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Frost Resistance of Polymers

V.I.Popov and V.A.Voskresenskii

Papers by Soviet and foreign authors on the problem of frost resistance are surveyed, and definitions are suggested for the concepts of the technical and the theoretical frost resistance of polymers. Existing qualitative methods for determining the frost resistance of various types of polymeric materials are discussed, together with quantitative methods proposed by Soviet authors, in particular those based on the thermomechanical method of investigation. Data are reported on the dependence of frost resistance on the previous history of the production and processing of polymers, the nature and duration of aging, the action of plasticisers, fillers, etc. The bibliography contains 91 references.

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1. History of Problem

The value of polymers in technology is continually increasing, and in the near future the volume of the production and consumption of polymers will exceed that of the manufacture and use of metals and alloys. In spite of their many valuable properties, however, polymers are not devoid of defects in several respects, one being the partial or complete loss of working properties at low temperatures, i.e. limited frost resistance. The experimental data show that the mechanical, dielectric, relaxation, and other properties of linear polymers vary substantially with temperature. Little work has been done on the behaviour of polymers at low temperatures, which is frequently an obstacle to their use in goods operating in the cold.

The tendency of polymers to crack when deformed below the brittle point is explained by the growth of stresses resulting from the retardation of processes in the macromolecular chains which lead to stress relaxation. It is therefore concluded that the frost resistance of polymers may be improved by the introduction of plasticisers[1] and by suitable chemical modification[2], since this enables the rate of relaxation processes to be increased and the development of cracks to be largely suppressed.

The ability of polymers themselves to retain their flexibility and elasticity at low temperatures is usually the main prerequisite for high frost resistance in polymeric materials based on them[2-5].

Aleksandrov[6] defines frost resistance as the ability of polymers to maintain their mechanical and other properties at low temperatures. A quantitative index of frost resistance is the temperature below which articles made of the given type of polymeric material disintegrate or suffer a sharp diminution in their physicomechanical properties under the influence of specified deforming forces. Brittle fracture of polymers thus begins with the finest inhomogeneities (microcracks), which are foci of considerable overstressing. When the overstresses become equal to the tensile strength of the material, a crack begins to grow at these sites, and leads to brittle fracture of the specimen at a specified frequency of deformation[7]. A roughly similar definition of the frost resistance of polymers is given in the relevant Soviet Standard[8].

Chernaya and Vol'chenko[9] and also Tager[10] regard the workability of a polymer at a definite low temperature limit of operation for a specified time as the main criterion of frost resistance. Sedlis[11] defines frost resistance as the ability of a polymer to retain flexibility and elasticity at low temperatures. Tinius[12] characterises frost resistance by the temperature at which specimens of the polymer become brittle with a given temperature–time operating schedule.

A provisional Soviet Standard for artificial leather and for film materials[13] notes that the temperature of frost resistance serves only for the comparison of these materials under given test conditions: it does not determine the lower temperature limit for goods to function, since this limit is determined by the actual conditions of operation.

In fact existing definitions of frost resistance are qualitative and applied in character, and to some extent serve merely as an indication of the technical (relative) frost resistance of a given polymeric material.

In addition to the concept of technical frost resistance it is useful to introduce that of the theoretical frost resistance, which should provide a more accurate measure of the true frost resistance of a polymer. The definition of frost resistance as the temperature threshold for the occurrence of segmental mobility in polymer chains, given by Kargin and Shteding[14], may correspond in considerable measure to the concept of theoretical frost resistance. In this case a thermomechanical method of investigation enabled the authors to find a boundary temperature between two zones—that in which segmental mobility appeared in practice and that in which it was absent—which was interpreted as the temperature of frost resistance.

The temperature of technical frost resistance of a polymer should obviously always lie somewhat above the level of theoretical frost resistance, since structural defects, foreign inclusions, internal and surface cracks, and residual stresses present in the material will promote the appearance of brittleness and disintegration of the material at higher temperatures than that at which segmental mobility disappears in the chain macromolecules. In view of the above, technical and theoretical frost resistance can obviously be defined as follows.

Technical frost resistance must be regarded as the ability of a polymeric material to maintain its operating properties at low temperatures for a certain length of time, i.e. to retain the ability to develop specified deformations or withstand disintegration.

Theoretical frost resistance is the lower temperature limit for the start of segmental mobility of the macromolecular chains, i.e. at which minute relaxation processes appear in the polymer for given rates of action of deforming forces of given magnitude, which prevent fracture of the polymer specimens.

2. Methods for Determination of Frost Resistance

Because of the very broad technical importance of frost resistance and the great difference in the conditions of operation of polymers a large number of test methods have been proposed. These methods differ significantly in the character, degree, and rate of deformation of the specimens, so that data on frost resistance obtained for the same material by different methods often differ considerably and are difficult to compare. The frost resistance of polymers is determined mainly from test results obtained by impact, single and multiple flexing, stretching, compression, torsion, etc.

Existing methods of testing polymers for frost resistance have been divided[15] into those based on determining the temperature at which a sample undergoes brittle fracture under the influence of a certain type of load (mostly impact) and those in which the temperature is determined at which a specimen under load acquires a predetermined deformation. The former type are most often used, and can usefully be further divided according to the type of load.

In an early form of apparatus proposed[16,17] for impact tests at low temperatures a weight of ~200 g fell on the frozen test specimen from different controlled heights. In an analogous instrument the weight was dropped from a constant height, but there were separate chambers for cooling and for testing the specimen. The limiting frost resistance of the polymer specimen was assessed from the appearance of cracks.

In test methods for rubbers[18] the brittle point is determined by bending the cooled specimen, fixed horizontally at one end, by the application of an impulsive load to the free end. The temperature at which cracks become visible to the naked eye or at which the specimen fractures is regarded as the brittle point.

In a study of the plasticising action on poly(vinyl chloride) of certain low-molecular-weight substances the frost resistance was determined[19] in a pendulum instrument by the impact on the frozen specimen of a weight of 500 g falling from a height of 300 mm. Specimens were regarded as withstanding the test if after impact no cracks were visible under a lens giving tenfold magnification.

In England polymeric film-forming materials are tested for frost resistance at low temperatures by Williams' method[20], in which a specimen 0.58 mm thick, made up of two halves, is frozen and then subjected to impact from a hammer driven by a spring.

A review[21] of existing methods and equipment for testing polymers for frost resistance divides the methods into those in which specimens may undergo disintegration and those in which the modulus of elasticity is measured. Such tests of films for frost resistance are made in a special impact apparatus.

The frost resistance of a new modification of polypropylene (poprolin), obtained by plasticising with dioctyl sebacate and applying a cross-linking agent to the polymer, was determined[22] from the brittle point at which 50% of the test specimens break down. A specimen was cooled to a definite temperature, and bent to a specified deflection by application of an impact load.

An impact method of loading has been used[23] to determine the frost resistance of films at temperatures from −73°C and above. In a test specimens were mounted on a frame, brought to the specified temperature, and punctured by a loaded rod moving at different speeds (from 14 to 38100 cm min^{-1}) depending on the test conditions. The load necessary to pierce the film, the corresponding deformation, the critical speed, and the brittleness of the specimens were determined. The results were rather high compared with values obtained by other methods.

Standards adopted in several countries for measuring frost resistance are based on determining impact strength at low temperatures: i.e. tests are made in which a specimen is subjected under standard conditions to the action of a falling weight of definite size. This technique is described, for example, in a Dutch Standard[24] for cables having poly(vinyl chloride) insulation and in other standards[25,26]. Turner[27] suggested a method for determining the frost resistance of polymers which had several advantages over the standard method[25]. A rapid method for determining the brittleness of rubber at low temperatures has also been suggested[28].

A German patent[29] proposed a special method for testing cable insulation. A piece of wire 1.5 m long is covered with the insulation and slowly cooled. After every 5 deg the wire is swung sharply (to imitate a whiplash). The frost-resistance temperature of the polymeric coating is then determined from the appearance of cracks.

Sorokobatkina[30] suggested apparatus for determining frost resistance from the brittle point in which the main variables—temperature and rate and magnitude of deformation—could be controlled.

There are several methods other than those involving impact for testing the frost resistance of polymers. For example, a Soviet standard[31] uses two ways—bending a specimen (fixed horizontally at one end) a specified amount, and compressing a loop of a polymer film 0.5 mm thick—for determining the brittle point. The frost resistance is taken to be the temperature at which 50% of the specimens tested yield cracks or break down at the specified deformation.

The principle of flexing a film through 180° is used also in testing cable rubber and resin on an ergometer[32] and in a small bath[33].

In the test for leathercloth[8] the specimen is not only bent through 180° but also smoothed out by weights totalling 1 kg. In another method[8] a loop of the film is pulled through a slit (1 mm wider than twice the thickness of the film) at 100 mm min^{-1}. The frost resistance is found from the load required to draw the loop through the slit at a certain temperature without rupture of the specimen or the appearance of cracks.

Schulz and Mehnert[34] suggest that the frost resistance of a film can be measured by the temperature at which a specimen in the form of a loop of precisely defined dimensions can still be pulled without breaking, through a slit of standard size, by a sharp jerk.

A method of testing frost resistance is often used in which a sample of the polymeric film is wound in the form of a tape at a specified rate on a spindle of definite diameter, without the appearance of cracks or breaks. This method is known as "cold bending". A British standard[35] provides that a poly(vinyl chloride) plastic tape 1.27 mm thick should be wound on a 0.5-cm spindle at a rate of 1 rev/sec. This method is widely used for testing cable insulation. The diameter of the spindle can be varied

according to the thickness of the specimen, which enables more or less comparable results to be obtained when different samples of the same material are tested. Another test method is also given: the specimen is cooled to the specified temperature, and subjected to a constant load (105.5 kg cm^{-2}) for 30 s, after which the elongation of the specimen is measured.

A method of testing rubber for frost resistance is also based on comparing the elongation of a specimen at normal and low temperatures[36]. In this case a coefficient of frost resistance is obtained by dividing the elongation at normal temperature under a definite load into the elongation of the working part of the specimen cooled to a particular temperature.

Sedlis and Lel'chuk[37,38] suggested that the frost resistance should be measured by the temperature at which a specimen of a polymer film extends by a definite amount under the influence of a load for a controlled period of time. These workers suggested both a method for determining frost resistance and empirical formulae for calculating this temperature.

In another method[39] a sample of artificial leather was kept in a cold chamber for 1 h, after which its bending strength was tested in a Herfeld apparatus. Hofman[40] pointed out that a single flexing of a sample of artificial leather will lead to erroneous conclusions on frost resistance, so that more prolonged bending tests are necessary.

The frost resistance of polymer films can be determined also from the number of double flexings required for the appearance of cracks or destruction of the specimen[41]. Tests by this method showed that the frost resistance of polymer films is increased by raising the plasticiser content and increasing the extent of gel formation.

Wormald[42] used a specially designed apparatus to determine the number of flexings (external diameter of curved specimen six times the thickness) leading to destruction of a poly(vinyl chloride) film at a specified temperature, as a function of the type and content of plasticiser. This method established that tritolyl phosphate was not effective in the production of frost-resistant plastics. It was concluded that the frost resistance is improved by partial replacement of dioctyl phthalate in the film by a linear plasticiser—dioctyl sebacate.

Several papers recommend the use of compressive forces for determining the frost resistance of plastics. For rubber under compression the method[43] consists in measuring the deformation of specimens in a special instrument at normal temperature and comparing the results with the deformation obtained under the same applied load at low temperatures. The temperature at which the frost-resistance coefficient of the rubber is 0.1 is adopted as the index of frost resistance. This method is applicable only to block specimens: to determine the frost resistance of film materials a specimen in the form of a cylinder (a roll of film 20–200 μm thick) can be deformed under a definite compressive load[44]. The deformed sample is removed from the chamber and inspected with the naked eye. The presence of cracks is the criterion from which the frost resistance of the material is assessed.

Several workers[45] recommend testing artificial leather for frost resistance in an attachment to a Schopper cold chamber. It is characterised by the load required to compress a cooled specimen of the film in the form of a tube (of diameter 65 mm and length 100 mm) fixed in special clamps in a deformometer.

Since fracture of a material is a more critical indication than a temporary increase in rigidity in the cold, tests of frost resistance in which the brittle point is determined are employed more often than methods involving determination of the limiting "temperature of cold twisting"[46]. The method consists in measuring the angle of rotation of the upper portion of a standard specimen, firmly attached to a movable upper clamp, under the action of a definite rotating moment about a fixed lower clamp, and hence calculating the modulus of elasticity at a specified temperature. These tests yield the temperature at which a standard modulus of rigidity is reached. When published results are considered, however, it must be remembered that in many cases different values are used for the standard modulus of rigidity. The frost resistance characterised by the torsional modulus is determined according to the standards.[47,48]

However, a modified method was used in several investigations[50]. Although the tests were made according to the standard[48], the frost resistance was measured by the temperature at which the specimen breaks down when twisted through 360°, not 200°. The frost resistance was shown to have considerably diminished in specimens which had aged under natural conditions.

Hayes and Lannon[51] proposed a method for determining the flexibility of plasticised poly(vinyl chloride) by measuring the angles through which specimens were twisted by a definite twisting moment (5.68×10^5 dyn cm). The frost resistance was characterised by the temperature which a specimen should have for the angle of twist produced by the given moment to be 200°.

Study of frost resistance from the increase in rigidity has established[52] that the thickness and linear dimensions of specimens influence the rigidity of film materials.

Since the flexibility of a polymer can be measured by the apparent modulus of elasticity in bending and twisting tests, and since a linear relation exists between the plasticiser concentration and the temperature at which a specified Young's modulus is reached, it is possible to find[53] the temperature at which a specified modulus will be achieved with a given plasticiser content: i.e. a qualitative determination of frost resistance can be made by this method.

Bartenev and Zuev[54] studied the relation between the frost-resistance coefficient and the maximum mechanical losses of rubberlike polymers during multiple deformations in the region of vitrification (the coefficient of frost resistance was defined[55,56] as the ratio of the amplitude of deformation at the specified temperature to the amplitude of vibration at +20°C).

It is evident from the above discussion that methods of determining frost resistance employed in various branches of technology are qualitative in character, insensitive, cumbersome, laborious, and applicable only to quite specific conditions of use of the articles made from polymers. The type of deforming force, its rate of application, and other test conditions are chosen purely empirically. The result produced by the deforming force—the appearance of cracks or other defects in the specimens—is usually determined visually. According to the above methods specimens are brought to destruction, which is not always possible or advisable.

Several new methods have recently been proposed for studying the frost resistance of polymers. Kanavets and Yartsev[57] have suggested adopting the reversible elastic deformation on stretching, characteristic of the intact internal structure of the material, as index of frost resistance. In this case the temperature of frost resistance is found from the plot of percentage elastic deformation against temperature.

Shteding and Kargin[14] have shown the theoretical possibility of determining the frost resistance of polymers by means of the thermomechanical deformation—temperature characteristics obtained by the uniaxial stretching of specimens in a special instrument, a deformometer[58]. As noted above, this method involves finding the temperature of the boundary between the zone in which segmental mobility of the chain macromolecules is absent and the zone in which it is present, an external indication of this being the observed appearance of a minimum deformation. This temperature was taken to be an index of the frost resistance of polymeric film materials. The proposed method represents a considerable advance in determining frost resistance, but it necessitates the construction of a special and quite complicated instrument—the deformometer.

Kargin and Shteding's suggested principle has been used[59,60] to determine the frost resistance of polymer films, but the instrument was a specially adapted version of apparatus used in industry to determine the frost resistance of rubbers[36], certain changes and additions being introduced into its design and especially into the method of measurement[59], which improved the accuracy and permitted the use of an existing manufactured instrument. With our proposed modifications[60] to the Kargin–Shteding method not only can the absolute frost resistance of polymeric films be determined more accurately but also the effect on polymers of various external factors (type and amount of plasticiser, processing schedule, aging, etc.) can be followed quantitatively. The experimental results correlate well with those obtained by other physical methods of investigation, e.g. thermomechanical and rheological.

3. Dependence of the Frost Resistance of Polymers on Various Factors

An early qualitative observation[11] was that the frost resistance of polymeric materials depends primarily on the physicomechanical parameters of the polymers themselves. The higher the flexibility and extensibility of the polymers at room temperature the higher is usually the frost resistance of materials based on them. A high degree of polymerisation and great uniformity of molecular weight, a low content of fractions of low molecular weight, and the necessary flexibility of the macromolecular chains also favour the production of frost-resistant polymeric materials.

The most important procedures for improving frost resistance are plasticisation with polymeric plasticisers and with low-molecular-weight plasticisers for amorphous polymers, and copolymerisation and modification for crystalline polymers, i.e. changing the properties of the polymers by chemical reaction with modifiers of low molecular weight[9], e.g. by processing mixtures together on rolls, in mixers, etc. Simultaneous enhancement of frost resistance and lowering of the glass point of crystalline polymers usually requires the introduction of mixtures of plasticisers and modifiers or the use of copolymerisation followed by plasticisation of the resulting copolymers. The frost resistance of polymers depends very substantially on the content of plasticisers[61] and obviously on their chemical structure.

Nevertheless, Bauer and Cox[62] who examined the main classes of plasticisers usually employed to increase the elasticity of vinyl polymers at low temperatures, detected no dependence of efficiency on the type of plasticiser (at contents below 50%), and suggested that plasticisers should be selected only on the basis of their compatibility with the polymer, incombustibility, low volatility, etc. These workers found that mixtures of plasticisers possess no synergic action, but this is disproved by later work: the frost resistance of poly(vinyl chloride) cable insulation can be improved appreciably[63] by the use of mixtures of plasticisers—a monoester of low molecular weight and a polyester of high molecular weight, obtained from phthalic anhydride, triethylene glycol, sebacic acid, and an aliphatic alcohol.

Experiments by other workers[19,64] have shown that the frost resistance of samples of plasticised poly(vinyl chloride) depends substantially on the chemical structure of the plasticisers. With equimolecular contents of tributyl phosphate and tritolyl phosphate in the polymer, for example, films with the former plasticiser, which has linear side-chains, are the more frost-resistant.

The use of a plasticiser having a low freezing point does not always guarantee improved frost resistance in a polymer[65]. For example, the frost resistance of a p.v.c. film plasticised with dioctyl adipate (f.p. −75°C) is lower than that of films having an equimolecular content of dioctyl sebacate (f.p. −48°C).

Forman[66] showed that non-volatile plasticisers of higher viscosity, higher boiling point, and low vapour pressure exert a greater plasticising effect on neoprene rubbers at low temperatures.

Fedotova and Karp[67] used a mixture of a gel-forming plasticiser and a grease to improve the frost resistance of plasticised p.v.c.

Kozlov et al.[68] discovered an interesting phenomenon in a study of the action of mixed plasticisers on polystyrene. A mixture of a plasticiser of low molecular weight (phenyltributóxysilane) and an oligomer (polydiphenyloxysilane) gives a significant synergic plasticising effect: a mixture of such plasticisers produces a considerably greater shift in the glass and flow points.

Plasticisers of different types are obtained depending on the presence of polarisable groups[69]: those containing polar and aliphatic groups (e.g. trioctyl phosphate) are not readily compatible with poly(vinyl chloride), but raise the frost resistance of the polymer substantially; those of polar–aromatic structure (tritolyl phosphate) form gels readily with p.v.c., but improve its frost resistance only very slightly. The frost-resistant plasticisers which are normally widely employed[15,70–73] are diesters of aliphatic dicarboxylic acids, such as adipic, sebacic, etc.

The quantity of frost-resistant plasticisers in a composition is determined by the elasticity which the plasticised material should possess at low temperatures. With a given total quantity of added plasticiser a linear relation exists between the quantity in the mixture and the softness of the poly(vinyl chloride) plastic, the limiting temperature of "cold twisting", and the logarithm of the bulk resistance.

Plasticisers prepared from linear alcohols[74] have recently become widely used, as also have epoxystearates[15], for the production of frost-resistant compositions. Polymers were shown[75] to acquire the greatest frost resistance when esters of organic acids containing 6–8 carbon atoms in the chain were used as plasticisers. Esters containing a larger number of carbon atoms in the chain are not so compatible with polymers and tend to freeze out of the compositions at low temperatures. The degree of branching in the structure of the initial alcohol also has a great effect on the frost resistance of the polymer material,

lowering it substantially[76]. For example, the frost resistance of p.v.c. diminished in the sequence—*n*-octyl > isohexyl > 2-ethylhexyl > iso-octyl > 2-ethyl-2-methylpentyl—on the introduction of different esters of phthalic acid with alcohols containing eight carbon atoms. The presence of several aromatic rings or polar groups in phthalic esters has an adverse effect on the frost resistance of the plasticised polymer[77]. Isophthalic diesters confer high frost resistance on p.v.c. [78]. Although phthalates are widely used to plasticise p.v.c., they are not sufficiently frost-resistant, and are also flammable[79]. Phosphates having aromatic side-chains are characterised by low flammability but low frost resistance. Linear plasticisers—sebacates and adipates—confer fairly high frost resistance on p.v.c., but are flammable. To obtain frost-resistant polymeric materials, even in this case it is advisable to use mixtures of plasticisers, including chloroalkanes and other halogenated compounds. The frost resistance of p.v.c. containing nitrophthalic esters is higher than with equivalent molar quantities of phthalates.

Fillers and pigments usually lower the frost resistance of plastics[11,42,81,82] and require additional quantities of plasticisers. From an examination of the viscoelastic properties of poly(vinyl chloride) plasticised with tritolyl phosphate and dioctyl adipate, however, Eirich has shown[83] that small amounts of a very finely disperse limestone filler act as an additional plasticiser, somewhat lowering the moduli and increasing the relative elongation under tension.

The frost resistance of polymers is improved by orientation and by preliminary drawing. Aleksandrov[6] notes that highly oriented polymers retain their flexibility at temperatures several tens of degrees below the glass point. Drawn poly(vinyl chloride) acquires flexibility which varies little with fall in temperature[11]. The effect of drawing is greater the lower the plasticiser content. The greatest effect was achieved by combining a frost-resistant mixture with a softener and mechanical drawing. Several other workers[84,19] have observed an improvement in frost resistance on drawing.

Orientation is especially valuable in the manufacture of films. Compared with unoriented p.v.c. films, oriented films possess superior mechanical properties and good frost resistance[85,86].

Several workers have established[87] that atmospheric aging influences the temperature of impact brittleness more than other mechanical properties. Atmospheric conditions have a greater effect on the frost resistance of films plasticised with a single plasticiser the greater the plasticiser content. All methods aimed at stabilising polymers usually maintain also the frost resistance of materials based on them. On the whole, however, insufficient study has been made of the variation in the frost resistance of polymers during aging.

The increase in the frost resistance of linear polymers due to the introduction of a sufficient quantity of gel-forming plasticisers is usually accompanied by a decrease in strength. In some cases, however, the frost resistance of materials can be enhanced with a simultaneous increase in strength by partial "cross-linking" of the polymers[88,89].

Kargin et al.[90] have established that several properties of polymers depend on the character of the supermolecular secondary structures. Conferring the optimum structure on polymers[91] will probably enable their physical properties to be influenced, including the frost resistance of materials obtained from them. Such investigations would be of great scientific interest.

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Department of Plastics, Kazan
Institute of Civil Engineering