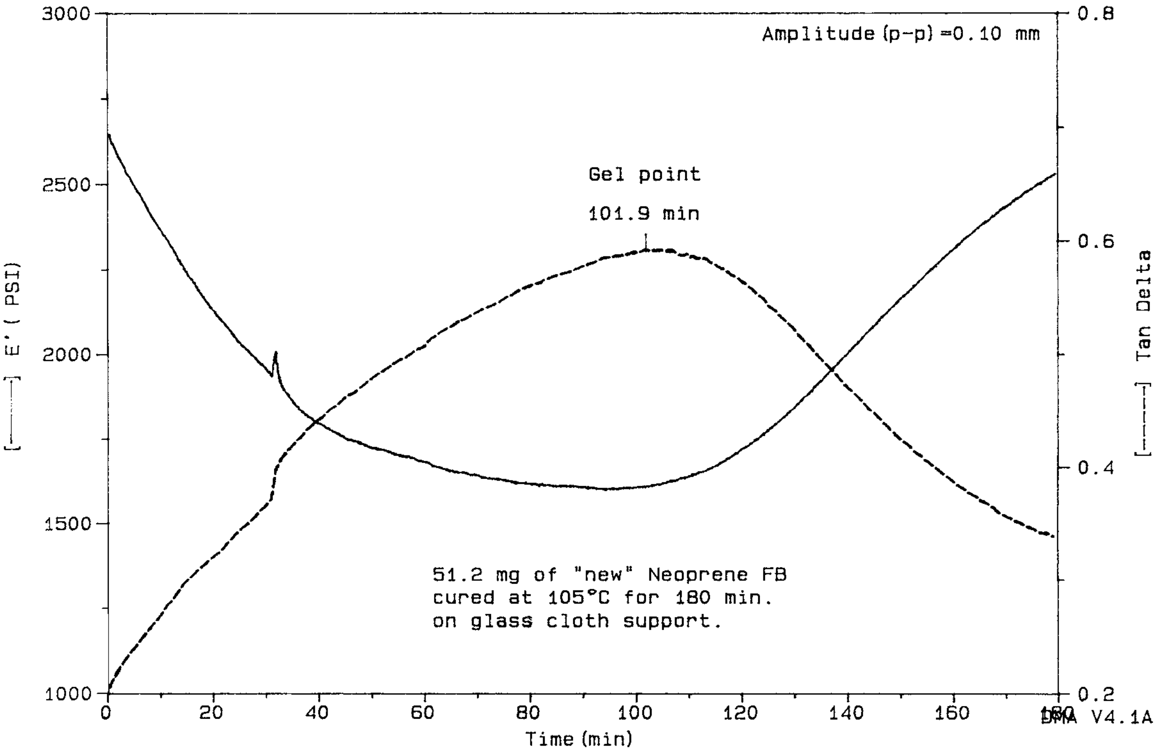

Fig. 6. DMA isothermal cure of 'new' Neoprene FB for 180 min at a set point cure temperature of 105°C and a frequency of 1 Hz.

Another rectangular sample of 'new' Neoprene FB was subjected to a similar temperature/frequency sweep, from −100 to −20°C at four frequencies with a temperature increment of 2°C. A TTS master curve was also created for this sample, and an Arrhenius fit through the shifted segments yielded an E_a value of 168.9 kJ/mol (40.3 kcal/mole), which is considerably higher than the E_a of cure for Neoprene FB. This again shows that the E_a of cure for the Neoprene FB can be extrapolated to lower temperatures, provided those temperatures are sufficiently above the T_g region, and lower than the onset of the melting region.

The data summary for calculated Arrhenius activation energies is as follows:

DMA temperature range (°C)	Type of DMA experiment	DMA activation energy (kcal/mol)	
		'New' Neoprene FB	'Old' Neoprene EB
95 to 115	Isothermal cure	26.6	22.9
−40 to 28	Temperature/frequency sweep	23.1	–
−100 to 20	Temperature/frequency sweep	40.3	–

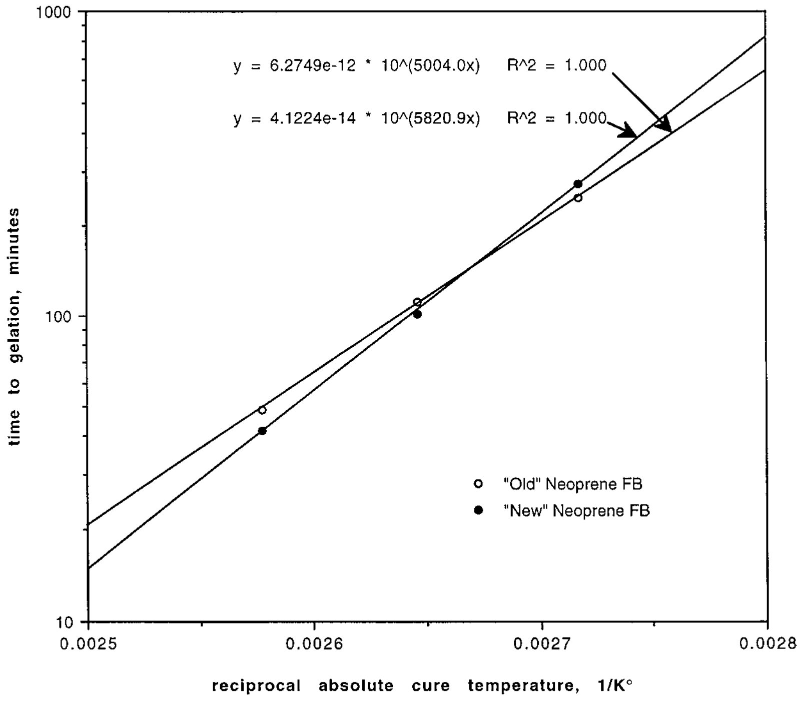

Fig. 7. Arrhenius plot of DMA log(gelation time) vs. reciprocal absolute cure temperature for ‘new’ and ‘old’ Neoprene FB.

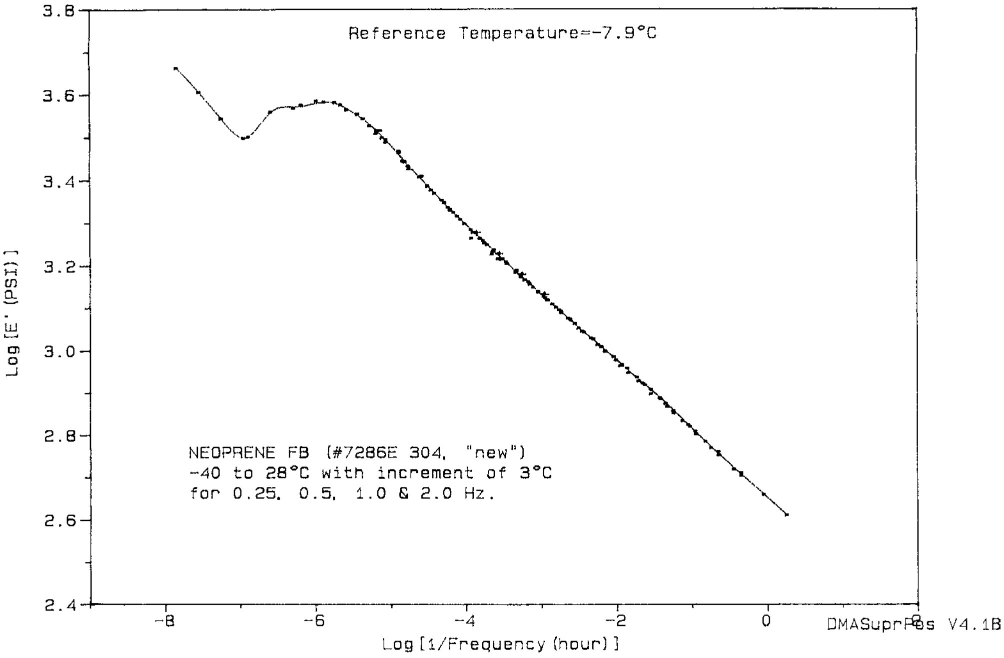

Fig. 8. DMA master curve for ‘new’ Neoprene EB created by time–temperature superposition (TTS) over a range from −40 to 28°C at four frequencies.

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