



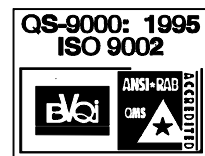
LOW TEMPERATURE TESTING OF ELASTOMERS

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LOW TEMPERATURE DATA

Two basic questions (as suggested by John Ferry, 1986 [4]) that an engineer designing a rubber seal might want to ask are:

1. After a sudden stress how long will it take for the elastomer to adjust its shape to maintain the seal?
2. If there are oscillating stresses, will there be sufficient time in the period of oscillation for the elastomer to adjust its shape to maintain the seal?

Correct answers to these questions may have saved the lives of the astronauts aboard the Space Shuttle "Challenger." Thus it is imperative that we find the answers, prepare for the future and avert similar tragedies.

A third question for a design or R&D engineer might want to ask is:

3. What tests can I use in the lab to analyze and verify my design?

In this paper we will discuss various historical attempts to answer these questions and propose alternate methods.

PURPOSE OF ENGINEERING DATA

The key question we must ask here is why do we do these various tests for rubber properties? The primary answers are 1) Quality Control and 2) to use the test results to predict performance under design conditions. For example, if we want to design a rubber hanger to support 500 lbs., we can use the tensile strength of the material as a design tool. From the equation:

$$\text{Eq. 1} \quad S_U = \frac{P_{Max}}{A}$$

Strength = Max Load/Cross Sectional Area, we know the tensile strength of the material and the maximum load corresponding to a given cross sectional area. For our design, we know the load to bear, and the strength of the material. The unknown is the size (cross sectional area) of the hanger. Rearranging, we can solve for the required area:

$$\text{Eq. 2} \quad A_{Min} = \frac{P_{Design}}{S_u}$$

For our example, let's assume a tensile strength of 2,500 psi. The load to bear is 500 lbs. Thus the cross section must be at least 0.2 in²; for a square cross section, the length of a side is about 0.45 inches (the square root of 0.2).

This example assumes that design conditions are (nearly) the same as test conditions. That is, the loading is (nearly) static and tensile, and the temperature is the same as test conditions. Tensile strength is a well-defined test, easily correlated for use in design*.

The whole purpose of engineering data is to classify and characterize the properties/behavior of engineering materials in order to predict their behavior under other geometric, loading, or temperature conditions. This reduces the amount of "trial and error" engineering and significantly reduces cost and increases speed of design. Tests that cannot be correlated to other sets of conditions are of little use to the design engineer. Mooney viscosity and many of the low temperature tests are just a few examples.

* This is presented as a simple example for linear materials; other factors are involved for elastomeric materials.

EXAMPLE OF POOR USE OF ENGINEERING DATA

Mooney Viscometer

As a quick example, let's look at the typical industry use of the Mooney viscometer or cure rheometer. Generally it is used as a quality control tool for various rubber compounds. Torque versus time is plotted as the rotor either rotates (constant speed) or oscillates (constant frequency). Be aware that viscosity (and consequently the measured torque) varies with shear rate. That is, the ratio of torque to rotor speed is NOT a constant value. In fact, the viscosity of many polymer melts actually looks like this:

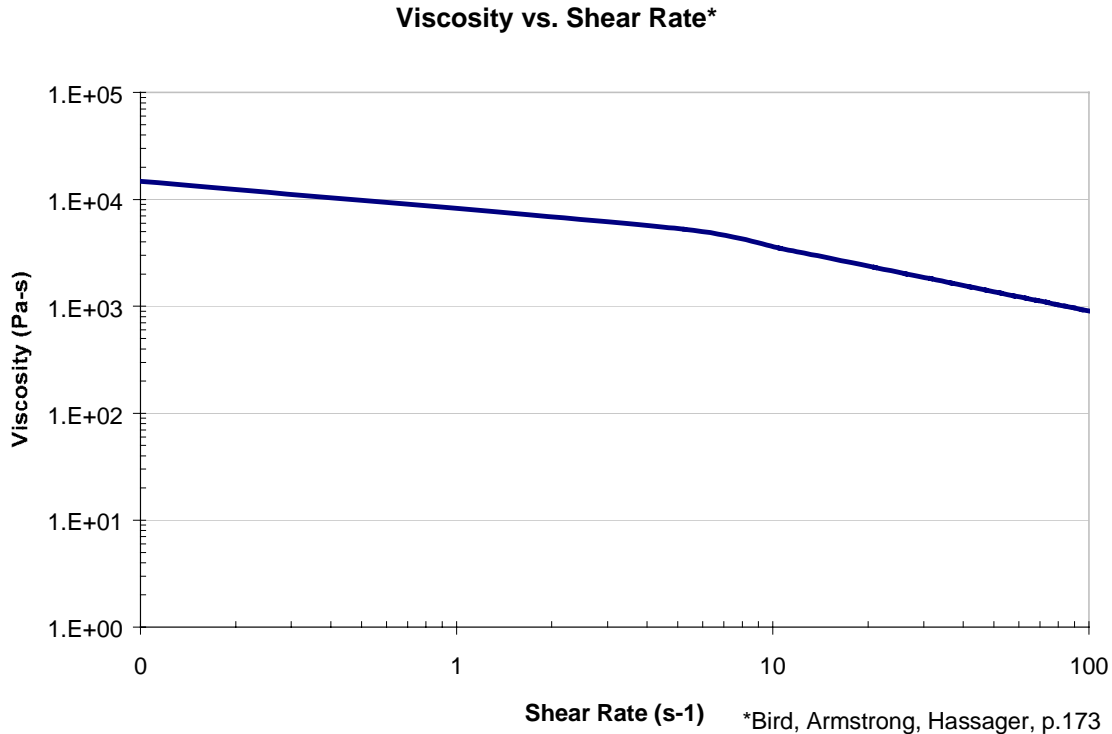


Figure 1

It is worth noting that Mooney viscometers impose a shear rate of approximately 1 s^{-1} , while typical shear rates in injection molding operations are in the neighborhood of 1000 s^{-1} . This information, combined with the chart above, should raise a red flag to anyone using a Mooney viscometer as a check for injection molding operations. Not only does the Mooney viscometer use a single (low) shear rate [6], but also its data cannot be used to predict behavior in other geometric configurations. That is, there is no definable "state of stress" for the sample in a Mooney viscometer.

INTRODUCTION TO MATERIAL BEHAVIOR

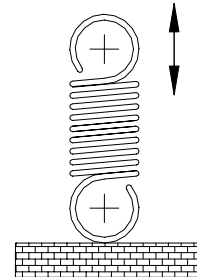
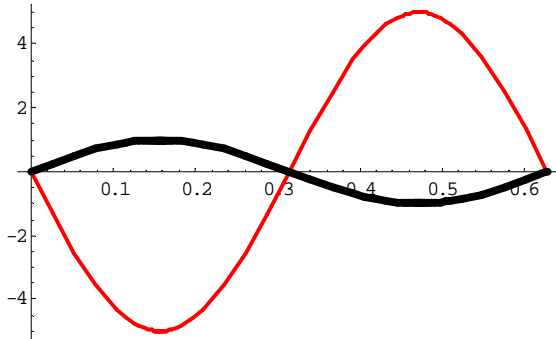
Perfectly Elastic Spring

Given a sinusoidal deflection (or similarly, strain) input, there will be a sinusoidal stress output with no phase lag- i.e. tan delta is zero. No dissipation is occurring. The following two curves show a sinusoidal strain input (black curve, y-axis is deflection in inches) and a perfectly elastic force response (red curve, y-axis in units of pounds force) versus time. The curves are exactly in phase. That is, the only difference between the two curves is in magnitude; both curves have the same argument, namely ωt . Thus the input deflection is:

Eq. 3 $y = A \sin(\omega t)$

and the measured force response is:

Eq. 4 $F = -kA \sin(\omega t)$



A Purely Elastic System- A Spring

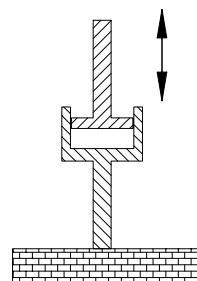
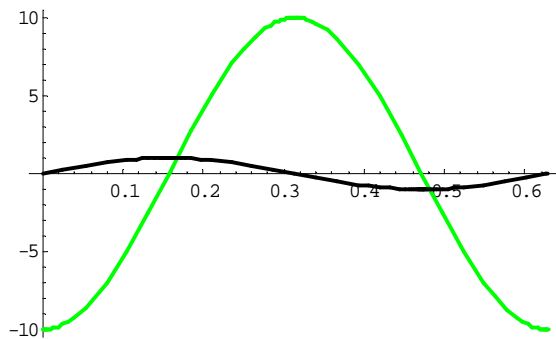
Figures 2a and 2b

As an example, think of a steel spring. The spring can be stretched between two fixed points and years later, the spring will not lose the stored energy. We can get the energy back and perform work even after a large amount of time. The further you stretch the spring, the more energy is stored, and it doesn't matter how *fast* you stretch the spring, only how *far*.

Purely Viscous Fluid

Given a sinusoidal deflection (or similarly, strain) input, there will be a sinusoidal stress output with a 90° phase lag. Therefore, tan delta is undefined. This means that the input and output curves will differ both in magnitude and in phase. The phase difference is exactly 90°. The fluid does not store any energy- all the work is dissipated. Thus the input deflection is the same as before, and the output force is:

Eq. 5 $F = [-c \dot{y}] = [-c \omega A \cos(\omega t)] = [-c \omega A \sin(\omega t + \pi/2)]$



A Purely Viscous System- A Dashpot

Figures 3a and 3b

As an example, think of a damper on an office door. The faster you push the door, the harder it is to close. Unlike the spring, if you push the door open, it will not close after you let go; the damper does not store any energy. The force it takes to move the damper doesn't depend on how far you move the damper, only how fast.

Viscoelastic Materials

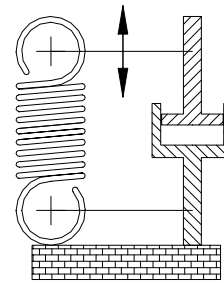
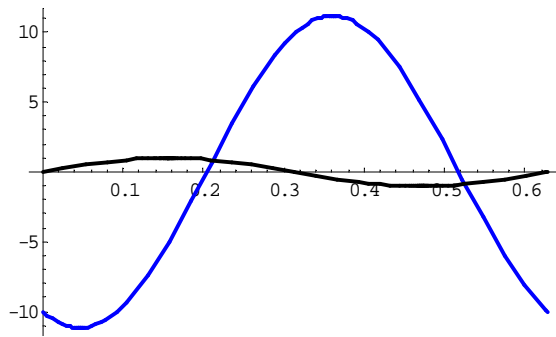
Sinusoidal Strain Input, Sinusoidal Stress Output- Phase Lag is somewhere between 0° and 90°; there is some storage and some dissipation. The sinusoidal deflection input is the same as before, but the output is a combination of the elastic and viscous responses:

$$\text{Eq. 6} \quad F = -kA \sin(\omega t) - c\omega A \cos(\omega t)$$

This response can also be expressed as a single sine wave as follows:

$$\text{Eq. 7} \quad F = -f \sin(\omega t + \delta), \text{ where the amplitude of the response is}$$

$$\text{Eq. 8} \quad f = \sqrt{A^2(k^2 + c^2\omega^2)} \text{ and the negative sign is simply an indicator of the direction of the forces.}$$



A Viscoelastic System- Polymers!

Figures 4a and 4b

As an example, think of a rubber band. There is some storage- you can stretch the rubber band and launch it (i.e. recover the energy). There is also some dissipation- stretch a rubber band while holding it over your upper lip and feel the heat buildup- this energy cannot be recovered!

Comparison of Responses:

We can plot all of the responses on the same axes to compare the results of a sinusoidal input. They show respectively, the response of a **purely elastic material**, a **purely viscous material** and a **viscoelastic material**.

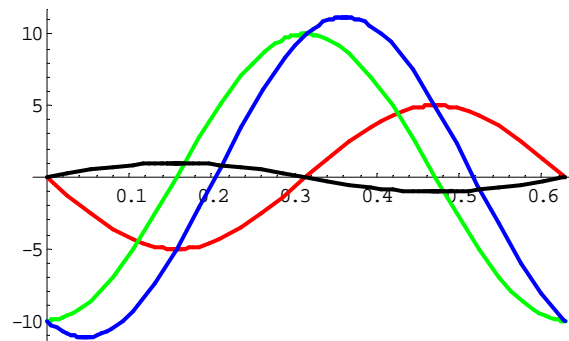


Figure 5

Tan Delta

To define tan delta, we must first define delta. Delta (usually shown with the Greek letter, δ) is the amount by which the sinusoidal force lags a sinusoidal displacement. Since the phase angle is somewhere between 0° (for perfectly elastic) and 90° (for purely viscous), it is used as a measure of how “viscous” a material is.

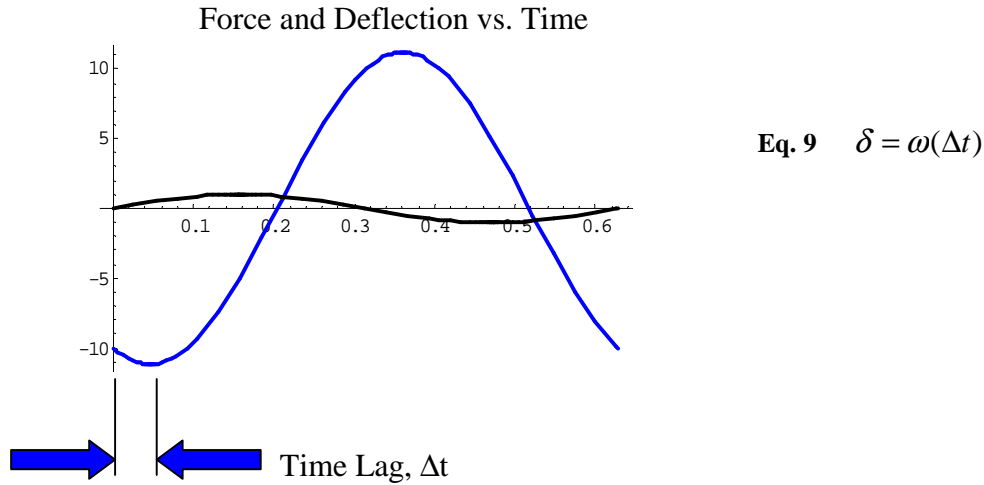


Figure 6

Loss Modulus

As we have seen, the response of a viscoelastic material to a sinusoidal input can be broken down into a viscous component and an elastic component. For a static test, we can calculate a modulus as the ratio of stress to strain. For a dynamic test, we can calculate a complex modulus as the ratio of stress and strain *amplitudes*. Thus a complex shear modulus, G^* , can be measured using a parallel plate rheometer. It can be shown that the phase angle, delta, relates to the ratio of viscous to storage (elastic) modulus via the following equation:

$$\text{Eq. 10} \quad \tan \delta = \frac{G''}{G'}$$

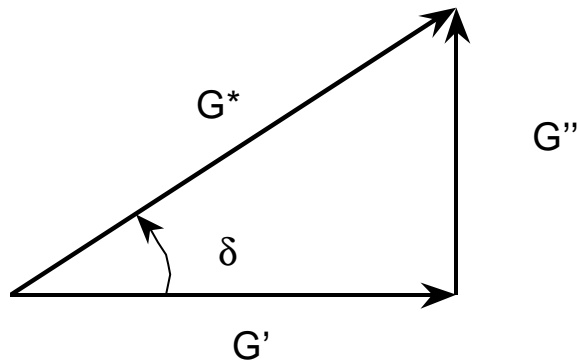


Figure 7

(which relates storage and loss modulus in terms of a right triangle and the Pythagorean Theorem) and that G' (storage modulus) and G'' (loss modulus) are related by:

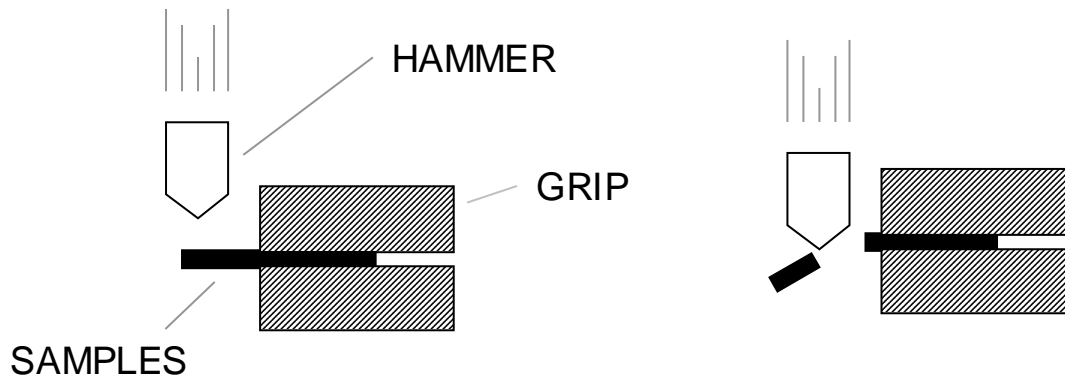
$$\text{Eq. 11} \quad G^* = \sqrt{(G')^2 + (G'')^2}$$

Thus, we can measure G^* and δ through simple experiments and calculate G' and G'' .

COMMON ASTM TESTS

Brittle Point, ASTM D2137:

This test uses a hammer of a specific mass, moving at a specified speed toward five rubber samples held by a grip. The samples and the grip are cooled to a low temperature. The hammer strikes the samples at the specified speed and continues moving past. The temperature at which fracture occurs in three of the five samples is said to be the brittle point of the material.



Figures 8a and 8b

This test has numerous flaws concerning its utility to the design engineer. The test samples are undergoing a combination of bending and shear under dynamic conditions (impact). Thus the state of stress in the material is not definable. Also, this is again a test that provides data at only one “shear rate” (i.e. speed of hammer at impact). Polymer liquids have a viscosity that is exponentially dependent on temperature as well as shear rate dependent at a given temperature. A design engineer cannot expect to use brittle point data to design for low temperature applications.

TR Test, ASTM D1329:

The “TR,” or “time-to-return,” test uses samples clicked from a sheet (or an o-ring for method D1414). The samples are stretched to a given extension in a sample rack. The samples and the rack are cooled to a low temperature and allowed to reach equilibrium. The samples are released from the rack and heated at a specified rate of 1°C per minute. Stretch is recorded over time, and the time at which the sample recovers 10% of the applied stretch is recorded as TR₁₀.

Among the flaws of this test is the fact that time and temperature are coupled via a specified heating rate of 1°C per minute. Again, with the temperature and shear rate dependent viscosity of polymer liquids, it is impossible to separate the effects of time and temperature using this test. Performing the test at a different heating rate would produce different results. This test does not account for the variations in thermal expansion among various compounds; i.e. the strain recovery is based on both the material’s elasticity and the fact that it expands as temperature increases. The TR test does not provide the design engineer with data that can be used for applications under conditions different than experimental.

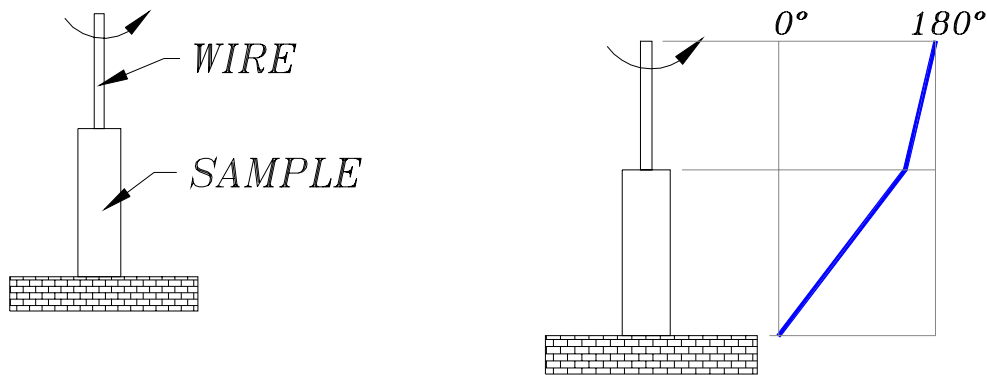
A more logical test might be the time it takes a given sample to recover 10% of its elongation performed at a fixed temperature (elastic recovery rate). However, even this test does not take into account the fact that it may have taken much more energy to deform one compound vs. another. That is, a 90 durometer compound requires more work input to deform to 50% elongation than does a 50 durometer compound. Thus, there is likely (depending on viscous losses) more energy stored in the stiffer compound than in the softer one.

This is basically a measure of viscosity as a function of temperature (elastic recovery rate), and can be done with a rheometer.

Stiffening at Low Temperature, ASTM D1053

This method employs a composite torsion rod. One section of the rod is made of a “torsion wire” whose torque vs. angular deflection curve is known. The other section of the rod is the rubber sample. The assembly is cooled to the test temperature. Then the top end of the composite rod is rotated 180°, while the other end is held stationary. The rotation at the interface is measured. From the relative rotation of the wire, the torque can be calculated. The shear strain in the sample can also be calculated from the measured rotation. The reference to time scale in this test is the time the technician waits to take a data point after the head has been set to 180° rotation (i.e. 10 seconds). The standard does allow for data to be taken over time as the sample remains at fixed temperature.

There are still many drawbacks to this test. First of all, the test is neither strain controlled nor stress controlled. It approximates a creep experiment, but the load changes with the displacement. Also, there is no mention of time dependence. Also, the composite rod is not necessary for this test; using grips on the sample combined with a torque transducer, we can perform this test easily- eliminating the “middle man” of the torsion rod. Furthermore, the test says “turn the torsion head quickly but smoothly 180°”; the interpretation of this statement can have a profound effect on the measured results if the material is highly viscous.



Figures 9a and 9b

Glass Transition Temperature: DSC Method, ASTM E1356

“DSC” stands for Differential Scanning Calorimeter. This type of device measures heat flow to a sample and the sample’s temperature. As the instrument displays heat flow versus temperature, we can see endotherms (as the sample absorbs heat energy) and exotherms (as the sample releases heat energy). As a polymer becomes crystalline or “glassy”, it undergoes a change that is similar to a change of phase. Consider water as an example: as water reaches 32°F, and we continue to remove heat, the temperature of the water remains constant throughout the phase change. A similar process occurs at the glass transition temperature for polymers. However, this process is strongly dependent on the rate of cooling. For example, the following chart shows glass transition temperature data from a DSC instrument for a VF₂ dipolymer fluoroelastomer.

T_g vs. HEATING RATE (DSC)

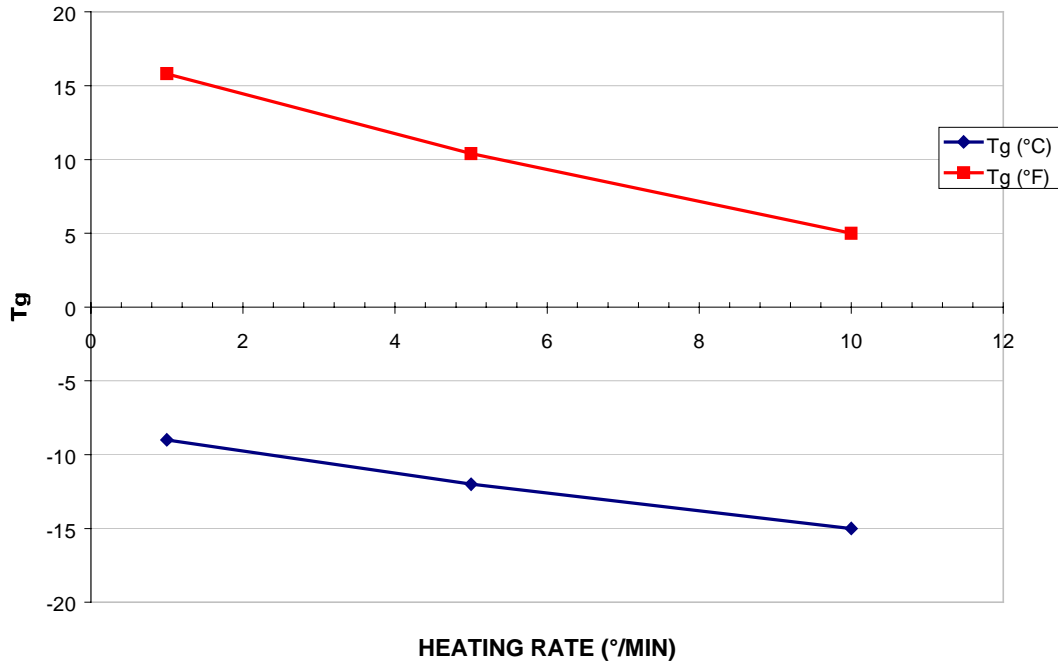


Figure 10, Data from Table 5

As the cooling rate increases, the glass transition temperature appears to decrease. Recall that the bosses of most lab technicians want high productivity from their technicians; the quickest way for a tech to get more tests done in a day is to increase the cooling rate! Thus, many materials might appear to have adequate low temperature properties at high cooling rates, while in actual applications the same material performs less than adequately. Think of your automobile as an example. How fast does it really cool down in winter? It is actually a relatively slow process. Thus it is irresponsible to report the glass transition temperature (as calculated from DSC data) as a single temperature given the strong dependence on cooling rate. Also, there is no indicator of how the elastomer will perform at temperatures close to, but above, the reported T_g. Should I not use the material for a seal that will see a minimum temperature of 10° above T_g, or will the seal function properly at 1° above T_g? This test/data does not have the capability to make such a determination.

Glass Transition Temperature: DMRT Methods, ASTM D5992

DMRT stands for Dynamic Mechanical and Rheological Testing. ASTM D5992 describes tests for determining glass transition temperature via DMRT and tan delta data. A frequency of oscillation is chosen, and the temperature is ramped up from a temperature well below T_g . (i.e. the test uses temperature sweeps at a given frequency). The point at which tan delta reaches a maximum is said to be the material's glass transition temperature. Once again, time and temperature are directly coupled via a specified heating rate, and again time and temperature effects are indistinguishable.

ASTM D5992 also describes a method of determining T_g using DMRT results for E'' , or loss modulus. The procedure is very similar to that for the tan delta method and has the same deficiencies.

Sample data are given below for the DMRT methods described in ASTM to show the test's dependence on frequency. The data is for a VF₂ dipolymer fluoroelastomer.

Table 1

T_g via DMRT and Tan Delta		
Frequency (Hz)	T_g (°C)	T_g (°F)
1	-20	-4
10	6.5	43.7
50	11	51.8

Table 2

T_g via DMRT and Loss Modulus, G''		
Frequency (Hz)	T_g (°C)	T_g (°F)
1	-8	17.6
10	-4.5	23.9
50	-2	28.4

Proper Use of DMRT

Let's now discuss a method that addresses the fundamental questions listed at the start of this paper. Consider a constant stress (creep) experiment. We can measure the time it takes a given material to reach its equilibrium configuration. In other words, let's say we hang a weight on a rubber band, and measure the time it takes to reach its full deflection. At room temperature, the response is nearly instantaneous, thus making time measurement a difficult task. At a very cold temperature, the time could be extremely long, thus making the experiment very time consuming. In any case, a quick response time is what the designer is looking for in an elastomeric seal material. For now, to limit the time it takes to perform a test we will consider (as proposed by Ferry) the time it takes the specimen to reach 90% of its equilibrium deflection and call this time t_{90} (as shown in Figure 11 below). For elastomers with short relaxation times (i.e. fast recovery rates), measurement of t_{90} will be nearly impossible; for non-glassy elastomers, this time is only a fraction of a second.

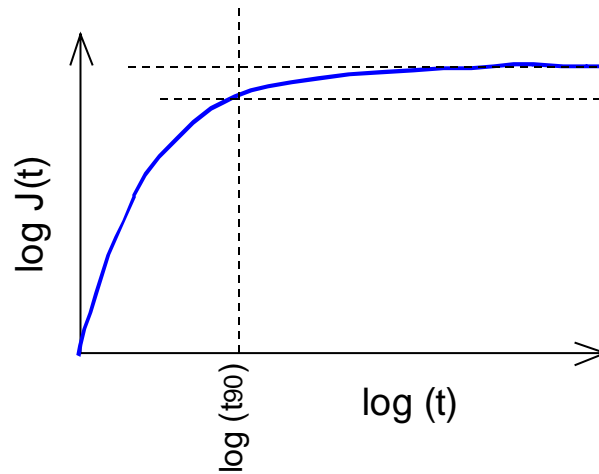


Figure 11

Let us now consider an application in which a seal undergoes oscillating stresses/loads. The response of a seal under such conditions can vary significantly with temperature and frequency. A good guideline for oscillating loads is to limit the vibrations to frequencies below that which cause a 10% increase in storage modulus. The frequency at which storage modulus increases by 10% is called f_{10} (as shown in Figure 12 below).

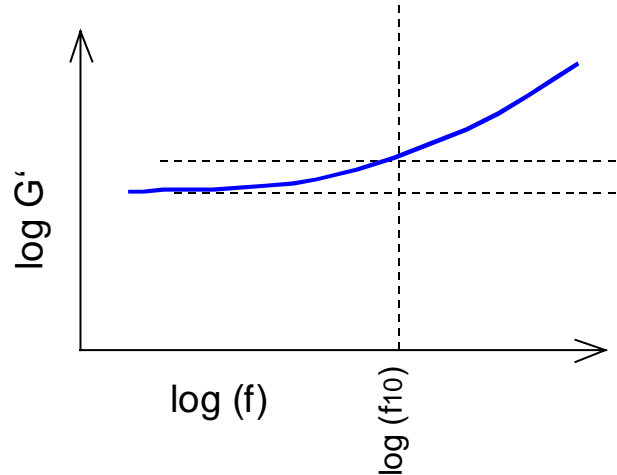


Figure 12

At a given temperature, the frequency at which the storage modulus, G' , increases 10% can be correlated to t_{90} as suggested by Ferry with the following equation:

$$\text{Eq. 12} \quad t_{90}(\text{sec}) \approx \frac{0.2}{f_{10}(\text{Hz})}$$

Using a simple geometry, such as circular parallel plates (as shown in Figure 13) or torsion, we can easily induce a definable strain field into a sample and conduct a test to find G' versus frequency at any specified temperature. Using torque transducers we can easily measure the material's response to various inputs.

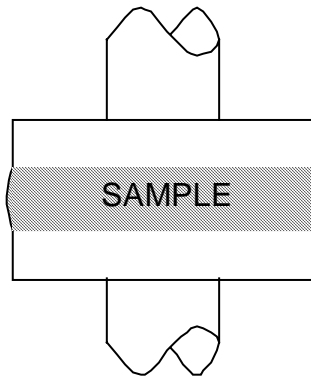


Figure 13

Examples of data from this type of test are shown below [4],[5]. The data compares two elastomers and their relaxation times at -25°C (-13°F) and 25°C (77°F). Using the data from the dynamic test, we can conclude that the polybutadiene material performs equally well over the entire temperature range, while the butyl rubber experiences a significant change in relaxation time as temperature drops. By performing more frequency sweeps at temperatures between -25°C and 25°C , we can determine the suitability of the elastomer for a given application.

Table 3 (References [4] and [5])

Temperature, $^{\circ}\text{C}$	1,4 Polybutadiene		Butyl Rubber	
	f_{10} (Hz)	t_{90} (sec)	f_{10} (Hz)	t_{90} (sec)
-25	13	0.015	0.005	40
25	250	0.0008	5	0.04

FREQUENCY TO INCREASE G' BY 10% VS. TEMPERATURE

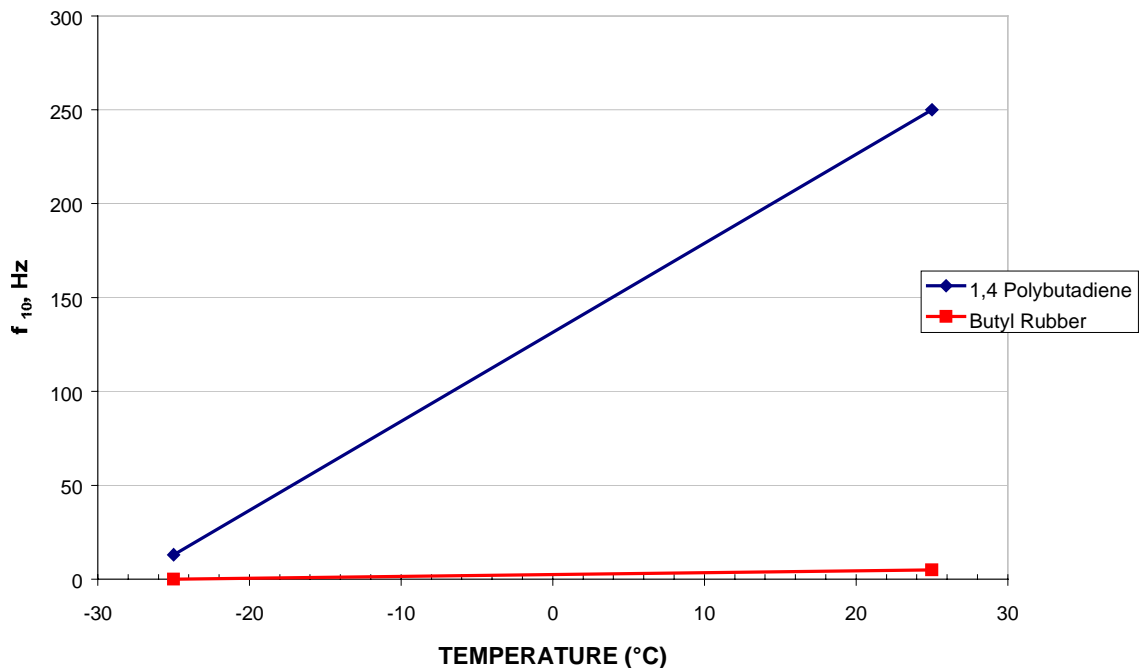


Figure 14, Data from Table 3

ESTIMATED t_{90} VS. TEMPERATURE

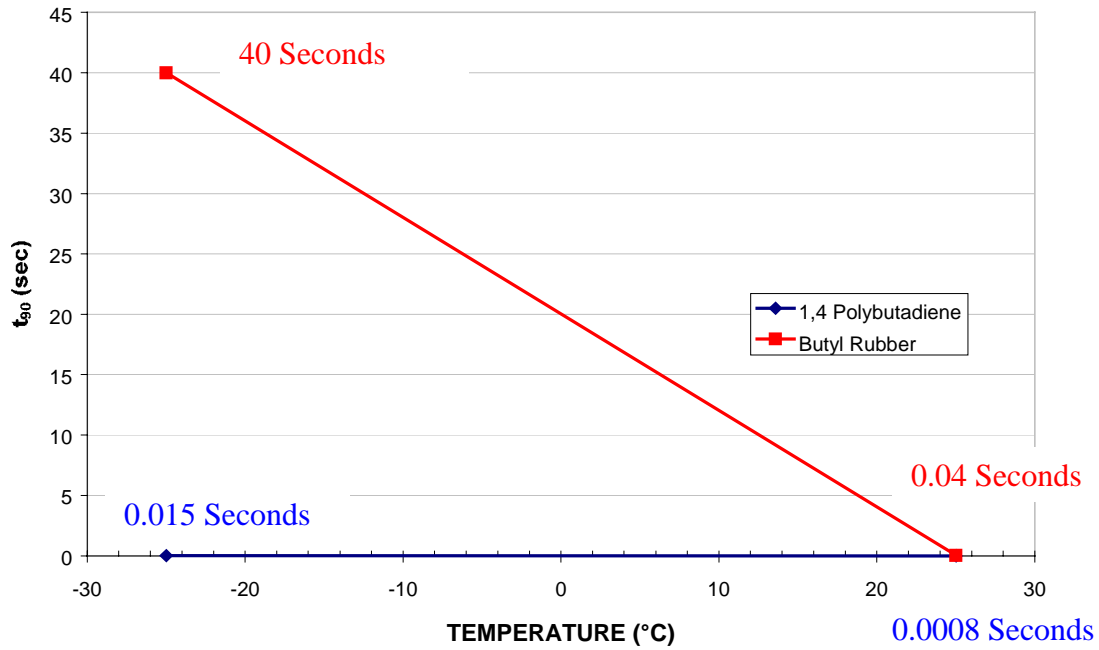


Figure 15, Data from Table 3

SUMMARY

In short, the various methods proposed by ASTM for evaluation of low temperature properties apply only to a limited set of conditions. In fact, the data produced by each of these methods does not even produce a unique value for glass transition temperature. Even if the methods showed agreement, there would be no scientific justification to enable prediction of material behavior in real-world applications. A summary of the data is presented below. All tests mentioned above were performed for the same material, and the calculated glass transition temperature (and brittle point) is plotted.

Tg FOR VF₂ DIPOLYMER ELASTOMER BY VARIOUS ASTM METHODS

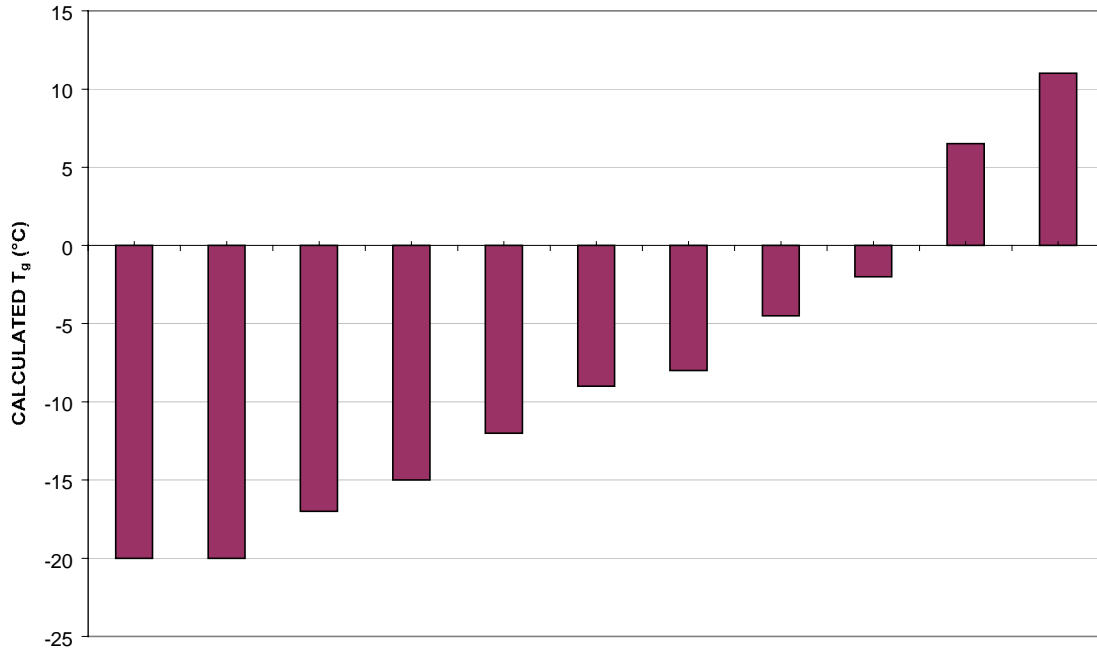


Figure 16, Data from Tables 4 through 8

Estimating elastic recovery rate as proposed by Ferry [4], [5] is a fast and useful method for estimating material performance at low temperature.

Low Temperature Properties for a Common VF₂ Dipolymer Fluoroelastomer

Table 4

TR₁₀	
T _g (°C)	T _g (°F)
-17	1.4

Table 5

T_g via DSC		
Heating Rate (°C/min)	T _g (°C)	T _g (°F)
10	-15	5
5	-12	10.4
1	-9	15.8

Table 6

T_g via DMRT Tan Delta		
Frequency (Hz)	T _g (°C)	T _g (°F)
1	-20	-4
10	6.5	43.7
50	11	51.8

Table 7

T_g via DMRT Loss Modulus		
Frequency (Hz)	T _g (°C)	T _g (°F)
1	-8	17.6
10	-4.5	23.9
50	-2	28.4

Table 8

Brittle Point		
Heating Rate (°C/min)	T _B (°C)	T _g (°F)
1	-20	-4

Table 9

Example from J. Ferry				
	1,4 Polybutadiene		Butyl Rubber	
Temperature, °C	f _{1.1}	t _{0.9}	f _{1.1}	t _{0.9}
-25	13	0.015	0.005	40
25	250	0.0008	5	0.04

SYMBOLS AND UNITS

Symbol	Description	Units (English, SI)
A	Cross sectional area of a specimen	in ² , m ²
A	Amplitude of deflection	in, m
c	Damping Coefficient	lb _f -s/in, N-s/m
f	Cyclic Frequency	cycles/sec
F	Force	lb _f , N
f	Amplitude of force response to a sinusoidal displacement input	lb _f , N
G*	Complex Shear Modulus	PSI, Pa
G'	Storage Shear Modulus	PSI, Pa
G''	Loss Modulus, Viscous Modulus	PSI, Pa
log	Base 10 logarithm	
P _{max}	Maximum measured load in a tensile test	lb _f , N
S _u	Ultimate Strength	PSI, Pa
T _g	Glass transition Temperature	°F, °C
y	Deflection of a spring, damper or system	in, m
δ	Phase angle between sinusoidal output and input curves	rad
π	Ratio of circle circumference to diameter; angular measure corresponding to 180°	Unitless
ω	Angular Frequency	rad/sec

Unit	Description
Pa	SI Unit of Pressure (Pascal)
s or sec	Seconds; unit of time measurement
Hz	Unit of frequency (cycles per second)
N	SI Unit of Force (Newton)
lb _f	English Unit of Force (pound force)
s ⁻¹	Units of shear rate, inverse seconds
Pa-s	Unit of Viscosity (Pascal seconds)
t	Time (seconds)
°	Unit of Angular Measurement (degrees)
°F	Unit of Temperature Measurement (degree Fahrenheit)
°C	Unit of Temperature Measurement (degree Celsius)

REFERENCES

[1] *1998 Annual Book of ASTM Standards*. Sections 9.01 and 9.02. The following standards were referenced:

D1053 Standard Test Methods for Rubber Property- Stiffening at Low Temperatures: Flexible Polymers and Coated Fabrics

D1329 Standard Test Method for Evaluating Rubber Property- Retraction at Lower Temperatures (TR Test)

D1414 Standard Test Methods for Rubber O-Rings

D2137 Rubber Property- Brittleness Point of Flexible Polymers and Coated Fabrics

D5992 Standard Guide for Dynamic Testing of Vulcanized Rubber and Rubber-Like Materials Using Vibratory Methods

[2] "Engineering Design with Natural Rubber." NR Technical Bulletin, 4th Edition. Malaysian Rubber Producers' Research Association (MRPRA), 1974. ISSN 09560-3856.

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[7] Stevens, R.D. and Albert L. Moore. "A New, Unique Viton® Fluoroelastomer With Expanded Fluids Resistance." Paper #32. Rubber Division, American Chemical Society. Cleveland, OH, October 21-24, 1997.

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