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RESISTANCE TO FREEZING AND GAS PERMEABILITY OF ELASTOMERS

[Comment: The following article by G. M. Bartenev, Doctor of Chemical Sciences, Scientific Research Institute of the Rubber Industry, was published in the September 1955 issue of the Moscow periodical Khimicheskaya Promyshlennost'.

Numbers in parentheses refer to the author's bibliography appended. Table and figures are also appended.]

The freezing resistance and gas permeability of elastomers and of materials based on elastomers are of great importance from the practical standpoint. While resistance to freezing is a desirable property, permeability to gas is an undesirable property in practical engineering applications. Although the two properties which have been mentioned are entirely different, there is a definite correlation between them which is based on the fact that the heat motion of links of polymer chains and the diffusion of gas molecules dissolved in the elastomer are interrelated.

The freezing resistance of elastomers is characterized by a conventional temperature of vitrification at which the material changes from an elastic state to a vitreous state. This resistance is determined by mechanical methods (static and frequency methods) and thermal methods (by determining the heat expansion or heat capacity).(1)

By using mechanical methods, the temperature T_k is determined at which the elasticity modulus of the elastomer increases by a factor k. The factor k is the coefficient of freezing resistance. It is numerically equal to that fraction of the high-elasticity deformation which has time to develop at low temperatures during a set interval of time or a set period of multiple deformation. In other words, the coefficient of resistance to freezing is numerically equal to a ratio of the magnitude of deformation ε at testing temperatures to the magnitude of deformation ε_∞ at high temperatures (e.g., 25°) at which the elasticity of the elastomer for all practical purposes reaches a limit.

By using thermal methods, the temperature T_g is determined below which the rotational freedoms of the long-chain molecule of the elastomer are lost.

At k = 0.01 the values of T_k for all practical purposes coincide with the values of T_g.

The gas permeability of elastomers varies within wide limits depending of the nature of the gas and the structure of the elastomer. In some cases the values of the gas permeability differ by factors amounting to several hundred. (3, 4) The highest gas permeability is exhibited by elastomers of normal structure which do not contain any polar groups in the molecule (NK, SKBM, etc). According to G. Amerongen, the gas permeability of natural rubber amounts to 37.4×10^{-8} cm^3/sec cm at for hydrogen and to 8.3×10^{-8} cm^3/sec cm at for air. The lowest gas permeability is possessed by polychloroprene and copolymers which contain strong polar groups in the molecule (SKN-26, SKN-40, etc).

In Table 1 the hydrogen and air permeabilities of elastomers at 25° according to Amerongen's data (4) are listed together with values of the resistance to freezing $T_{0.01}$ determined by us with the use of the static method on a Kargin balance (time of observation 30 sec) and values of T_g taken from the literature. (5) The gas permeabilities are given in percent of the permeability of natural rubber.

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The dependence between the gas permeability P of the elastomers and their temperature of vitrification ($T_{0.01}$ and T_g) is shown in figures 1 and 2.

It can be seen from the data cited that as the gas permeability drops, the resistance of elastomers to freezing also drops. The reason for this is quite obvious: as the intermolecular forces are reduced in the transition from polar elastomers to nonpolar elastomers, both the rate of diffusion of gas molecules and the mobility of the links of elastomer molecules are increased. The first condition brings about an increased gas permeability, while the second results in a preservation of the flexibility of the long-chain molecules of the elastomer down to very low temperatures.

It follows from this that an elastomer cannot be expected to have both a high resistance to freezing and a low gas permeability: these characteristics are mutually incompatible.

Strictly speaking, this conclusion applies only to pure high-polymer substances and not to compounded rubbers. By compounding the elastomer with additives, one may obtain materials which possess both a high resistance to freezing and a low gas permeability. If a dispersed filler which adsorbs gas is added, the gas permeability will be lowered while the resistance to freezing is preserved. To give another example, addition of a small quantity of plasticizer may greatly improve the resistance to freezing while a low gas permeability is preserved. Nevertheless, in working with material derived from elastomers it is necessary to keep in mind the relationship which has been formulated.

Table 1.   Resistance of Elastomers to Freezing and
Their Permeability to Hydrogen and Air

Elastomer	Temperature of Vitrification in °C		Permeability P at 25°C in %	
	$T_{0.01}$	T_g	To Hydrogen	To Air
Butadiene-styrene rubber SKS-10	-76	--	--	--
Natural rubber (NK)	-71	-73	100	100
Polybutadiene SKBM	-70	-66	86	81
Butadiene-styrene rubber SKS-30 (Buna ES)	-61	-61	81	76
Butadiene-nitril rubber SKN-18 (Perbunan-18)	-45	--	51	33
Polychloroprene (Neoprene)	-38	-36	27	15
Butadiene-nitril rubber SKN-26 (Hycar OR-25)	-26	-24	24	8.5
Butadiene-nitril rubber SKN-40 (Hycar OR-15)	-22	-20	15	3.4

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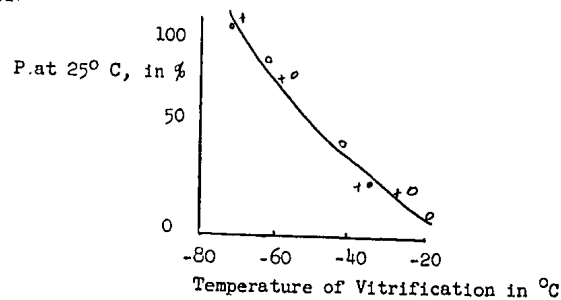
Fig 1. The Relationship Between the Permeability of Elastomers To Hydrogen at 25°C and Their Temperature of Vitrification (points indicated by circles represent values of T_g, those indicated by crosses values of $T_{0.01}$)
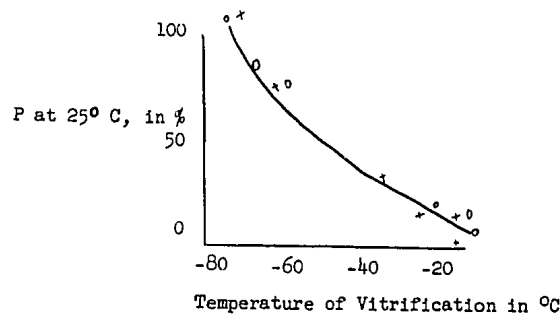

Fig 2. The Relationship Between the Permeability of Elastomers To Air at 25°C and Their Temperature of Vitrification (points indicated by circles represent values of T_g, those indicated by crosses values of $T_{0.01}$)

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