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Review' of Test Methods for Determination of Low-Temperature Properties of Elastomers

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ABSTRACT

Low-temperature properties of elastomers are important in Scandinavia. Requirements for low-temperature properties have long since been included in specifications, especially those of the Scandinavian automotive industry. These requirements are not always understood by manufacturers in warmer countries.

This paper describes what happens in rubber materials at low temperatures and how that affects the properties of the materials.

The most common test methods for determination of low-temperature properties will also be reviewed, and the interpretation of the results and the precision of the test methods will be discussed.

WHAT HAPPENS IN RUBBER AT LOW TEMPERATURES?

A high mobility of the molecular segments in a polymer is the condition for the rubbery state, i.e. high elastic elongation. With decreasing temperature the movements of the segments are reduced. At a certain temperature, the movements of the molecular segments are completely frozen and the material becomes a stiff plastic-like material with low elongation at break. This temperature is called the glass transition temperature, T_g.

The movements of the molecular segments can also be decreased by

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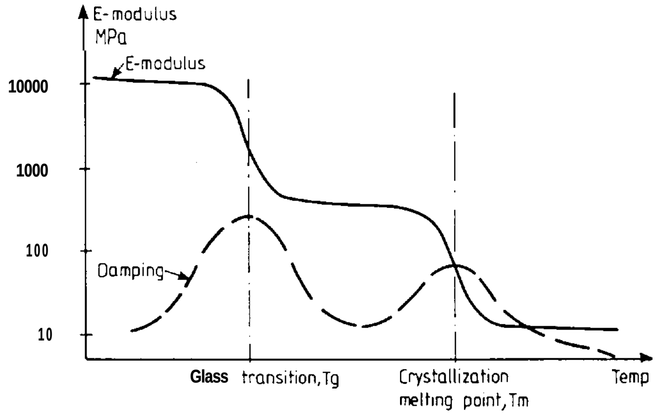


Fig. 1. Characteristic temperature-modulus curve for polymers.

crystallization, which means that parts of the molecules are arranged in a regular structure. The crystalline melting point, T_m, which gives the upper temperature limit for this transformation, is higher than the glass transition temperature. The crystallization assumes a certain mobility of the segments and happens therefore with the highest speed at a temperature between the glass transition and the crystallization melting point (see Fig. 1).

The condition for the rubbery state is consequently a low tendency to crystallization and a low glass transition temperature. If a rubber material is cooled down, the glass transition point, T_g, will sooner or later be reached and the material becomes stiff and eventually also brittle. This means that it is no longer useful as a 'rubber'. For example, the increased hardness and stiffness make hoses difficult to handle and rubber damping elements have completely different properties. If the rubber becomes brittle it will crack by bending.

The ability of a rubber material to keep its high elastic elongation and continue to be useful at low temperatures is described as its 'cold resistance'.

Changes in the viscoelastic properties of the rubber occur immediately when the rubber is cooled down. This is the dominating phenomenon when the cold resistance of rubber is discussed. Changes caused by crystallization, however, need a certain time to happen and it can take a long time to reach equilibrium. The crystallization effects are less important for rubber polymers, especially when they are crosslinked.

Most of the rubber materials have a lowest useful temperature in the

TABLE 1
Lowest Useful Temperature

Polymer	*Min. temp. (°C)*	*Polymer*	*Min. temp. (°C)*
Natural rubber	-60	Propylene oxide rubber	-60
Isoprene rubber	-60	Polysulphide rubber	-35
Butadiene rubber	-100	Silicone rubber	-110
Styrene butadiene rubber	-50	Fluorocarbon rubber	-25 to -40
Isobutylene isoprene rubber	-50	Fluro-silicone rubber	-60
Ethylene propylene rubber	-55	Kalrez	-20
Poly-norbornene rubber	-45	Polyphosfazene rubber	-20 to -65
Nitrile butadiene rubber	-40	Urethane rubber	-20 to -40
Hydrated nitrile butadiene rubber	-25	Styrene butadiene styrene TPE	-50
Chloro-ethylene rubber	-20	Styrene ethylene butadiene styrene TPE	-50
Acrylic rubber	-30	Thermoplastic natural rubber	-60
Ethyleneacrylate rubber	-35	Thermoplastic ethylene propylene rubber	-60
Chloroprene rubber	-40	Thermoplastic nitrile rubber	-60
Chlorsulphonated polyethylene rubber	-25	Thermoplastic urethane rubber	-40
Epichlorohydrin rubber	-45	Thermoplastic ethylene vinyl acetate rubber	-50
		Thermoplastic polyester	-60

interval -25 to -75 “C. Table 1 shows some typical values. The low-temperature properties can be affected by the composition, and especially by the type of softener used.

TEST METHODS FOR DETERMINATION OF COLD RESISTANCE

The cold resistance of rubber can be studied by several methods. These methods may not necessarily give the same values or even range the rubber materials in the same order.

Standardized test methods

Brittleness point: IS0 81.2
By brittleness point is meant, the lowest temperature at which rubber materials do not exhibit brittle failure when impacted under specified conditions.

When testing, test pieces in the form of strips 40 mm *x* 6 mm and 2 mm thick are clamped as shown in Fig. 2 and then immersed for 5 min in a cold bath. After 5 min they are subjected to a single impact blow, then examined to see if they show any cracks. If they have failed, new test pieces are tested at a temperature 2 °C higher. The test is then repeated at higher temperatures until no failure is observed. This temperature is recorded as the temperature limit for brittleness.

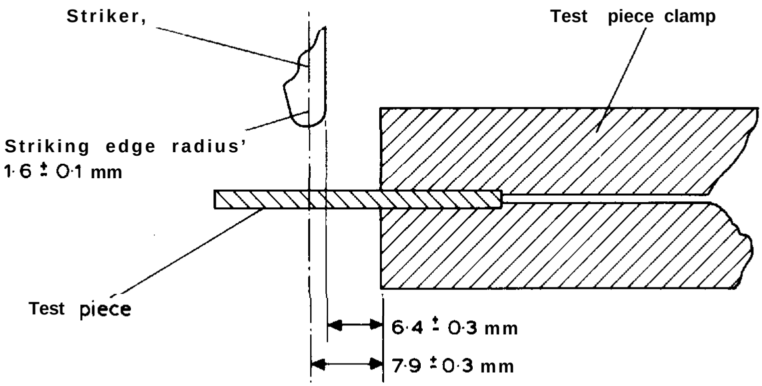
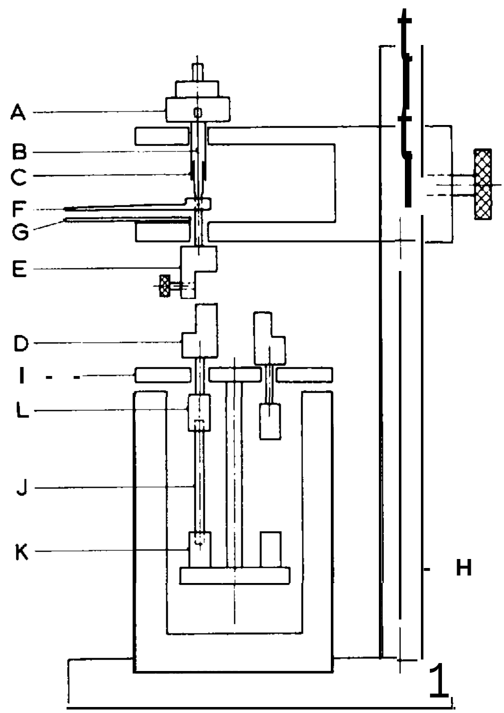


Fig. 2. Test piece clamp and striker.



A Torsion head
B Torsion wire
C Sleeve
D Clamp stud
E Screw connector
F Pointer
G Movable protractor
H Supporting stand
I Rack
J Test piece
K Bottom clamp
L Top clamp

Fig. 3. Apparatus for determination of stiffness characteristics (Gehman test).

Determination of stiffness characteristics (Gehman test): IS0 1432
The Gehman test is used to determine the relative stiffness characteristics of **vulcanized** rubbers over a temperature range of -150 °C to room temperature.

The principle for this test is that a rubber strip 40 mm x 3 mm *x* 2 mm is connected in series with a torsional wire. The rubber strip is placed in a cold liquid bath. When one end of this combination of torsion wire and rubber strip is twisted to a certain angle, the torsion will be divided between the rubber strip and the wire in inverse proportion to their torsion stiffness. The test is started at a low temperature and is then repeated at higher temperatures, increased stepwise. From the recorded twist angles a curve can be calculated and plotted of torsional modulus against temperature. The apparatus is shown in Fig. 3.

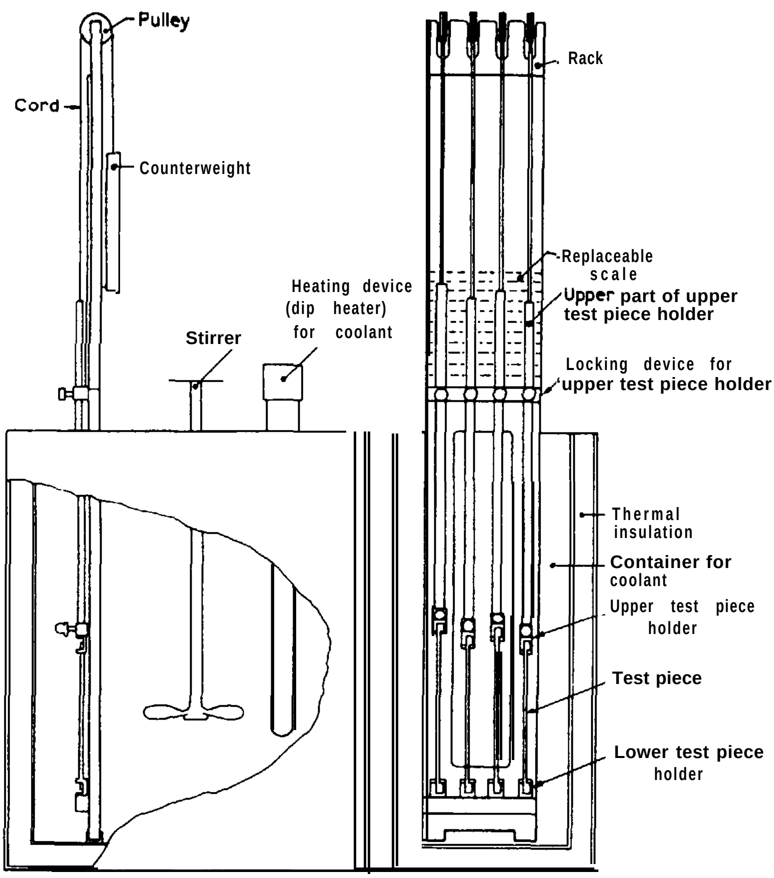


Fig. 4. Retraction apparatus.

Temperature retraction test (TR test): ISO 2921

The principle for this method is to elongate a rubber T 50 test piece, lock it and cool it to -70 °C in a cold liquid bath, for 10 min. After this time the test piece is released and the temperature is increased by 1 °C. The elastic retraction is then measured. The temperatures at which the rubber test piece has retracted 10, 30, 50 and 70% are then given as the result. The apparatus is shown in Fig. 4.

Compression set at low temperature: IS0 1653

The test piece, normally a cylinder, 29 mm in diameter and 12·5 mm high, is compressed to 75% of its original height between two plates equipped with a quick release device. After 30 min the jig is placed in a low-temperature cabinet at the test temperature. After 24 or 72 h the test piece is released, still at the test temperature, and the height is measured, normally after 10 and 1800 s. The compression set is then calculated in the normal way as the remaining deformation.

Increase in hardness: ISO 3387

This method describes a test based on hardness measurements for determining the progressive stiffening of rubber with time, caused by crystallization. The method is applicable to both raw and vulcanized rubbers. It is mainly of interest for rubber with a marked crystallization tendency at temperatures experienced in cold climates such as, for instance, chloroprene and natural rubber.

The test pieces are placed in a cold chamber at the test temperature and the first hardness measurement is done after 15 min conditioning time. The hardness measurements are then repeated after 24 and 168 h storage. If a curve is to be plotted, measurements can be made at intermediate times.

Determination of crystallization at low temperatures: ISO 6471

This method describes the determination of the tendency of vulcanized rubber to crystallize, and the time dependence of crystallization, by measurement of the recovery of compressed test pieces. Crystallization, which occurs more rapidly under high compression, reduces the elastic recovery of the rubber.

The test pieces are first compressed with low deformation and the recovery is determined without crystallization. The test pieces are then compressed with high deformation and the recovery is determined after crystallization. Normal holding times are 30 or 60 min, but if the time dependence is to be studied the results after different times are plotted on a graph. From this curve the half-time to crystallization can be determined. Figure 5 shows the equipment.

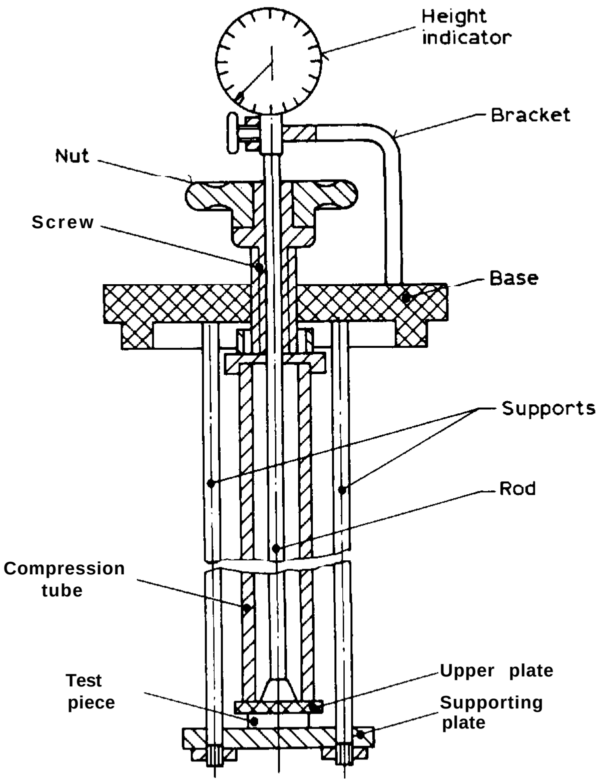


Fig. 5. Apparatus for determination of crystallization under compression.

Product tests

Coated fabrics, impact test: ISO 4646
This test is similar to the brittleness test.

Coated fabrics, bend test: ISO 4675
In this test a coated fabric is mounted in a bending jig and bent rapidly at low temperature; see Fig. 6.

Hoses, flexibility test: ISO 4672
This standard describes a method for assessing whether a rubber hose retains adequate flexibility at low temperature. The stiffness of a hose at low temperature is compared with the stiffness at room temperature.

To measure the stiffness, the hose is placed in a cold liquid bath and bent around a torque wheel, both at room temperature and at lower temperatures; see Fig. 7.

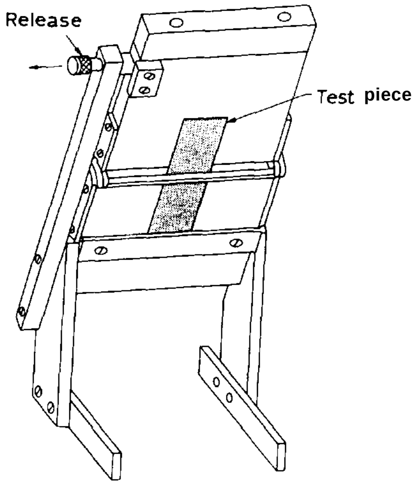


Fig. 6. Bending jig for coated fabrics.

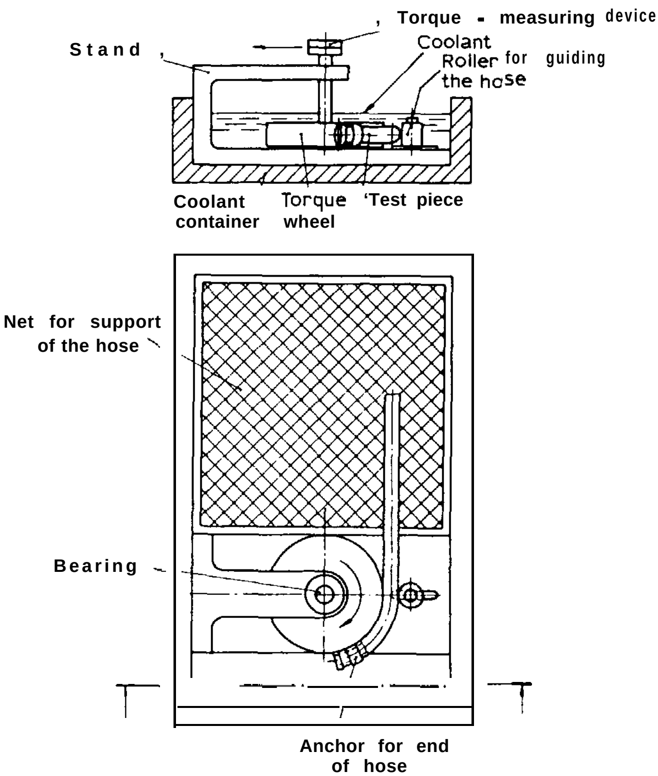


Fig. 7. Hose flexibility.

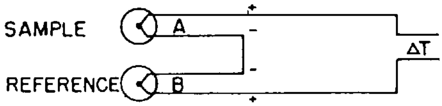


Fig. 8. Differential thermocouple.

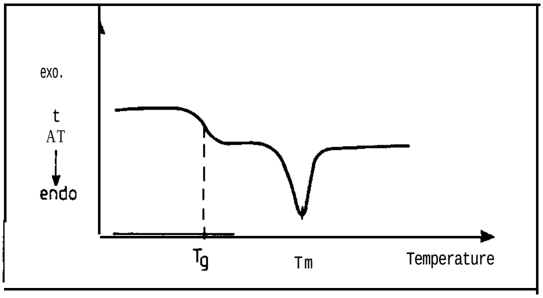


Fig. 9. Example of a DTA curve.

Non-standardized test methods

Differential thermal analysis (D TA)

In a DTA test the test sample and a reference sample are heated in a special oven, normally from low temperature to high temperature (for rubber from -150 to 100 “C). The reference sample should be an inert material which does not show any changes in the temperature interval used. The temperature difference between the two samples is measured with a differential thermocouple (Fig. 8) and gives the DTA signal. When the temperature reaches the glass transition of the rubber or the crystallization melting point, a certain amount of heat energy must be transferred to the rubber. This means that the temperature stops increasing in the rubber, while the temperature in the reference sample continues to rise. This gives a difference in temperature between the rubber sample and the reference sample. A melting is also called an endothermic process; see Fig. 9.

Dynamic mechanical measurements

Another way of determining the transformation points T_g and T_m is to measure the E modulus and the damping, tan δ as a function of temperature, see Fig. 10. This is done in special testing machines by applying a mechanical vibration on a rubber sample in compression, tension shear or bending.

INTERPRETATION OF THE RESULTS

The brittleness point gives the lowest temperature at which the rubber can be bent without damage.

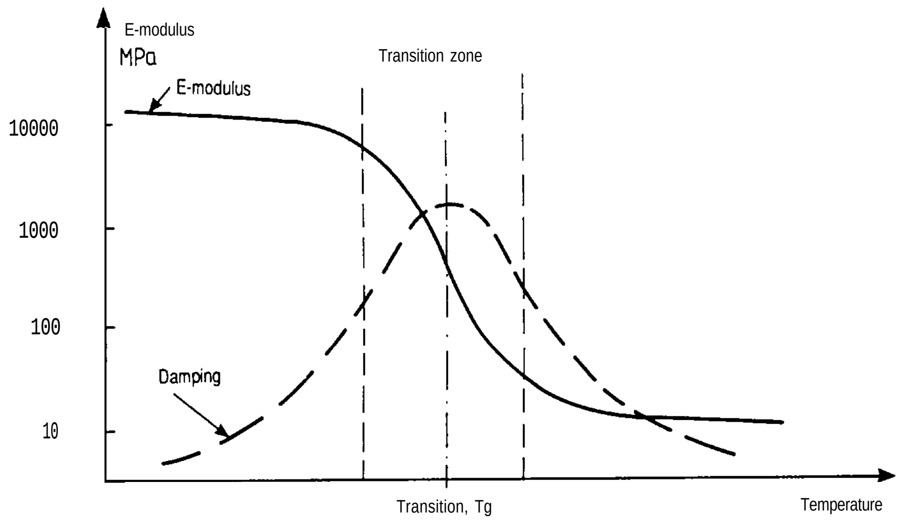


Fig. 10. **Example of a dynamic mechanical test.**

The Gehman test gives the relative stiffness at low temperature compared with the stiffness at room temperature.

The TR test shows the elastic recovery at low temperatures. TR,, is often considered to be close to the brittleness point. TR,, is often used in specifications.

Compression ***set*** at low temperatures gives a value of the elastic recovery at the measured temperature.

The hardness increase test shows the increase in hardness caused by crystallization.

The crystallization test shows the tendency of vulcanized rubbers to crystallize and the time dependence of crystallization.

The DTA test gives the T_g and T_m temperatures or ranges.

The dynamic mechanical test also gives information about T_g and T_m plus information about the modulus and damping at different temperatures.

PRECISION OF THE METHODS

IS0 decided some years ago to include precision statements in the standards. This is done by interlaboratory tests were the reproducibility, ***R*** (between labs), and the repeatability, r (within labs), are determined.

In Sweden we have also been running a programme for interlaboratory tests during the last six years. The results from these tests often

TABLE 2
Precision of Test Methods

Method	*Reproducibility* [a]	
	R(°C)	(*R*) (%)
IS0 812, Brittleness	8.3	
IS0 2921		
TR_{10}	6.2	
TR_{30}	7.2	
TR_{50}	6.3	
TR_{70}	7·1	
IS0 1653, Compression set, -25 °C		
30s		67
1800 s		147

[a] Reproducibility is the value you can expect the results to be, between two laboratories, with 95% probability. ***R*** = reproducibility in actual measuring units; ***(R)*** = reproducibility as a percentage of the measured value.

show a poor precision. The low-temperature tests shown in Table 2 have been investigated.

The precision results are not too good, especially for the compression set test. But work is being started to improve the precision of the equipment and the test methods.

USE OF THE METHODS

In Scandinavia the dominating method is the TR test. This test is widely used both in material standards and industry specifications. The TR test is considered to give good information about low-temperature properties and the test is also the one showing the best reproducibility (but not good) of the low-temperature methods.

The second method is the brittleness test, followed by the Gehman test and compression set at low temperature.