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DESIGNING WITH ELASTOMERS FOR USE AT LOW TEMPERATURES

I. INTRODUCTION

1. The functionality of elastomer parts at low temperature involves many parameters. This functionality is best demonstrated by the part performance in actual or simulated service. For a more meaningful test of performance, however, the designer may need specific guidance in selecting candidate elastomer compounds for his test hardware. This will allow early success in hardware testing by eliminating obviously unsuited candidate materials. Presently, the designer often finds his guidance in prior successful experience, in information found in elastomer material specifications, in consultation with elastomer engineers in the rubber industry or with in-house materials engineers. This guidance may be excellent "engineering judgment" which, coupled with specific, pertinent data could form a basis for cause and effect when undertaking significantly new designs.

2. In sealing applications, the medium is all important. For instance, in missile design it has been shown that AN and MS O-rings that work well at -65°F (-54°C) in hydraulic and fuel systems perform poorly in pneumatic applications at the same temperature. Diaphragms and shock mounts require much better low temperature characteristics because of the widely different uses, including more dynamic service.

3. Many elastomer specifications contain a statement as to the useful temperature range of the materials covered. The designer does well to take note of the suggested low temperature limit. The more serious and dedicated designer, when selecting a candidate rubber compound, will not stop at this primitive approach but will use additional "engineering judgement" as to how his design and his specific media may differ from the experience upon which the suggested low temperature limit was predicated. He will also take note of the specific low temperature test method(s) used in the rubber specification so he will develop a feel for the enforceable low temperature qualities of the rubber product he is specifying.

4. Communication between design engineer and materials engineer is all important. Good "engineering judgements" can be made only when full environmental details and performance requirements are known and taken into consideration.

5. A brittle point or a TR-10 temperature (temperature at which rubber retracts 10% from a specified "frozen" stretch) in a rubber specification has been used historically as a go/no-go limit for design. Unfortunately, these tests, their relation to other similar tests found in the literature, and the way the rubber part performs in a specific component or system test must be correlated to be beneficial. Lastly, many component or system tests should simulate natural environments by allowing for known time-dependent phenomena such as crystallization, plasticizer extraction, swelling and set to occur.

6. This AIR is intended as an early effort to mitigate some problems, to familiarize design with the language involved, provide models for understanding possible mechanisms, indicate short comings of current practices and improve communications between various disciplines.

II. TERMINOLOGY

1. "Elastomers" constitute the collective name for polymers which are rubber-like in properties. In fact, this collective name is a contraction of "elastic" and "polymer." It replaces the older terminologies "natural and synthetic rubber," which are now not precise and hence must be dropped from common usage. (For example, natural rubber is now manufactured synthetically).

2. 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) long after polymerization to high molecular weight is completed. Elastomers are uniquely capable of high deformation and rapid recovery from such deformation.

III. TRANSITIONS IN ELASTOMERS

1. A transition is a change from one state to another, for example, ice to water, or water to steam. In elastomers, a transition often causes radical changes in mechanical and other properties at a definite temperature or temperature range. "An understanding of the mechanical properties of high polymers is impossible without first learning something about the types of transitions that occur in such materials".[1] The transitions that occur in the elastomeric high polymers of most immediate value to designers are:

   Second-order Transitions (vitrification or glass transition).
   First-order Transition (crystallization).[2]

IV. SECOND-ORDER TRANSITION (GLASS TRANSITION, Tg)

1. This name is derived from the essentially abrupt modification in the rate of change in a number of elastomer properties as temperature is lowered, resulting in a second-order differential mathematical expression. The older common way of determining this transition is by use of a dilatometer and plotting volume versus temperature.

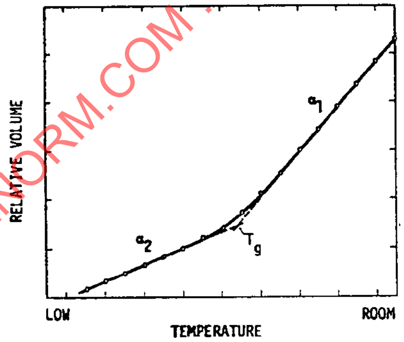

FIGURE 1. Determination of Tg by Volume Dilatometry
(α = Thermal Coefficient of Expansion)

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, α "is smaller by a factor of one-half to one-third" the former value.[3] 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 a vitrious glass or rigid, brittle plastic,[4] but above Tg, the polymer is elastomeric.

2. The current, quick, inexpensive way to determine Tg directly is by thermomechanical analysis (TMA), differential thermal analysis (DTA) or differential scanning calorimetry (DSC) using the DuPont 990 equipment, or similar. 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 as fixed and reproducible as is the freeze-thaw transition at +32°F (0°C) for water.

3. "The main difference between a rubber and a rigid plastic is that a rubber has a glass transition below room temperature while a plastic has a glass transition above room temperature".[5] This observation by a polymer physical chemist describes two of the states of matter of polymers, which are more complex than the usual solid, liquid, and gas states of classic physics. Being in the elastomeric or plastic state depends on what temperature region of its characteristics a polymer happens to be in. Practical commercial elastomeric compounds must fulfill many criteria in addition to being elastomeric at normal room temperatures, but they do fulfill that one criteria. Below their Tg temperature, the elastomers are, in fact, no longer in the elastomeric state, but are in the plastic (glass) state. Materials known as 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 of commerce. 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 in. 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".[6, 7,8,9,10,11]

5. There has been some reluctance in the precision seal area of technology 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. However, 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,[12] 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.[13]

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 JP 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.[14, 15]

V. PLASTICIZERS AND THE GLASS TRANSITION (Tg)

1. Nature gave each chemical structure elastomer its own unique Tg value. Often this is not as low as a design needs. The rubber compounder often adds several oils to the compound which are capable of acting as low temperature plasticizers, effectively lowering the Tg value. This is exactly the same effect as cited above by the usage fluid. The plasticizer oils or system fluid permeates throughout the elastomer volume, moving the polymer segments further 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 temperatures.[16]

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 o-ring can have a net shrinkage. (In tests by one aircraft manufacturer, MS29512 NBR o-rings shrank up to 5% below their virgin volume in the early weeks of water immersion.)[17, 18] The Tg of fuel extracted o-rings when dried out can be much higher than the specification value.[19] 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.

4. Where test hardware is placed into low temperature test before the rubber 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 the usage fluid.

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

VI. VISCOELASTIC EFFECTS

1. Unlike water, elastomers do not recover total mobility when warmed to just above the Tg value. They are, instead, like cold motor oil or molasses. The elastomers become more fluid and elastic as the temperature is raised far above Tg, and conversely become progressively and ever more radically 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 are 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. brittlepoint or TR-10 temperature. In order to intelligently design many components to work at low temperature, the designer should have in front of him a complete property versus temperature curve, so he knows 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.)* Note for the ethylene propylene compound that the brittlepoint 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 temperatures to high are TR-10, Tg and brittle point. More testing needs to be done to establish the general relationships of these various test methods.

2. A designer may need complete property versus temperature curves for several properties and test methods. Nowhere else in the age of computer aided design are modern designers faced with hazarding functionality on a complete absence of reliable constants, characteristic curves and known safety factors. The assistance of materials engineers in obtaining and interpreting these is required.

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*See note 1 at the end of this paper.

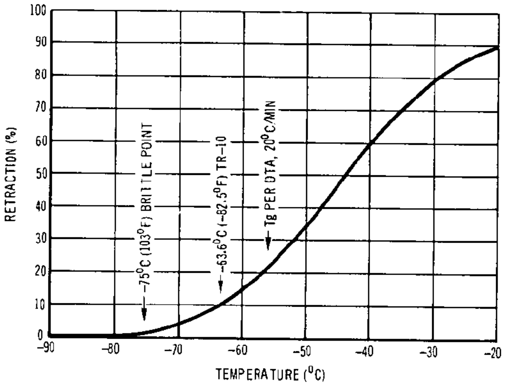

FIGURE 2 Relationship Between Glass Transition (T_g), TR-10 and Brittlepoint for a Specific Ethylene Propylene Rubber Compound, as Shown on a Complete Temperature Retraction Curve

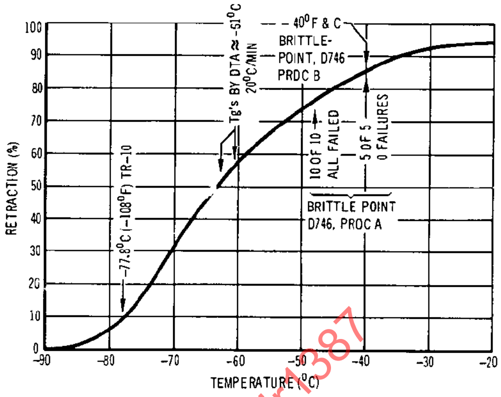

FIGURE 3 Relationship Between Glass Transition (Tg), TR-10 and Variously Defined Brittlepoints for One Chlorobutyl Rubber Compound, as Shown on a Complete Temperature Retraction Curve

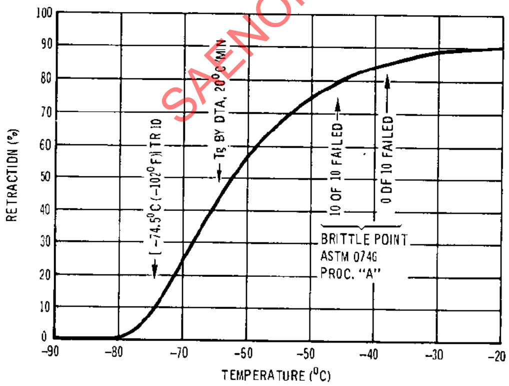

FIGURE 4 Relationship Between Glass Transition (T_g), TR-10 and Variously Defined Brittlepoints on a Second Chlorobutyl Compound, as Shown on a Complete Temperature Retraction Curve

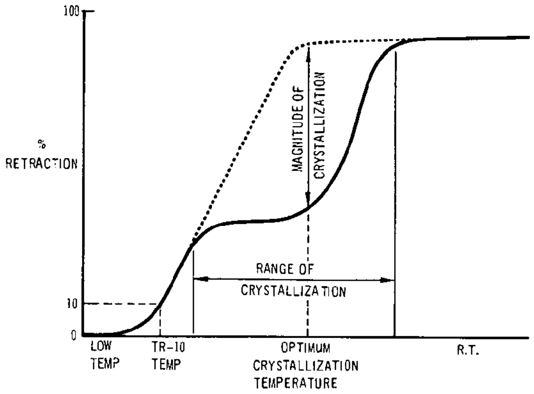

FIGURE 5 Temperature Retraction Curve for a Very Strongly Crystallizable Elastomer

VII. PRACTICAL LOW TEMPERATURE TEST METHODS FOR ELASTOMERS

1. Until recently, Tg could not be directly determined quickly and economically. Even today, this capability does not generally exist among the rubber fabricators due to their small size and the high cost and sophistication of the test equipment. Thus, many inventors have developed "practical" tests to measure the effects of low temperature on some selected mechanical property 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 Method A (or ASTM D746, Procedure B):

   This test establishes 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[20] states that "Tg changes only about three degrees with a change in time scale of a factor 10." Another text states that Tg's determined by slow dilatometry must be raised by about 27 deg F (15 deg C) for dynamic tests run at 10 cycles per minute (not per second).[21] This same text, when dealing with stiffness, states "a change of a factor of 10 in rate being equivalent to 6-8°C change in temperature.[22]" Still another author indicates the Tg phenomena as related to fracture of polymers with sufficiently rigid macromolecules may expand to hundreds of degrees by the speed factor.[23]

   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.

   An older, obsolete brittleness test was ASTM D736. In it, the striker was hand operated and not rate controlled. This test is not reproducible, rates materials 10 to 15°F too low; its use should be discontinued.

b. Temperature Retraction, ASTM D1329:

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 deg C or 1 deg 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 sigmoid 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. 5. This sag will indicate the range of temperatures over which the crystallites were melting out, and the amount of departure from the sigmoid 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 finding general usage in military o-ring specifications from the U.S. Air Force, in the Aerospace Material Specifications (AMS) from the Society of Automotive Engineers, and in data sheets from the precision o-ring industry. The designer is well advised to become proficient in using TR-10 data in his o-ring designs. As above 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.

c. Young's Modulus in Flexure, ASTM D797:

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:

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 deg (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 the twisting. When the elastomer has changed to a glassy, rigid, plastic, the wire does most of the twisting. At intermediate temperatures, the wire and the rubber share the twist at some changing ratio. Designers should obtain the whole apparent modulus versus temperature curve (Fig 6); however, tabular data often shows T_2, T_5, T_{10}, and T_{100}. These are the temperatures where the rubber is 2, 5, 10 and 100 times, respectively, the apparent modulus at room temperature. Some authors use a "Gehman freeze point." This is found by extrapolating the steep linear portion of the sigmoid curve to the zero degree twist axis. This test method is used in one U.S. Army Military specification and data in Gehman terms is often published by the polymer manufacturers on "typical" compounds using their polymer.

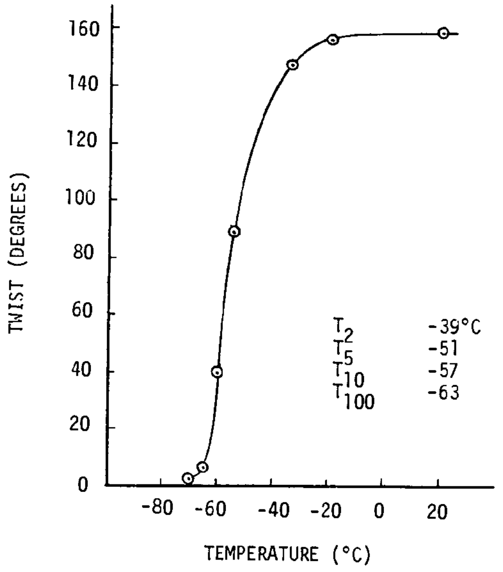

FIGURE 6. Gehman Torsional Stiffness Curve (ASTM D1053) for a New Experimental, Mineral Filled, Polyphosphazene Elastomer Compound

e. Torsional Stiffness (Clash Berg) Test, ASTM D1043:

This torsional test is similar to the Gehman except dead weights are used instead of a torsion wire. The results are best used as a complete curve of apparent modulus versus temperature. Some authors report a temperature where the apparent modulus is very high, perhaps 10,000 or 45,000 psi (68.9 or 310.2 MPa). The modulus increases steeply as the temperature is lowered until it takes on the values associated with rigid plastics, which of course the rubber has become.

f. Low-Temperature Compression Set, ASTM D1229:

This test measures the lack of elastic recovery from compression, whereas the temperature retraction tests measures the same, but in tension. A rubber button is compressed at room temperature between metal plates to a deformation set by spacers, then placed in a cold chamber. After 22 or 94 hr. the sample is released from compression and allowed to recover for 30 min. while still in the cold temperature. The amount the sample fails to recover from deformation is cold set expressed in percent. As the rubber approaches the plastic state, the cold set approaches 100%. The meaning for pneumatic o-ring service is thus immediately apparent. If the test is run at the optimum crystallization temperature, the set after 94 hr may be grossly higher than after 22 hrs. If the crystallization is allowed to continue to an asymtotic condition (see Table I), the cold set will exceed 100%, say 103%. This "shrinkage" is due to the more ordered state of a partly crystalline as compared to an amorphous elastomer. Again, the implication to sealing power is apparent. Any shrinkage of a seal is usually considered decidedly undesirable. This test has been used in development testing but not in specifications. It could be used very advantageously to cut down on component testing required.

VIII. FIRST ORDER TRANSITIONS (CRYSTALLIZATION)

These transitions derive their name from being expressed mathematically in first order differential functions. The coefficient of thermal expansion curve obtained by dilatometry can also be used to find and define the effects of crystallization as shown in Fig. 7 :

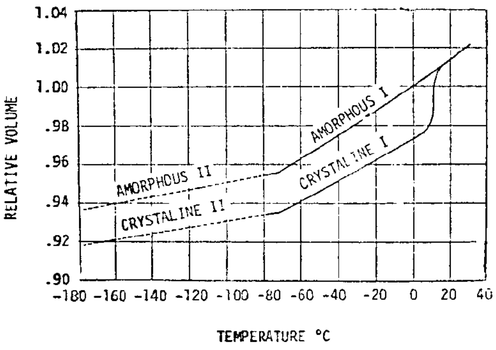

FIGURE 7. Determination of Crystallization by Volume Dilatometry

It will be noted that crystallization involves a significant volume decrease (first order differential) under isothermal (constant temperature) conditions. Because designers are not aware of crystallization phenomena, hardware qualification tests at low temperature are often unintentionally run in too short a time span to allow this phenomena to develop. When it fully develops in natural outdoor winter environments, many catastrophic failures can and do occur. Not only is the time of test too short, but temperatures that are optimum for crystallization are unintentionally bypassed when test hardware is quenched from room temperature to -65°F (-54°C). This supercools 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% maximum) so 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.

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 latice to grow.

There is an optimum temperature 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. 8.

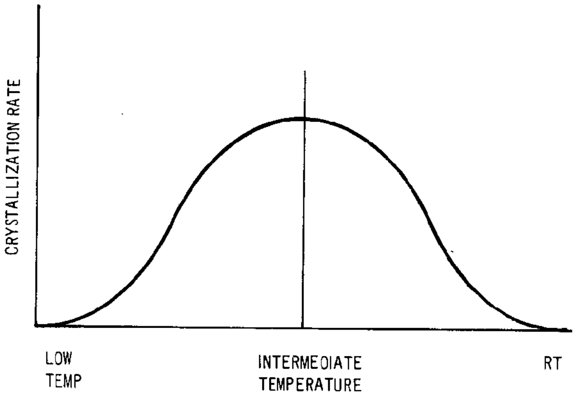

FIGURE 8. Optimum Temperature and Range of Crystallization