AEROSPACE INFORMATION REPORT

AIR1387™ REV. D

Issued 1976-03
Revised 2016-01

Superseding AIR1387C

(R) Designing with Elastomers for use at Low Temperatures, Near or Below Glass Transition

RATIONALE

AIR1387C is now due for review. The template has been revised to meet the document standards of SAE. The addition of glass transition (Tg) and temperature retraction tables, new low temperature hydrocarbon and fluorocarbon elastomers, and new test methods to characterize low temperature properties of elastomers has been made to the last revision.

1. SCOPE

To ensure 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.

There are no static applications of rubber. The Gaussian theory of rubber elasticity demonstrates that the elastic characteristic of rubber is due to approximately 15% internal energy and the balance, 85%, is entropy change. In other words, when an elastomer is deformed, the elastomer chain network is forced to rearrange its configuration thereby storing energy through entropy change. Thermodynamically, this means that rubber elasticity is time and temperature dependent (Reference 25).

The purpose of this report is to provide guidance on low temperature properties of rubber with the 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 material properties together with the many other factors involved in the design process.

2. REFERENCES

1. Nielsen, Lawrence E., Mechanical Properties of Polymers, Reinhold Publishing Corporation, New York, 1962.

2. Ferry, John D., Viscoelastic Properties of Polymers, Third Edition, John Wiley and Sons, Inc., New York, 1983.

3. Morton, Maurice, Rubber Technology, Second Edition, Van Nostrand Reinhold Co., New York, 1973.

4. Mears, Patrick, Polymers, Structure and Bulk Properties, Van Nostrand Reinhold Co., New York, 1965.

5. Tobolsky, Arthur V. and Mark, Herman F., Polymer Science and Materials, John Wiley and Sons, New York, 1971.

TO PLACE A DOCUMENT ORDER: **Tel: 877-606-7323 (inside USA and Canada)**
Tel: +1 724-776-4970 (outside USA)
Fax: 724-776-0790
Email: CustomerService@sae.org
SAE WEB ADDRESS: **http://www.sae.org**

SAE values your input. To provide feedback on this Technical Report, please visit
http://www.sae.org/technical/standards/AIR1387D

6. Allen, P.W., Lindley, P.B., and Payne, A.R., Use of Rubber in Engineering, Maclaren and Sons Ltd., London, 1967.

7. Bikales, Norbert M., Characterization of Polymers, Wiley-Interscience, New York, 1971.

8. ASTM D832, Rubber Conditioning for Low-Temperature Testing.

9. ASTM D797, Rubber Property - Young's Modulus at Normal and Subnormal Temperatures.

10. Ohlberg, Stanley M., Alexander, Leroy E., and Warrick, E.L., "Crystallinity and Orientation in Silicone Rubber, I-X-ray Studies," Journal of Polymer Science, Volume XXVII, pp. 1-17 (1958).

11. Warrick, E.L., "Crystallinity and Orientation in Silicone Rubber, II - Physical Measurements," Journal of Polymer Science, Interscience Publishers, Inc., Volume XXVII, pp. 19-38 (1959).

12. ASTM D1329, Evaluating Rubber Property - Retraction at Low Temperature (TR Test).

13. ASTM D2137, Rubber Property - Brittleness Point of Flexible Polymers and Coated Fabrics.

14. ASTM D746, Brittleness Temperature of Plastics and Elastomers by Impact.

15. ASTM D1053, Rubber Property - Stiffening at Low Temperatures: Flexible Polymers and Coated Fabrics.

16. ASTM D1043, Stiffness Properties of Plastics as a Function of Temperature by Means of a Torsion Test.

17. ASTM D1229, Rubber Property - Compression Set at Low Temperatures.

18. Smalley, A.J., Darlow, M.S., and Mehta, R.K., "Stiffness and Damping of Elastomeric O-Ring Bearing Mounts," NASA CR-135328.

19. Tanabe, T.M. and Yoshioka, E.N. (Lockheed Missiles & Space Co.) and Anisman, A.M. (JEDTCO Corp.), "Composite Silicone Rubber Seal for the Space Telescope Program," design and evaluation of seal materials for use down to -170 °F, ACS Rubber Div., October 5-7, 1984.

20. Rogers, W.P. (Chairman), "The Report of the Presidential Commission on the Space Shuttle Challenger Accident," U.S. Government Printing Office, Washington, DC, 1986.

21. Bower, Mark V., "Viscoelastic Properties of Elastomeric Materials for O-ring Applications," SAMPE Quarterly, pp. 24-31, July 1989. NASA Contract NGT 01-002-099, in support of Challenger investigation.

22. Quoted from New Yorker Magazine, November 10, 1986.

23. ASTM E756, Measuring Vibration-Damping Properties of Materials.

24. Madigosky, W.M., "Dynamic Mechanical Materials Characterization and Analysis Using a Dynamic Mechanical Thermal Analyzer," Naval Surface Warfare Center Report NAVSWC TR 91-90, January 1991.

25. "Engineering With Rubber - How to Design Rubber Components," A.N. Gent, Ed., Oxford University Press, New York, NY, 1992.

26. Laird, J.L. and Liolios, "TA (Thermal Analysis) Techniques for the Rubber Laboratory," Rubber World, January 1990.

27. Ratliff, O.D., "The Use of a Differential Scanning Calorimeter to Determine the State of Cure of Rubber," ACS Rubber Division, April 8-11, 1986, Paper No. 100.

28. Babbit, R.O., "Rubber Handbook," R.T. Vanderbilt, Norwalk, CT, 1978.

29. Bhowmick, A.K. and Stephens, H.L., "Handbook of Elastomers - New Developments and Technology," Marcel Dekker, Inc., New York and Basel, 1988.

30. AMS7258, Rings, Sealing, Butadiene-Acrylonitrile (NBR) Rubber, Fuel Resistant, Low Shrinkage, 65-75.

31. RMA O-ring Technical Information Bulletin OR-8, "O-Ring Low Temperature Performance - Comparison of Test Methods," Approved 1977. Recommends ASTM D1329 for evaluating O-ring material at low temperatures.

32. ASTM D3418, Transition Temperatures and Enthalpies of Fusion and Crystallization of Polymers by Differential Scanning Calorimetry.

33. ASTM D7426, Assignment of the DSC Procedure for Determining Tg of a Polymer or an Elastomeric Compound.

34. ASTM E1545, Assignment of the Glass Transition Temperature by Thermomechanical Analysis.

35. ASTM E1640, Assignment of the Glass Transition Temperature by Dynamic Mechanical Analysis.

36. ASTM D1418, Rubber and Rubber Latices - Nomenclature.

37. Stevens, R., Thomas, E., Brown, J., and Revolta, W., "Low Temperature Sealing Capabilities of Fluoroelastomers," SAE Technical Paper 900194, 1990, doi:10.4271/900194.

38. AMS7254, Perfluoroether Elastomer.

39. AMS7287, Fluorocarbon Elastomer (FKM) High Temperature / HTS Oil Resistant / Fuel Resistant Low Compression Set / 70 to 80 Hardness, Low Temperature Tg -22 °F (-30 °C) For Seals in Oil / Fuel / Specific Hydraulic Systems.

40. AMS7379, Rubber: Fluorocarbon Elastomer (FKM) 70 to 80 Hardness, Low Temperature Sealing Tg -40 °F (-40 °C) for Elastomeric Seals in Aircraft Engine Oil, Fuel and Hydraulics Systems.

41. AMS3208, Chloroprene (CR) Rubber Weather Resistant 45 - 55.

42. AMS3209, Chloroprene (CR) Rubber Weather Resistant 65 - 75.

43. AMS3238, Butyl (IIR) Rubber Phosphate Ester Resistant 65 - 75.

44. AMS7270, Rings, Sealings, Butadiene-Acrylonitrile (NBR) Rubber Fuel Resistant 65 - 75 .

45. AMS7255, Rings, Sealing, Tetrafluoroethylene/Propylene Rubber (FEPM) Hydraulic Fluid and Synthetic Oil Resistant 70 to 80.

46. AMS3216, Fluorocarbon (FKM) Rubber High-Temperature - Fluid Resistant Low Compression Set 70 to 80.

47. AMS3218, Fluorocarbon (FKM) Rubber High-Temperature-Fluid Resistant Low Compression Set 85 to 95.

48. AMS7259, Rubber: Fluorocarbon (FKM) High Temperature/Fluid Resistant Low Compression Set/ 85 to 95 Hardness for Seals in Fuel Systems and Specific Engine Oil Systems.

49. AMS7276, Rubber: Fluorocarbon (FKM) High-Temperature-Fluid Resistant Low Compression Set for Seals in Fuel Systems and Specific Engine Oil Systems.

50. AMS7257, Perfluorocarbon (FFKM) Engine Oil, Fuel and Hydraulic Fluid Resistant 70 to 80 Hardness for High Temperature Seals in Engine Oil Systems, Fuel Systems and Hydraulic Systems.

51. AMS3337, Silicone (PVMQ) Rubber Extreme-Low-Temperature Resistant 65 - 75.

52. AMS3338, Silicone (PVMQ) Rubber Extreme-Low-Temperature Resistant 75 - 85.

53. AMS3304, Silicone, Rubber General Purpose 70 Durometer.

54. AMS-P-83461, Packing, Preformed, Petroleum Hydraulic Fluid Resistant, Improved Performance at 275°F (135°C).

55. AMS-R-83485, Rubber, Fluorocarbon Elastomer, Improved Performance at Low Temperatures.

56. MIL-DTL-25988C, Rubber, Fluorosilicone Elastomer, Oil-and-Fuel Resistant, Sheets, Strips, Molded Parts, and Extruded Shapes (Inactive for new design).

57. NAS1613, Packing, Preformed, Ethylene Propylene Rubber.

3. SUMMARY

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

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

a. Prior successful experience

b. Information in elastomer specifications

c. Consultation with elastomer specialists

d. Consultation with experienced materials application engineers

e. Specific, pertinent data in rubber reference handbooks, current literature, supplier brochures, material test data, and application test data

f. Perceptive engineering judgment

CAUTION: Specifications, as a necessary part of the procurement process, provide production property limits. These may not fairly represent typical or actual properties of a material, especially with regard to environmental resistance, creep, or other time dependent behavior. Test methods used in elastomer specifications are often low cost methods to ensure lot to lot consistency, and may not define all criteria needed for design.

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. When the seal is no longer in contact with the fluid, its characteristics may change. For seals which must perform at extremely high temperatures as well as low temperatures, the fluid swelling versus 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. It should also be recognized that low temperature requirements for static applications are more forgiving than that for dynamic applications.

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 viscoelastic effects, swelling, compression set, and slow crystallization.

4. TERMINOLOGY

4.1 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 not precise and hence may cause some difficulties in technical usage.

4.2 POLYMER

A macromolecule formed by the chemical union of combining units is 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. 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 process subsequent to their polymerization to high molecular weight. Elastomers are uniquely capable of high deformation and rapid recovery from such deformation.

5. 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 can occur in 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 (Reference 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.

6. GLASS TRANSITION TEMPERATURE (Tg) (SEE FIGURES 1 AND 2)

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 versus temperature (Figure 1).

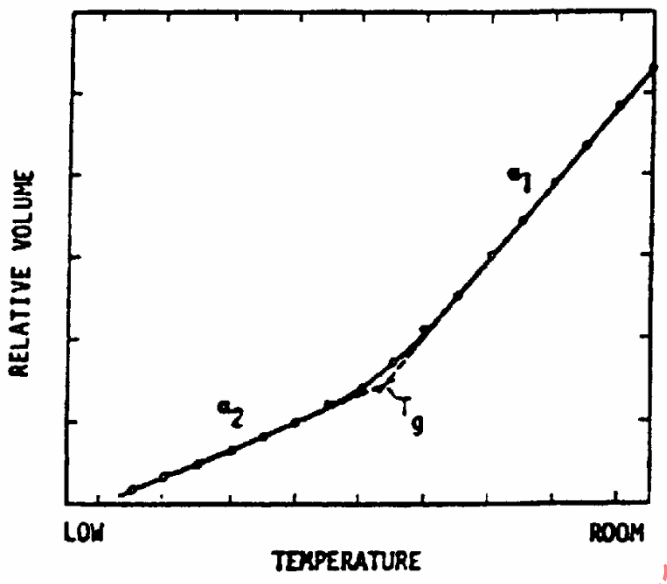

Figure 1 - Determination of Tg by volume dilatometry
(α = thermal coefficient of expansion)

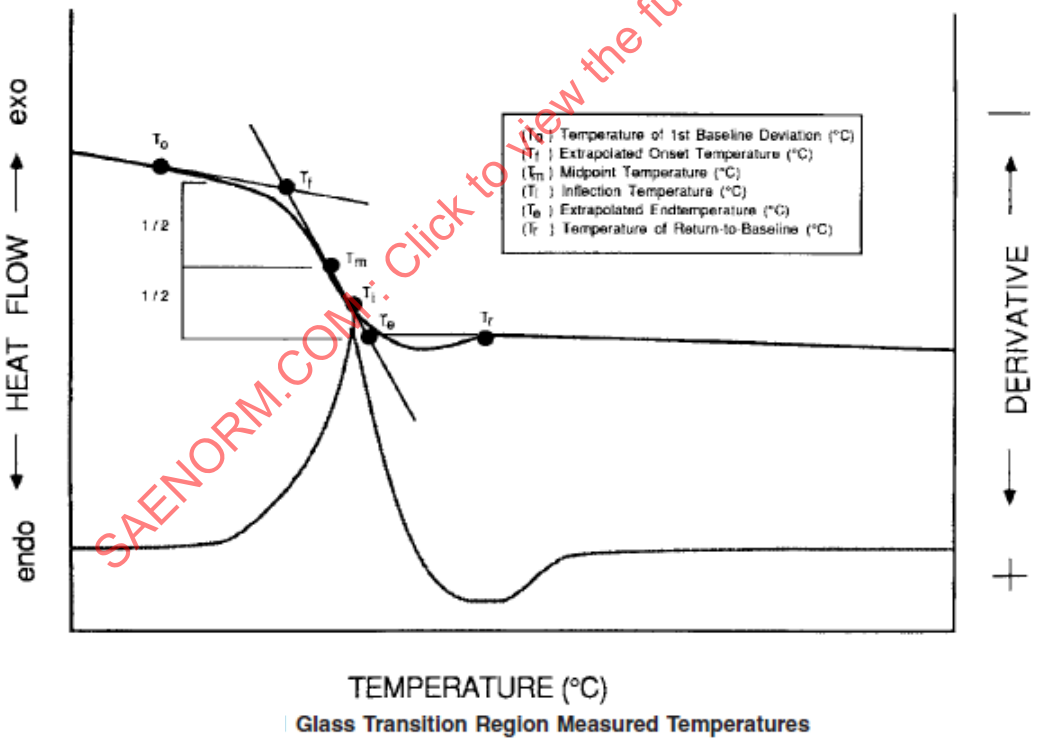

Figure 2 - Determination of Tg by DSC

Table 1 - Typical glass transition temperature ranges

Elastomer Class Designation (ASTM D1418)	AMS	Tg Range (°F)	Tg Range (°C)	Tg Midpoint (°F)	Tg Midpoint (°C)
CR	3208 / 3209	no data	no data	no data	no data
Butyl	3238	-74 to -56	-59 to -49	-74	-59
NBR (low ACN)	AMS-P-83461	-80 to -65	-62 to -54	-72	-58
NBR (med ACN)	7270	-25 to -16	-32 to -27	-22	-30
HNBR	none	-18 to -13	-28 to -25	-17	-27
EPDM	NAS-1613 (Rev. 6)	-76 to -65	-60 to -54	-72	-58
FEPM	7255	+34 to +43	+1 to +6	+37	+3
FKM (Type 1)	3216 / 3218 / 7259 / 7276	+1 to +9	-17 to -13	+1	-16
FKM (Type 3)	AMS-R-83485 / 7287	-20 to -25	-32 to -29	-22	-30
FKM (Type 3)	7379	-38 to -44	-42 to -39	-40	-40
FFKM	7257	+25 to +34	-4 to +5	+34	-2
PVMQ	3337 / 3338		-114 to -106	-168	-111
VMQ	3304	-56 to -47	-49 to -44	-51	-46
FVMQ	MIL-DTL-25988 (type 1 class 1)	-96 to -80	-71 to -62	-89	-67
Perfluoroether	7254	-89 to -81	-67 to -63	-85	-65

NOTE: Tg per ASTM D3418 or D7426 (midpoint data).

a. 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 (Reference 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 (Reference 3), but above Tg, the polymer is elastomeric.

b. The current, quick, inexpensive way to determine Tg directly is by the thermomechanical analysis (TMA), differential thermal analysis (DTA), or differential scanning calorimetry (DSC - Figure 2) (References 26, 27, 32, 33, 34, 35). 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. Note that the elastomeric to glass state transition is a physical change and can be reversed by increasing temperature. Table 1 provides typical Tg values and ranges for some of the significant elastomers used in aerospace sealing applications.

c. 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 (Reference 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.

d. 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 (References 1, 2, 4, 5, 6, 7).

e. 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 (Reference 4).

f. 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.

7. PLASTICIZERS AND THE GLASS TRANSITION (Tg)

a. 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.

b. 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 (Reference 8).

c. 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, MS 29512 NBR O-rings 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 AMS7258 (Reference 30), a low-shrink nitrile O-ring 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-rings are soaked in reference fuels for 70 hours at 77 °F (25 °C) and then allowed to dry out for 48 hours at 77 °F (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 AMS-P-5315 nitrile compound.

d. 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.

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

8. VISCOELASTIC EFFECT

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 elastomeric properties and test methods at low temperature may not be as direct as would be assumed from simple molecular motion theory. (See Figures 3, 4, and 5.)

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.

9. 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 versus temperature curve obtained by dilatometry can be used to find and define the effects of crystallization of an elastomer as shown in Figure 6.

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.

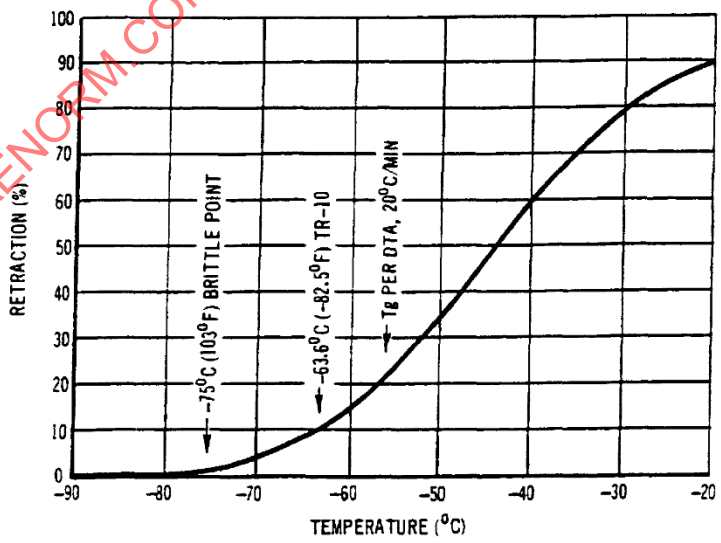

Figure 3 - Relationship between glass transition (Tg), TR-10 and brittle point for a specific ethylene propylene rubber compound, as shown on a complete temperature retraction curve

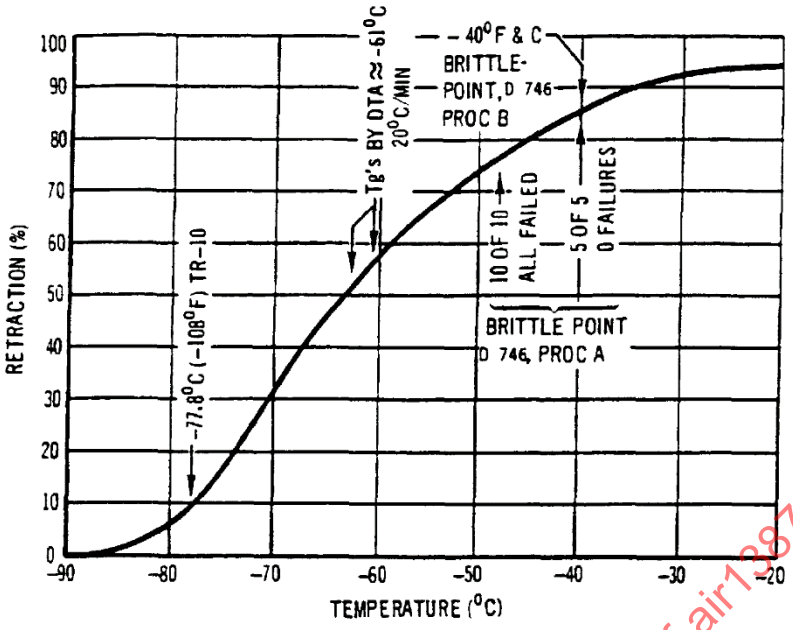

Figure 4 - Relationship between glass transition (Tg), TR-10 and variously defined brittle points for one chlorobutyl rubber compound, as shown on a complete temperature retraction curve

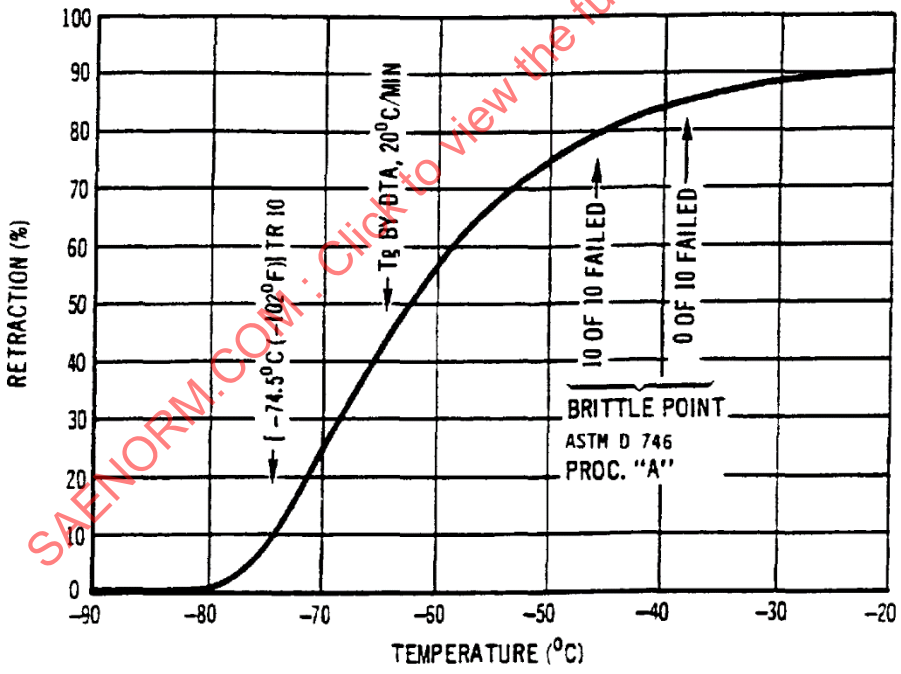

Figure 5 - Relationship between glass transition (Tg), TR-10 and variously defined brittle points on a second chlorobutyl compound, as shown on a complete temperature retraction curve

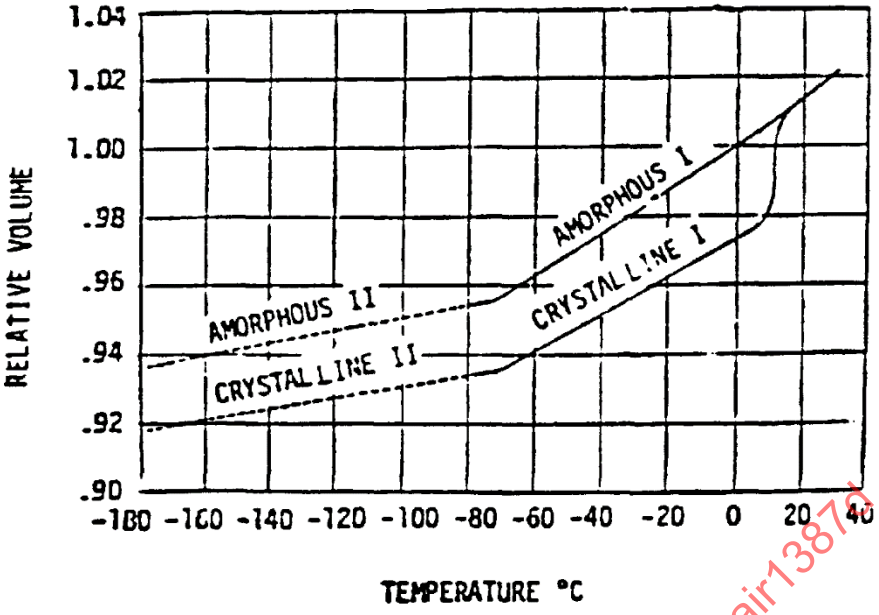

Figure 6 - Determination of crystallization by volume dilatometry shown also are the effects of supercooling (amorphous states) as compared to equilibrated crystalline states.

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 1 of ASTM D832 (Reference 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 Figure 7.

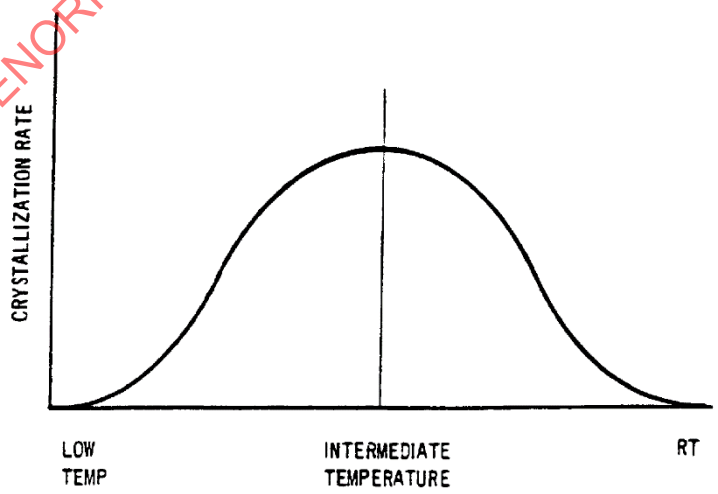

Figure 7 - Optimum temperature and range of crystallization

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 2 (References 8 and 9):

Table 2 - Crystallizable elastomers

Crystallizable Elastomer	Optimum Crystallization Temperature	Approximate Time for Strong Crystallization of Unstretched Elastomer at Optimum Crystallization Temperature[2]
Neoprene[1]	+14 °F (-10 °C)	2 weeks
Polyurethane	+14 °F (-10 °C)	Unknown
Natural and 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 (References 10, 11)	-67 °F (-55 °C)	Very Short
Methyl Phenyl Silicone (References 10, 11)	-76 to -120 °F[3] (-60 to -84 °C)	Very Short

NOTES:

[1] Various neoprene homopolymers and copolymers vary significantly in the degree and rate of crystallization.
[2] Stretching or any deformation greatly speeds crystallization.
[3] 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 (References 3, 7). The technically best method is to run temperature-retraction (ASTM D1329) (Reference 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.

10. RESPONSE TO SUDDEN TRANSIENT SHEAR STRESS

The behavior of elastomers is, in general, nonlinear, viscoelastic, and temperature dependent. In the Space Shuttle Challenger accident, the temperature dependent behavior of the elastomer used in the field joints of the solid rocket booster has been cited as a contributing factor in the accident (References 20, 21). After the January 1985 mission, in tests conducted on the O-rings, engineers learned that at 100 °F (38 °C) the rings maintained their ability to seal at an approximation of launch pressures, at 75 °F (24 °C) they lost it for 2.4 s, and at 50 °F (10 °C) they lost it for 10 min or more. Cold weather made the O-rings and the putty less resilient, and therefore slower to fill the gap - a gap that was bigger than the one they had been designed to fill in the first place (Reference 22).

Time period response of an elastomer in reaction to sudden stress or to changing stress pattern becomes more sluggish as temperature is reduced. Depending on the dynamics of the design requirement, unsatisfactory behavior may occur at a temperature well above the Tg. A more complete explanation on time/temperature response behavior of elastomers may be found in Chapter 1 of Reference 25.