REAFFIRMED 12/91

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AEROSPACE
INFORMATION
REPORT

SAE AIR 1387A

Issued 3-76
Revised 9-85

Superseding AIR 1387

Submitted for recognition as an American National Standard

DESIGNING WITH ELASTOMERS FOR USE AT LOW TEMPERATURES

I. INTRODUCTION: To insure success in design of elastomeric parts for use at low temperature, the design engineer must understand the peculiar properties of rubber materials at these temperatures. The purpose of this report is to provide guidance on these properties with their terminology, test methods, and mathematical models applicable to rubber, and to present some practical experience. In this way, it is hoped that mistakes can be avoided, particularly in selection of rubber materials, enabling the design engineer to weigh low temperature materials properties together with the many other factors involved in the design process.

II. SUMMARY: The design for performance of an elastomer at low temperature, whether used as an O-seal, a vibration damping device, a diaphragm, a flexible hose or whatever, requires an understanding of the material transitions of elastomers.

Specific guidance is needed by the designer in selecting candidate elastomers for his prototype designs, to eliminate unsuitable materials and allow early success. Sources of guidance, in addition to this report may include the following:

- o Prior successful experience
- o Information in elastomer specifications
- o Consultation with elastomer specialists
- o Consultation with experienced materials application engineers
- o Specific, pertinent data in handbooks, literature, supplier brochures
- o Perceptive engineering judgement

Many good computer based information services now exist which abstract current literature. For example, a particularly pertinent list of articles on chemistry, low temperature properties and applications of elastomers may be obtained from American Chemical Society and Chemical Abstracts Service.

Each of these sources must be weighed for validity. For example, an elastomer specification containing a statement as to useful temperature range does not provide a complete nor reliable approach by itself. Such temperature ranges are predicated on the intended use and test methods which may or may not be relevant to the requirements of a new design.

In sealing applications, the fluid media being sealed is extremely important. Since the fluid may act as a plasticizer to depress the glass transition range, a seal which may work well in a fluid may not perform well in pneumatic service at the same temperature, that is, there is not the benefit of the fluid media. For seals which must perform at extremely high temperatures as well as low temperatures, the fluid swelling vs. temperature characteristics must be well understood.

Certain dynamic devices such as shock and isolation mounts and diaphragms require particular attention to low temperature transitions and effects of fluid media.

Lastly, performance is best demonstrated by actual service. However, reliable data by this route is often difficult to obtain, and the actual environment may be difficult to define. The designer must rely upon simulated service testing, or test methods intended to simulate the environment. Such testing can be biased or even totally inappropriate if it fails to provide for the possibilities of time-dependent effects. The designer must be aware of the hazards of time dependent visco-elastic effects, swelling, compression set and slow crystallization.

III. TERMINOLOGY:

A. Elastomer - A collective name for a polymer which is rubber-like in properties, a contraction of "elastic" and "polymer." The older terminologies "natural and synthetic rubber," are now not precise and hence may cause some difficulties in technical usage. For example, natural rubber is now manufactured synthetically. However, ASTM D1566 defines elastomer as "a term often used for rubber and polymers that have properties similar to those of rubber", and notes "This term should not be used in standards for rubber".

B. Polymer - A macromolecule formed by the chemical union of combining units called monomers. A polymer is composed of long chains of atoms going to extremely high molecular weight (length or size). Well known polymers are plastics, elastomers, fibers and muscle. Plastics are generally highly branched* and often highly organized into repeating units in three dimensions (crystalline). In contrast, elastomers are usually strongly linear (straight line chains), usually free from or low in crystalline content, and usually deliberately cross-linked between chains (cured) by a

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*Noteable exceptions include polyethylene which is straight chain, and GR-S rubber which is not straight chain.

III. (Continued):

process subsequent to their polymerization to high molecular weight. Elastomers are uniquely capable of high deformation and rapid recovery from such deformation.

IV. TRANSITIONS IN ELASTOMERS: Materials can exist in one of three classical states of matter: solid, liquid or vapor. A transition is a change from one state to another, as for example from ice (solid) to water (liquid), or from water to steam (vapor). Specialized forms of matter occur within the states of matter, such as elastomeric form, vitreous (plastic, glassy or amorphous) form, crystalline form, plus colloids and plasmas. In elastomers, transitions occur at low temperatures which are not unlike transitions among the classical states of matter, causing major changes in mechanical and physical properties. These transitions will occur in very narrow temperature spans. An understanding of the mechanical properties of elastomers and high polymers in general requires an appreciation of the types of transitions that occur in such materials.[1]

The elastomeric form is analogous in many respects to the liquid state, the vitreous form to a supercooled liquid, and the crystalline form to true solid state. The transitions among the elastomeric, vitreous and crystalline forms are of most immediate impact in design at low temperature.

V. GLASS TRANSITION TEMPERATURE (Tg): An abrupt modification in the rate of change in a number of elastomer properties as temperature is lowered occurs at what is called the Glass Transition Temperature, a second-order differential mathematical expression. The older common way of determining this transition was by use of a dilatometer and plotting volume vs temperature.

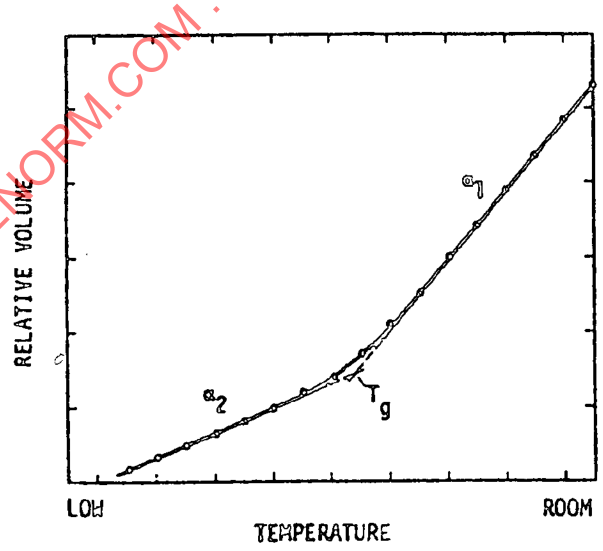

FIGURE 1. Determination of Tg by Volume Dilatometry
(α = Thermal Coefficient of Expansion)

1. It will be noted that the slope of the curve is the thermal coefficient of expansion (α) of the elastomer and that at some low temperature, is smaller by a factor of one-half to one-third the former value.[2] The straight line portions of the curve are projected to an intercept, which is defined as the glass transition, symbol Tg. At temperatures below Tg, the polymer is vitreous glass or rigid brittle plastic,[3] but above Tg, the polymer is elastomeric.

2. The current, quick, inexpensive way to determine Tg directly is by the thermomechanical analysis (TMA) differential thermal analysis (DTA) or differential scanning calorimetry (DSC). The absolute temperature value of Tg will vary somewhat depending on the material property being sampled, the test method used and the cooling rate utilized. However, for a fixed set of test parameters, the Tg of an unimmersed elastomer compound is almost as fixed and reproducible as is the freeze-thaw transition at +32°F (0°C) of water.

3. A major difference between an elastomer and a rigid plastic is that the elastomer has a glass transition below room temperature, while the plastic has a glass transition above room temperature.[1] Being in the elastomeric or plastic state therefore depends at what temperature a polymer happens to be exposed.

   Practical commercial elastomeric compounds may have to fulfill many criteria in addition to being elastomeric at normal room temperatures, but they do fulfill that one criterion. Below their Tg, the elastomers are, no longer in the elastomeric state, but are in the plastic (glass) state. Elastomers in normal commerce can be used far below Tg as plastic seals, e.g. cryogenic seals. Cryogenic seals involve special design concepts and are beyond the scope of this document. This document is limited to seals that utilize the elastomeric properties of the cured elastomeric compounds.

   Similarly, polymers that are in their plastic state (below Tg) at room temperature often can be heated above Tg until they are in, or pass through, an elastomeric state. These changes of state are very useful in forming and processing plastics.

4. Below the glass transition temperature Tg, molecular motion is frozen. At Tg the polymer has expanded to the extent that there is enough free volume available in the material for molecular motion to begin. Molecular segments occasionally have room enough to jump from one position to another with respect to their neighbors at this temperature. Because of the change in molecular mobility in the transition region, the viscosity changes by many decades within a few degrees.[1,2,4,5,6,7]

5. In the precision seal area of technology it is important to accept the implications of Tg on performance at low temperature. Such sealing involves a large number of parameters. Further, very satisfactory sealing is generally obtained in fluid systems considerably below the Tg value measured on the dry seal material. If the Tg is measured on the elastomer compound after it is fully swollen in the working fluid, the Tg is found to be significantly depressed, and the apparent anomaly is resolved. There exist theoretical formulas for computing the depression of Tg by fluid swell if the pour point of the fluid is lower than the Tg of the rubber.[4]

6. Stated conversely, the usual empirical experience with successful elastomer seals at low temperature in hydraulic and fuel systems cannot be projected into pneumatic systems. By example, a fluorocarbon elastomer seal that has shown sealing down to -38°F (-39°C) in jet fuel applications in bench tests had to be rated no lower than +25°F (-4°C) to give reliable performance in specific pneumatic applications.

VI. PLASTICIZERS AND THE GLASS TRANSITION (Tg):

1. Each chemical class of elastomer has its own characteristic Tg value. When, for a particular elastomer this is not as low as the design needs, the compounder may add one of a number of oils or organic compounds to lower the Tg. This has the same effect as cited above where a usage fluid permeates the elastomer. The plasticizer oil permeates the elastomer structure, moving polymer segments apart and allowing molecular motion at lower temperatures.

2. Several types of low temperature plasticizing oils are used so that the solubility limit of each plasticizer in the polymer is not exceeded. Some authorities believe that the reduced solubility at low temperatures can cause troubles even if there is no solubility problem at room temperature.[8]

3. There are also other recognized problems with the use of low temperature plasticized rubber compounds. The plasticizer can be extracted by the system fluid, with several results. The extracted plasticizer is a contaminant in the fluid system. The extracted seal can have a net shrinkage. (In tests by one aircraft manufacturer, MS29512 NBR O-seals shrank up to 5% below their virgin volume in the early weeks of water immersion.) The Tg of fuel extracted seals when dried out can be much higher than the specification value. The true working Tg of a seal is its Tg value after complete equilibrium with its usage fluid environment. This has generally not been measured in the past but must be measured in all future systems tests.

As a means to combat the leakage that occurs when an aircraft has been in a hangar for an extended period (60 days or more) and is then refueled, the USAF has developed a low-shrink nitrile O-seal material, which takes advantage of the fuel acting as a plasticizer. The specification includes a test for fuel soak with dry-out in which O-seals are soaked in reference fuels for 70 hours at 25°C and then allowed to dry out for 48 hours at 25°C, for three cycles. The volume change is specified at not more than 1% loss. This compares to an 8% loss in volume for a qualified MIL-P-5315 nitrile compound.

4. Where test hardware is placed into low temperature test before the compound comes into equilibrium with usage fluid, the test results may not be representative of actual long term hardware performance. Conversely, repaired assemblies placed immediately back into low temperature service may not perform as well as before repair until the rubber has had time to come to equilibrium with usage fluid.

5. Low temperature plasticizers can also cause fungus growth problems. Only selected low-temperature plasticizers are non-nutrient to fungus growth.

VII. VISCOELASTIC EFFECT:

1. Elastomers do not recover total mobility when warmed to just above the Tg value. The elastomers become more elastic as the temperature is raised above Tg, and conversely become progressively stiffer and lose elastic recovery power as Tg is approached during lowering of temperatures. These effects are called the viscoelastic effects, i.e. they are a combination of viscosity and elasticity in changing ratios. How elastic a rubber compound has to be to function properly at low temperatures has no fixed value but, rather, depends on what the specific application demands of the rubber part. Elastomer specifications which give fixed low temperature performance limits may be misleading in this regard. A pressure switch may become erratic when its rubber diaphragm doubles in modulus, whereas a static packing may still function with the elastomer compound a thousand times as stiff as at room temperature. Most elastomer specifications contain, at best, only some go/no-go low-temperature test value, e.g. Brittle Point or TR-10 temperature. In order to design many components to work at low temperature, the designer should have complete property versus temperature curves, to know in what part of the curve he is working and how properties are changing over the intended service temperature range. In fact, recent tests on a limited number of generic types of elastomers indicate the interrelationships among various elastomer properties and test methods at low temperature may not be as direct as would be assumed from simple molecular motion theory. (See Fig. 2, 3 and 4.)

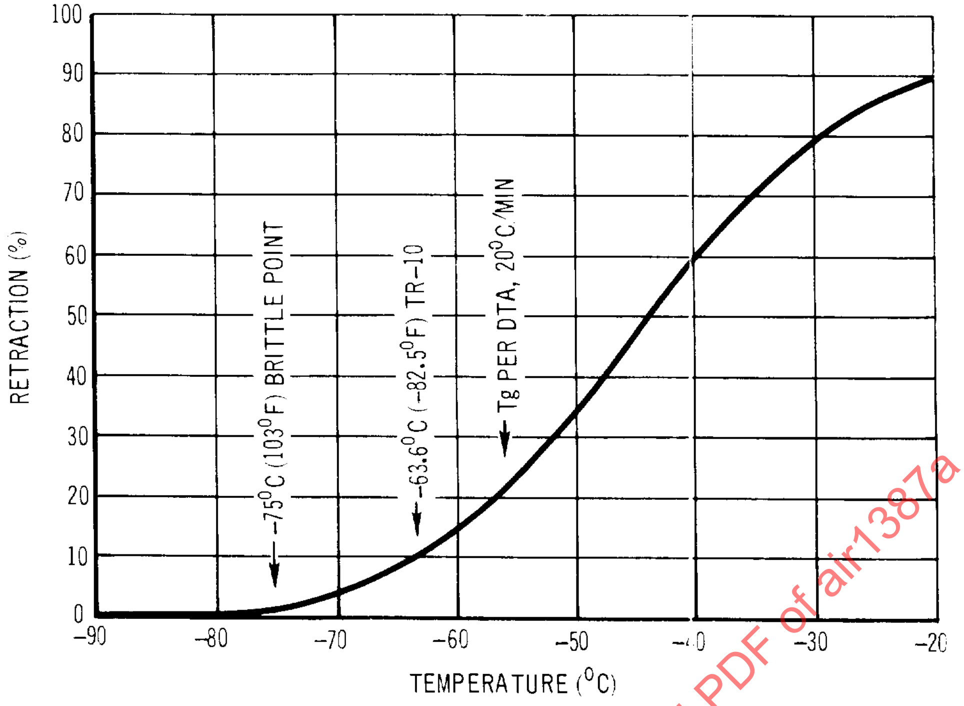

FIGURE 2 Relationship Between Glass Transition (T_g), TR-10 and Brittlepoint for a Specific Ethylene Propylene Rubber Compound, as Shown on a Complete Temperature Retraction Curve

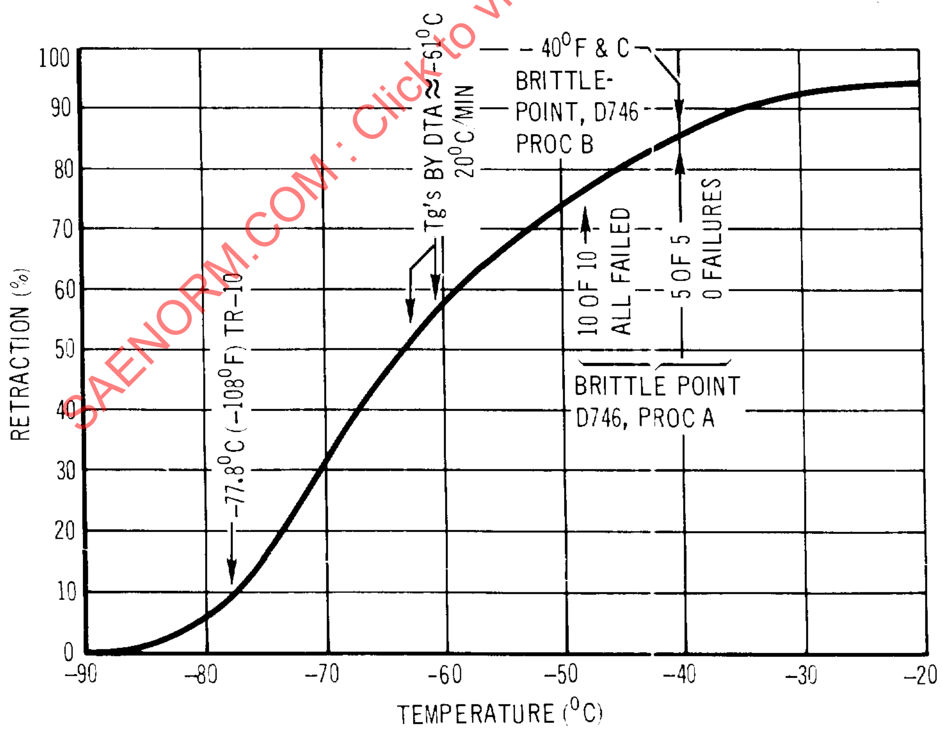

FIGURE 3 Relationship Between Glass Transition (Tg), TR-10 and Variously Defined Brittlepoints for One Chlorobutyl Rubber Compound, as Shown on a Complete Temperature Retraction Curve

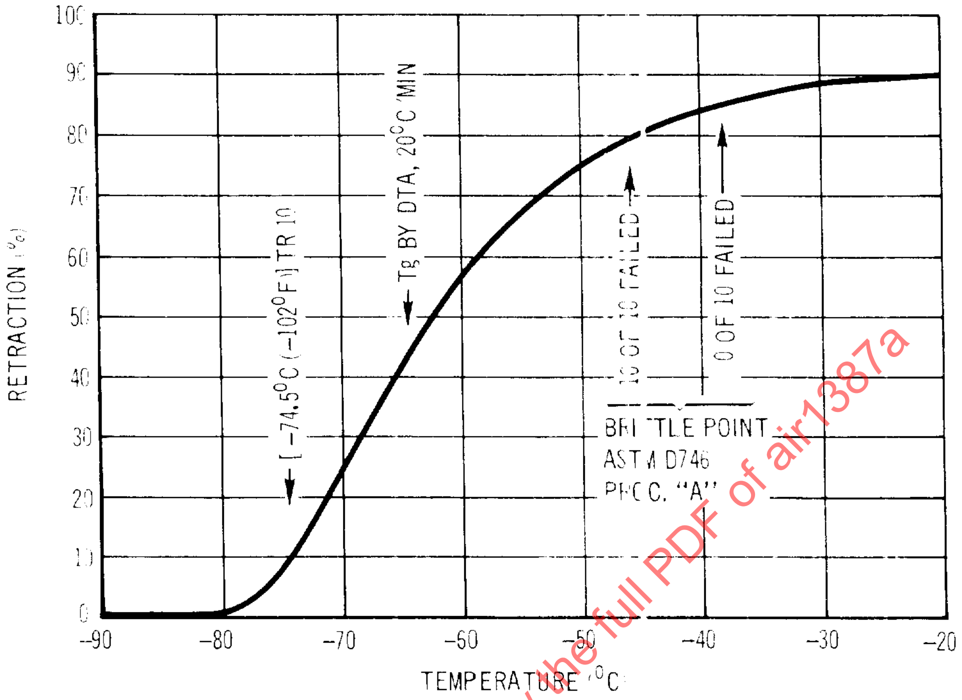

FIGURE 4 Relationship Between Glass Transition (T_g), TR-10 and Variously Defined Brittlepoints on a Second Chlorobutyl Compound, as Shown on a Complete Temperature Retraction Curve

Note for the ethylene propylene compound that the Brittle Point occurs at very low TR curve values, next the TR-10 and then Tg by fast DTA.

On the chlorobutyl compounds, the order from low temperature to high is TR-10, Tg and Brittle Point.

VIII. CRYSTALLIZATION TRANSITIONS: These transitions are capable of being expressed mathematically in first order differential functions, as contrasted to glass transition, a second order function. The coefficient of thermal expansion vs. temperature curve obtained by dilatometry can be used to find and define the effects of crystallization of an elastomer as shown in Figure 5.

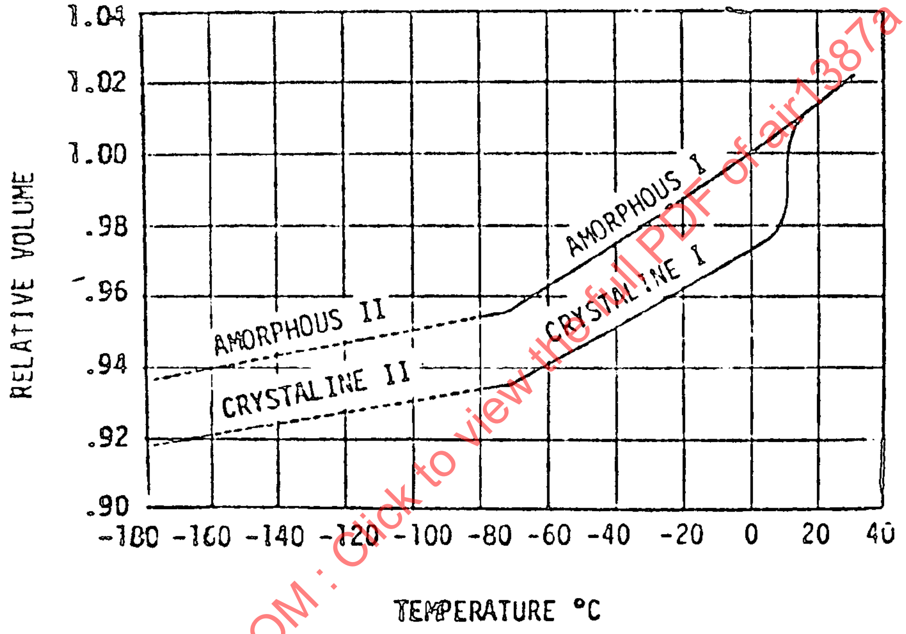

FIGURE 5. Determination of Crystallization by Volume Dilatometry Shown also are the effects of supercooling (amorphous states) as compared to equilibrated crystalline states.

It will be noted that crystallization involves a significant volume decrease (first order differential) under isothermal (constant temperature) conditions. Because designers may not be aware of crystallization phenomena, hardware qualification tests at low temperature are often unintentionally run in too short a time span to allow this phenomenon to develop. When it develops fully, for example in natural outdoor winter environments, catastrophic failures can occur. Not only can the time of test be too short, but also temperatures that are optimum for crystallization may be unintentionally bypassed when test hardware is quenched from room temperature down to say -65°F (-54°C). This can supercool the elastomer which remains an amorphous liquid rather than crystallizing.

The mechanical property effects of crystallization are a total loss of elastic recovery capability, significant stiffening, slight shrinkage, and hence over 100% compression set. Contrary to expectations, crystallized elastomers do not become brittle (silicones excepted). Unlike the crystalline plastics, the degree of crystallization remains low (32% or less) so that the crystallites are embedded in an amorphous, flexible matrix. This provides freedom from brittleness. An excellent comparison of glass transition and crystallization effects is given in Table I of ASTM D832[8].

Fortunately, the vast majority of elastomers do not crystallize. The copolymers and terpolymers which contain significant quantities (over 15%) of a second monomer would not be expected to crystallize since the resulting randomness does not allow a repeating structure crystalline lattice to grow.

There is an optimum temperature for rate of crystallization for each crystallizable elastomer, and a considerable range of temperatures above and below this optimum temperature where the tendency to crystallize remains strong, as shown in Fig. 6.

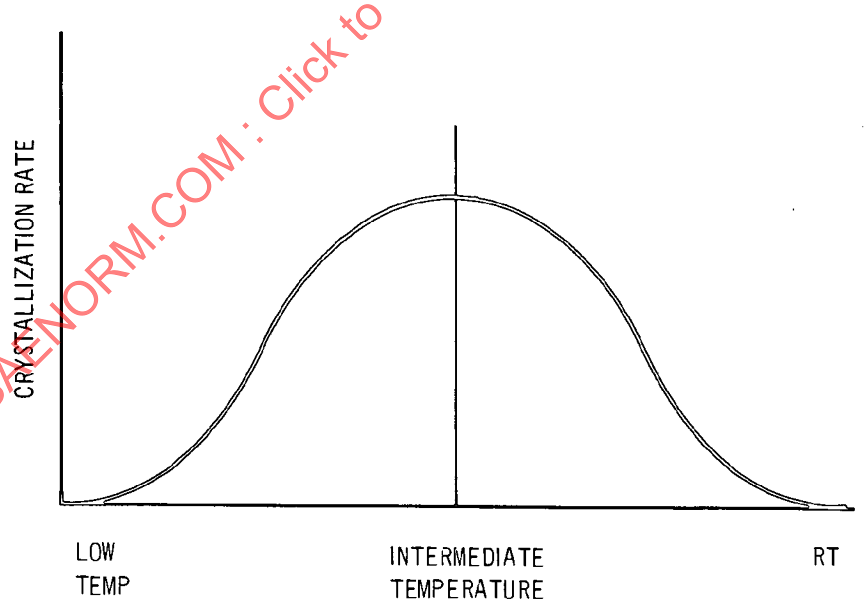

FIGURE 6. Optimum Temperature and Range of Crystallization

This crystallizable range is undesirable from a design standpoint, and it should be avoided. A better approach is not to use elastomers which crystallize strongly in intermediate and low temperature applications if they are to be used at these temperatures.

A list of elastomers which are strongly crystallizable, together with the optimum crystallization temperature and an estimate of the time for high relative orders of crystallization is presented in Table I:[8,9]

TABLE I - CRYSTALLIZABLE ELASTOMERS

Crystallizable Elastomer	Optimum Crystallization Temperature	Approximate time for strong Crystallization of unstretched elastomer at optimum crystallization temperature**
Neoprene*	+14°F (-10°C)	2 weeks
Polyurethane	+14°F (-10°C)	Unknown
Natural & Synthetic Cispolyisoprene Rubber	-13°F (-25°C)	1 Month
Low Styrene SBR	-40°F (-40°C)	Very Short
Polybutadiene	-40°F (-40°C)	Very Short
Butyl	-40°F (-40°C)	Requires Stretch
Dimethyl Silicone[10,11]	-67°F (-55°C)	Very Short
Methyl Phenyl Silicone[10,11]	-76 to -120°F*** (-60 to -84.4°C)	Very Short

* Various neoprene homopolymers and copolymers vary significantly in the degree and rate of crystallization.

** Stretching or any deformation greatly speeds crystallization.

*** Estimated

The fast and economical method today for finding crystallization is the Differential Thermal Analysis (DTA) test. However, it may be inaccurate on elastomers having long crystallization times.[3,7] The technically best method is to run temperature-retraction (ASTM D1329)[12] with the sample stretched the maximum possible amount. For the doubters as to the reality of crystallization, conventional x-ray diffraction can be used.

IX. PRACTICAL LOW TEMPERATURE TEST METHODS FOR ELASTOMERS:

1. Until recently, Tg could not be directly determined quickly and economically. Even today, this capability may not exist among the smaller rubber fabricators due to the high cost and sophistication of the test equipment. Thus, many older and "practical" tests have evolved to measure the effects of low temperature on selected mechanical properties of rubber. These tests have long been world standards published by the American Society for Testing and Materials (ASTM). The rubber fabricator may possibly have one or more of these test instruments. Various specification-publishing agencies favor now one, now another, of these test methods. They all show the gradual change of some chosen property, or a go/no-go limit, as temperature is lowered through Tg. As such, any one (or combination of tests) is of great value to the designer in visualizing the changes taking place, even if an exact interrelationship is not yet empirically and statistically tested out among the various practical tests, nor with Tg.

2. As an aid to design, each common ASTM low-temperature test method is briefly described as to property measured and technique used:

a. Brittleness Temperature, ASTM D2137[13], Method A (or ASTM D746[14], Procedure B):

This test established a go/no-go temperature below which the material becomes brittle under a fixed impact. This is probably the most generally specified test method, but not necessarily the best.

Specifically, this test method determines the lowest temperature at which an impact of a specific geometry striker at 6.5 ± 0.5 ft/sec does no damage to any of five identical cantilevered samples. If the using design will allow impacts at a higher impact rate or with a sharper striker, the design may still fail by brittle fracture at some higher temperature than indicated by this test. The temperature at which brittle fracture occurs might possibly be raised to room temperature or above if explosive impact or shock wave is involved. Conversely, the material may possibly not show brittle fracture at temperatures considerably below the ASTM D2137 brittleness temperature if the rate of impact is lower.

Some inference of the change of Brittle Point due to change of impact speed might possibly be inferred from published data on the effect of speed on Tg and modulus values. One author[2] states that "Tg changes only about three degrees with a change in time scale of a factor of 10." Another text states that Tg's determined by slow dilatometry must be raised by about 27°F (15°C) for dynamic tests run at 10 cycles per minute.[6] This same text, when dealing with stiffness, states "a change of a factor of 10 rate being equivalent to 6-8°C change in temperature."

As noted above for Tg, Brittle Points on elastomer compounds for use in fluid media must be run on samples at equilibrium swell with the intended usage fluid. Further, if the compound is low temperature plasticized, the plasticizer must also have been leached out to a final condition.

For those exceptional designs and cases where the design usage will occur before equilibrium swell will occur (e.g., one-shot missile fuel systems equipped with upstream valves or burst diaphragms), the test samples should only be preconditioned to the same extent as they would see in service. Where repair parts will see both initial and equilibrium swell conditions, brittleness temperature tests may have to be run on samples at both extremes of conditioning to insure total service reliability.

b. Temperature Retraction, ASTM D1329[12]:

This test measures the amount of elastic recovery from deformation of an elastomer compound as a function of temperature. The characteristic "snap back" of an elastomer at room temperature becomes "crawl back" at low temperatures. An elastomer sample is stretched and then cooled well below Tg to a rigid frozen plastic column which does not recover at all upon release. The released sample is heated at a fixed rate (1°C or 1°F per minute) and the percent retraction versus temperature curve plotted (See Figs. 2, 3 and 4). For elastomers which do not crystallize (see following section), the resulting curves are sigmoidal, or "S" shaped. For elastomers in which crystallization was induced by high elongation and intermediate cool temperatures, there will be a decided sag in the curve, Fig. 7. This sag will indicate the range of temperatures over which the crystallites were melting out, and the amount of departure from the sigmoidal curve is an indication of the degree of crystallinity.

The complete TR curve can be used directly by the designer to note the degradation of elastomeric recovery with dropping temperature. This test is generally run as a go/no-go test using the temperature where ten percent retraction occurs (TR-10 temperature) for a specimen at low elongation (50%). This go/no-go test is in general usage in military O-seal specifications in the Aerospace Material Specification (AMS) from the Society of Automotive Engineers, and in data sheets from the precision O-seal industry. The designer is well advised to become proficient in using TR-10 data in his O-seal designs. As in the case for Tg and Brittle Point, the TR-10 at equilibrium swell conditions in the system fluid should also be run for closer correlation with system performance.

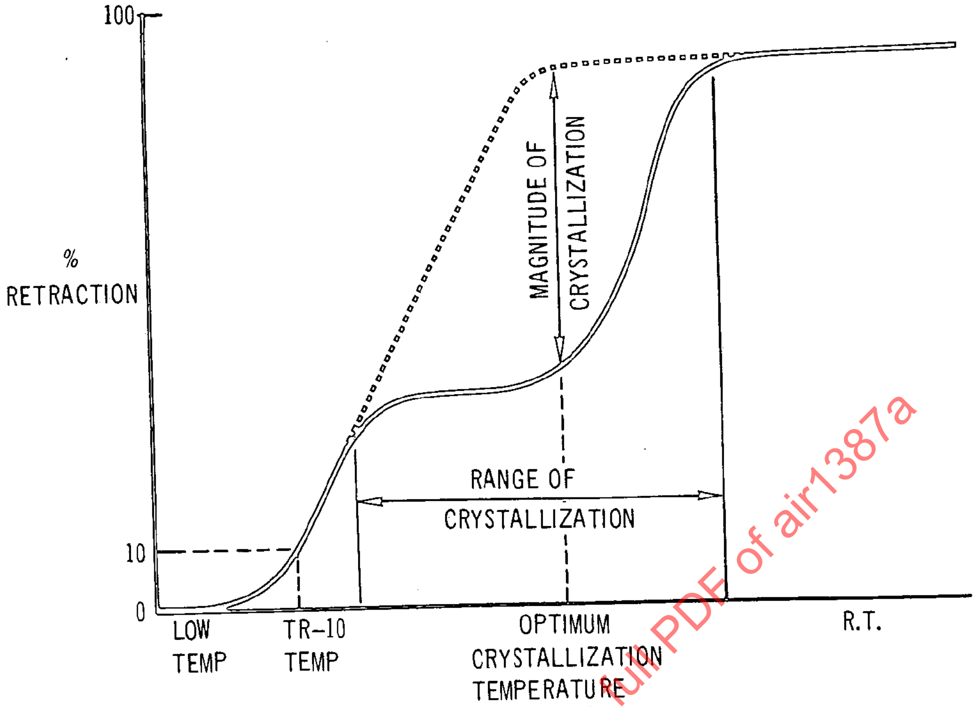

FIGURE 7 Temperature Retraction Curve for a Very Strongly Crystallizable Elastomer

c. Young's Modulus In Flexure, ASTM D797[9]:

The stiffness of a beam of rubber is measured at low temperature in the Young's Modulus test. By arbitrary definition, the lower usage temperature of the elastomer compound is sometimes said to be where Young's Modulus equals 10,000 psi (68.9 MPA). Young's Modulus is one of three low temperature tests invoked in Federal Specification ZZ-R-765 covering silicone rubber, being used as a go/no-go test at specified temperatures and stated maximum modulus values. ASTM D797 makes provision for measuring crystallization and other time dependent effects; however, the specified 72 hours cold soak is not nearly long enough for many elastomers to reach ultimate crystallization, even at the given optimum crystallization temperatures. (See Table I for an indication of times that should be used.)

d. Torsion Wire (Gehman) Stiffness, ASTM D1053[15]:

The torsional stiffness of a rubber specimen is measured as a function of temperature. One end of an assembly consisting of an elastomer sample and a calibrated metal wire is rotated 180° (3.14 rad) at succeeding low temperatures to measure the relative stiffness of the elastomer and the wire. At room temperature, the rubber does most of