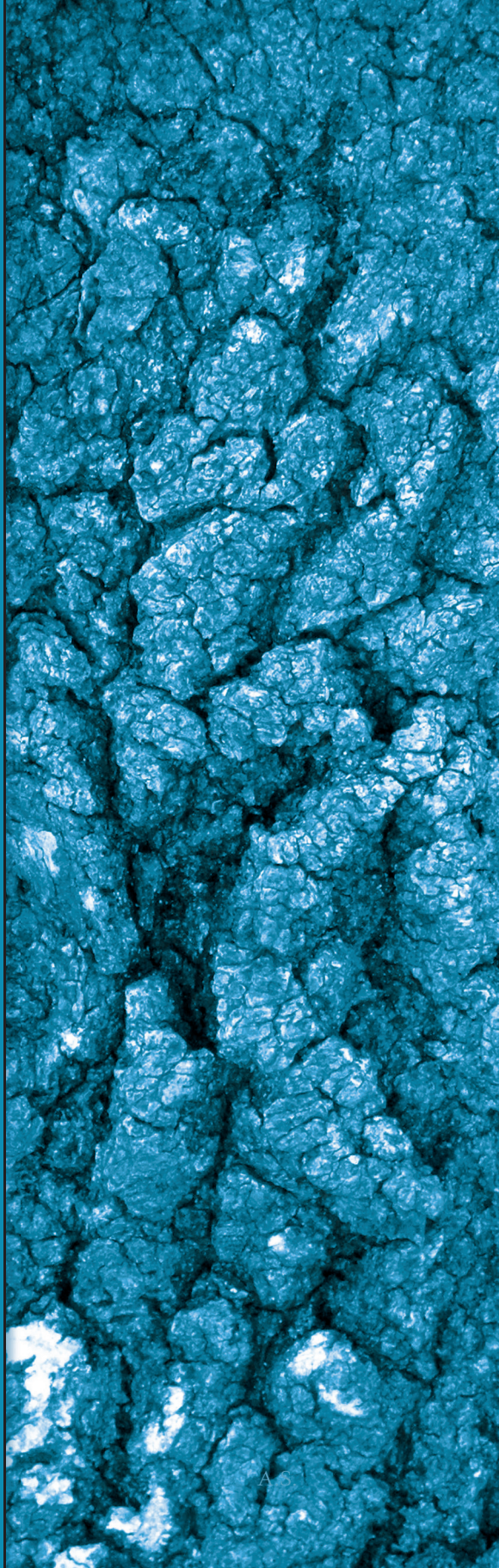


New Concepts in Polymer Science

Low-Temperature Behaviour of Elastomers

M.F. Bukhina
S.K. Kurlyand

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Low-Temperature Behaviour of Elastomers

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Foreword

Intensive development of many engineering fields, aerospace including, raised the problem of a significant broadening of the operational temperature range of elastomeric materials.

In a number of cases, one of the essential factors determining the performance of elastomers and elastomeric goods is low-temperature resistance. This factor preserved its significance for space-system and aviation components, in developing new aircraft and helicopters. In the ostensibly advancing era of global warming, unusual local temperature drops in the normally warm areas make low-temperature resistance of elastomers even more an issue.

The currently existing ways of increasing low-temperature resistance by developing novel elastomeric materials and composites with new efficient ingredients and their combinations make it possible to significantly broaden the temperature ranges of elastomer applications.

There are two most studied physical processes determining the low-temperature resistance of elastomers: glass transition and crystallization. Extensive information has been accumulated on the relation of these processes to the structural and molecular parameters of rubbers, their compositions and deformation conditions. These processes have been found to contribute to the low-temperature resistance of elastomeric materials and articles. Ever-widening applications and development of elastomers of regular structure make one to consider the low-temperature resistance of elastomeric materials in a new light. Attention of investigators is currently attracted by microcrystallization, a specific manifestation of the crystallization of elastomers. There are grounds to believe that this process determines the properties of a number of relatively new elastomers, which are copolymers including rapidly crystallizing sequences.

Due to the inclement climate of Russia, low-temperature studies of elastomers have been vitally important for the successful development of industries and transport in Extreme North regions and Siberia. That is why these studies have been the most intensive namely in Russia. The book written by specialists of two Russian research institutes (Research Institute of Elastomeric Materials and Articles (Moscow) and Lebedev Synthetic Rubber Research Institute (St.-Petersburg)), where such studies have been carried out for many years, summarizes the results of these works and other numerous investigations by Russian and Western scientists. The book was published in Russian in 1989. That was the year when a major cycle of works on the low-temperature behaviour of elastomers had been completed. Those works, however, are little known to specialists from other countries. The book also includes the results obtained by Russian and Western specialists in the recent years. Major attention is given to Russian publications, not always known to investigators and engineers in other countries. The results published in special Russian editions [220, 377, 439] and reported at special Russian and international conferences [23, 99] are also considered.

The book also contains reference material, which could help specialists in choosing the compositions of rubbers and the designs of rubber articles intended for low-temperature applications. The authors also strived to analyze the not-yet solved scientific and technical problems, essential for increasing the quality of these items.

Considerable attention is given in the book to the effect the compositions of rubbers and the conditions of their processing have on low-temperature resistance. Herewith, the issues related to chemical changes that occur in rubbers are not discussed. The interested reader can find respective data in many other books. These are, for instance [178, 180, 346, 372, 373, 390, 391].

For convenience, the authors thought it expedient to give a list of references and recommended literature in the end of the book in an alphabetical order (by the first author's names).

Chapters 1–3, 6 and 7 were written by the authors with participation of N.M. Zorina and N.L. Severina (Moscow). In preparation of the text of the present edition, the authors used the data by N.N. Petrova (Yakutsk). The authors thank G.D. Garmashova, G.V. Novikova and G.P. Petrova (St.-Petersburg) for their assistance in preparing the material and for valuable comments; and B.M. Polyakova, N.N. Kutsankina (Moscow), G.P. Maksimchuk and G.S. Solodovnikova (St.-Petersburg) for their help in preparing the manuscript of the Russian edition. The authors use the occasion to sincerely thank Prof. V.A. Shershnev, who took upon himself an uneasy task of reviewing the manuscript of the Russian edition. The great majority of his numerous comments were taken into account.

The book will be of use for researchers and engineers working in the field of elastomers, developing and using elastomeric materials and articles, and also for university students, postgraduates and teachers studying the physics of elastomers and majoring in this field.

Introduction

The purpose of Introduction is to remind the reader of basic information on the mechanical properties of elastomers, required to understand the physical processes that occur in these materials at low temperatures.

The major differences of elastomers from all other materials are their capability of large reversible deformation, low rate of deformation, low rigidity, large difference between shear modulus and bulk modulus, and significant losses of mechanical energy in dynamic deformation. These unique properties are realized in the temperature range close to room temperature. The low-temperature resistance of elastomers is their ability to preserve this set of unique mechanical properties at a temperature decrease.

When considering deformation of polymers, we distinguish between three of its components:

- Purely elastic deformation similar to elastic deformation of common solids, with elasticity modulus of $\approx 10^3$ MPa. It is reversible and is related to the change of intermolecular and interatomic distances, as well as angles formed by valent bonds, which connect atoms in macromolecules; the development of elastic deformation is accompanied with a change of internal energy of the system.
- Rubberlike deformation characteristic of only polymers in the rubberlike state; it is also reversible but is related to the change of macromolecular conformation, i.e., to the change of system's entropy. The entire set of unique mechanical properties of natural and synthetic rubbers is determined by this type of deformation.
- Plastic deformation related to the irreversible motion of macromolecules relative to one another. This type of deformation plays an especially important role in raw rubbers and raw rubber compounds. In deformation of vulcanized rubbers, i.e., elastomers that possess a three-dimensional network of chemical bonds, this third component of deformation develops only when chemical bonds are broken, i.e., as the result of chemical ageing.

Depending on the deformation conditions of an elastomer, the ratio of its deformation components changes, which is determined by the difference in the rates of each type of deformation: the rate of elastic deformation is very high, and it develops in a negligibly small time. The rate of the rubberlike deformation component is hundreds of times lower even at high temperatures, and it sharply drops down at a temperature decrease. Thus, by changing the temperature of an elastomer, the predominant development of each of these types of deformation can be realized.

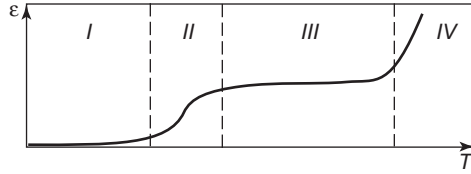


Figure 1 A temperature dependence of deformation ε under a given load. *I*, glassy-state region; *II*, transition region; *III*, region of the complete development of rubberlike deformation (rubberlike-state plateau); *IV*, viscous-flow region.

Figure 1 is a schematic representation of a temperature dependence for an elastomer. In region *I*, where the elastomer is in the glassy state, mainly elastic deformation develops. Transition region *II* is characterized by the coexistence of elastic and rubberlike deformations. On the plateau of the rubberlike state *III*, rubberlike deformation determines the unique mechanical properties of elastomers. Mainly plastic deformation develops in the viscous-flow region *IV*; it determines the processing properties of elastomers.

The low temperature performance of an elastomer is mainly determined by its behaviour in region *II* – in transition from the rubberlike to the glassy state (or the other way round, from the glassy to the rubberlike state).

The difference of the temperature dependence and the absolute values of the rates of three deformation types peculiar to polymers leads to the change of their properties in time, i.e., to the occurrence of a set of their relaxation properties.

The main type of physical relaxation processes observed in polymers is related to the transition from “instantaneous” elastic to “slow” rubberlike deformation. These relaxation processes are called the major physical relaxation processes or α -processes of relaxation.

Besides physical relaxation processes, polymers are characterized by chemical processes related to the change of their chemical structure: rupture or formation of new chemical bonds, i.e., to chemical ageing.

In the deformation of rubbers at a very low rate, obviously lower than the rate of rubberlike deformation, the latter develops completely. However, for raw rubbers and rubber compounds the development of rubberlike deformation is obligatorily accompanied by plastic deformation, so that no equilibrium deformation can be achieved at a given load. For a three-dimensional-network elastomer, which vulcanized rubber is, a certain equilibrium value of deformation corresponds to each value of stress, and, vice versa, a very certain value of equilibrium stress different from zero corresponds to each value of deformation.

A typical dependence between a nominal equilibrium stress f and a deformation ratio λ at an uniaxial tension is presented in Fig. 2.

Here

$$f = P / S_0, \quad (1)$$

where P is the load on the specimen, measured after an equilibrium has been established; S_0 is the cross-section area of the specimen before the deformation. Note that the length of the specimen in these measurements should be considerably larger than the dimensions of its cross section. The dependences between the true equilibrium stress σ and the elongation ratio λ are represented in Fig. 2 by curves 2. Here, the true cross-section area S was calculated from the assumption of incompressibility:

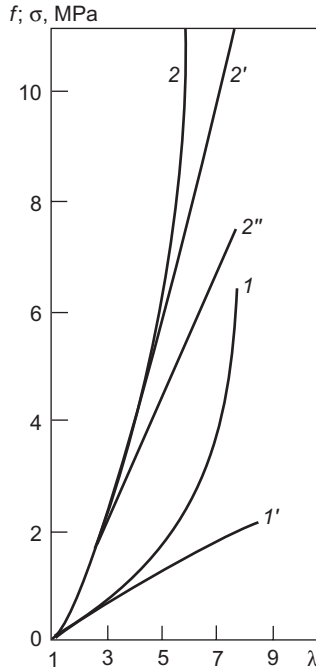


Figure 2 Dependence of the equilibrium stress, normal f ($1, 1'$) and true σ ($2, 2', 2''$), on the deformation ratio λ at a uniaxial tension of unfilled vulcanized natural rubber: $1, 2$, experiment; $1', 2', 2''$, calculation: $1'$, by (6); $2'$, by (7); $2''$, by (3).

$$Sl = l_0 S_0, \quad S = S_0 / \lambda. \quad (2)$$

where l_0 is the length of the undeformed specimen; l , the length of the deformed specimen. For the values of λ close to unity the dependence $\sigma - \lambda$ (or $\sigma - \varepsilon$, where the deformation $\varepsilon = \lambda - 1$) can be considered to be linear [55]:

$$\sigma = E\varepsilon. \quad (3)$$

Here E is the Young's modulus. For a deformation not accompanied by a volume change, $E = 3G$, where G is the shear modulus, and the Poisson ratio $\mu = 0.5$.

Complex (three-axial) deformation is described by the dependence of strain energy function W , i.e., the specific work of deformation, on the extension ratio $\lambda_1, \lambda_2, \lambda_3$ along the three principal axes of deformation.

Considering an individual molecule as a statistical set of segments, and a specimen as a whole as a network formed by the statistical set of molecules, and accepting that rubber-like deformation of elastomers is of entropic nature, an expression for the specific work of deformation or for strain energy function was obtained in the form:

$$W = \frac{1}{2} NkT (\lambda_1^2 + \lambda_2^2 + \lambda_3^2). \quad (4)$$

Here N is the number of molecular segments forming the network, k is Boltzmann's constant and T is absolute temperature, and

$$NkT = G, \quad (4')$$

where G is the shear modulus.

The dependences between the principal stresses and deformations are determined by differentiation

$$\partial W / \partial \lambda_i = f_i, \quad i = 1, 2, 3. \quad (5)$$

For uniaxial tensile/compressive deformation, from the relation (4) for normal f and true σ stresses it follows:

$$f = G(\lambda - 1/\lambda), \quad (6)$$

$$\sigma = G(\lambda^2 - 1/\lambda). \quad (7)$$

Figure 2 presents the dependences of $f - \lambda$ from the relation (6), curve 1', and $\sigma - \lambda$ from the relation (7), curve 2'.

The difference of the values of σ obtained by (3) and (7) does not exceed 5% in the region* of $-0.5 < \varepsilon < 2.5$ at $G < 5$ MPa; as G is increased, the deformation limits within which (3) and (7) virtually coincide become narrower. The experimental results obtained at an equilibrium uniaxial tension of unfilled vulcanizates based on most natural rubbers is described well by eq. (3) [44, 55]. The applicability limits of (3) and (7) are the broader the smaller G (or E) is.

The expression for strain energy function can be also obtained without using representations of the nature of a deformation. Thus, based on the assumption of the linear dependence between stress and deformation in simple shear for an isotropic incompressible material, an expression, which is usually called the Mooney or Mooney–Rivlin strain energy function, was obtained [715]:

$$W = C_1 (\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3) + C_2 (1/\lambda_1^2 + 1/\lambda_2^2 + 1/\lambda_3^2 - 3). \quad (8)$$

At $C_2 = 0$, it changes to (4).

The relation between stress and deformation at uniaxial deformation, which follows from (8):

$$f = 2(\lambda - 1/\lambda^2)(C_1 + C_2/\lambda), \quad (9)$$

* The negative values of ε correspond to compression.

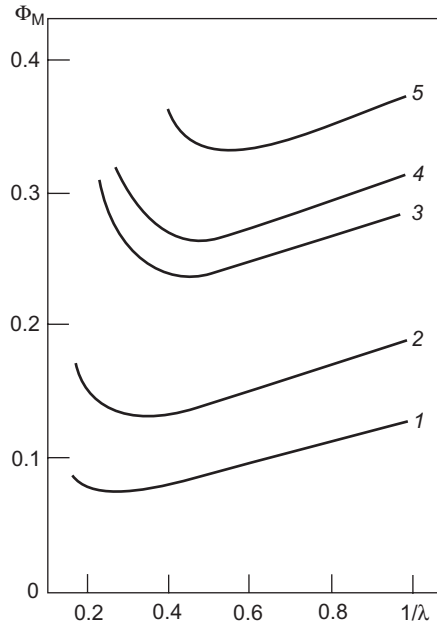


Figure 3 Dependence of $\Phi_M = f/(\lambda - 1)\lambda^2$ on $1/\lambda$ for natural rubbers vulcanized with various amounts of dicumyl peroxide (numbers at the curves, %).

describes the experimental data in the region of large deformation better than (6). At $C_2 = 0$ and $2C_1 = NkT$, eq. (9) changes to (6).

In the case of the validity of relation (9), experimental data form straight lines in coordinates $\Phi_M = f/(\lambda - 1)\lambda^2$ and $1/\lambda$ (Fig. 3). The slope of these lines gives the values $2C_2$; and the segment cut on the ordinate axis, $2C_1$. As a rule, at large λ (small $1/\lambda$) one observes deviations from this dependence, which are due to a steeper character of the curve $f - \lambda$ than it follows from eq. (9). For natural and polychloroprene rubbers these deviations are related, first of all, to the development of stress-induced crystallization (see Chapter 4).

The fact that the classical theory of rubberlike elasticity fails to describe deformation curves at large tensions implies that its assumptions are not fulfilled for real elastomers. Introduction of additional restrictions for the motion of molecular chains between chemical junctions made it possible to describe experimental data better. However, more new additional assumptions need to be introduced for the data to coincide with the experiment.

Considering the constant C_2 in eqs. (8) and (9) as a measure of deviation of experimental data from classical theory, we can assume that its significance is the greater, the larger the number of physical junctions in the network is and the more intensively they are formed in the process of deformation. There is no common point of view on the nature of the physical junctions. Presumably, the greatest role in the deformation of elastomers is played by the physical junctions, which are pre-phase fluctuations and are structurally close to crystals. They become stable crystals only when their size exceeds the critical size of the nucleus* (see Chapter 3). Therefore, understanding of the mechanism of crystallization, in

* Formation of junctions of this nature is also possible in non-crystallizing elastomers, but they fail to become stable under any conditions there.

particular, that of stress-induced crystallization, can also be of help in describing the deformation properties of elastomers.

When considering the entropic component of deformation, we do not have to take into account the change of volume during the deformation. However, we can not neglect the volume change both in the case of large tensile deformations and at large compressions, as well as in compression of specimens with a large shape factor $\Phi = S_{20}/S_{10}$, for which the area of the loaded surface S_{20} is considerably greater than that of the free surface S_{10} , i.e., when the process is close to volume compression. In this case, the contribution of elastic (or energetic) component of the deformation is great; this results also in some peculiarity of low-temperature resistance (see Chapter 2).

The low rate of rubberlike deformation as compared with elastic deformation, and its dependence on temperature, i.e., the relaxation behaviour, are manifested the most vividly in the dynamic loading of elastomers, when both the stress and deformation change in time.

A typical case of dynamic loading is a periodic application of a load. The higher the loading frequency ν , the smaller (at a constant amplitude of the stress) the time of the deformation development is and, respectively, the smaller the amplitude of the deformation for one cycle of loading. Due to the low rate of rubberlike deformation, it is delayed in phase from the load, so part of the mechanical energy is not returned completely but passes into heat, i.e., a hysteresis is observed.

The simplest way of periodic loading is the deformation at a constant frequency, so that deformation ε and stress f of the specimen change by a harmonic law:

$$f = f_0 \cos \omega t; \quad \varepsilon = \varepsilon_0 \cos(\omega t - \delta), \quad (10)$$

where t is time, ω is the angular frequency ($\omega = 2\pi\nu$); δ is the phase shift between the stress and deformation, which usually ($\tan \delta$) can serve as a measure of energy losses. The dynamic modulus of tension/compression $E = f_0/\varepsilon_0$.

The dynamic moduli of tension/compression E and shear G in harmonic loading are characterized by complex values:

$$E = E' + iE''; \quad G = G' + iG''. \quad (11)$$

where

$$E' = E \cos \delta; \quad E'' = E \sin \delta; \quad \tan \delta = E''/E'. \quad (11')$$

The relations for the shear modulus G are written down in a similar way. The values E' , G' and E'' , G'' are called, respectively, the storage and loss moduli.

The temperature dependence of the deformation amplitude at a given frequency ν has the same shape as the temperature dependence of deformation (see Fig. 1) at static loading.

The dependence of the real and imaginary components of the dynamic modulus on frequency is similar to that on temperature: as frequency is increased, G' and E' go up as they do when temperature is decreased, and $\tan \delta$, G'' and E'' pass through a maximum. The temperature and frequency dependences of the mechanical properties determine the low-temperature resistance of elastomers operated under dynamic conditions.

The interested reader can find out more about the peculiar features of the properties of elastomers in the books [27, 29, 44, 45, 97, 161, 178, 180, 198, 205, 340, 372, 373, 390, 391, 403, 462, 462a, 464, 550, 600, 624, 715].

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1 Glass Transition of Elastomers

Glass transition – the transition of a substance from the liquid state into the solid (but not crystalline) state – is characteristic of both polymers and many low-molecular-mass substances. A substance proves glassy when the energy of molecular motion, decreasing in cooling, approaches the energy of molecular interaction in the order of magnitude. Glass transition occurs when the cooling rate of a substance exceeds that of crystallization, i.e., it can be observed for substances with a low crystallization rate or those that do not crystallize at all. The higher the viscosity of a liquid, the more probable it is that it will pass into the glassy state when cooled. Due to the high viscosity of the melt, glass transition is realized, e.g., for low-molecular-mass silicate glasses. Vice versa, rapidly crystallizable substances are very difficult – and sometimes impossible – to obtain in the glassy state. This explains the fact that crystals are much more frequent than glasses among low-molecular-mass substances in the solid state.

Similar patterns are observed for polymers. The impossibility of crystallization (due to the non-regularity of the chain for a number of polymers) is also responsible for glass transition. For many polymers, the glass transition range is at room temperature and higher, which determines their use as structural hard materials. These are polystyrene, polymethyl methacrylate, polycarbonate and others. Rapidly crystallizable polymers, such as polyethylene, polypropylene, polyethylene terephthalate etc., occurring in the crystallized state at room temperature, can not in practice be produced in the glassy state due to the high rate and degree of crystallization. Only their amorphous part can undergo glass transition, and the properties of the amorphous part can be significantly affected by the crystallizable part (if the degree of crystallization is large enough, see Chapter 6).

In elastomers, where the degree of crystallization does not exceed 30–60%, cooling leads to glass transition. In high-crystallization rate elastomers only the amorphous part can be glassy, and low-crystallization rate elastomers can be produced completely glassy, the same way as non-crystallizable elastomers (Fig. 1.1). Since many elastomers do not crystallize at all or crystallize slowly, for most of them glass transition is the major process, which determines their low-temperature resistance.

1.1 Methods of glass-transition temperature determination

1.1.1 Structural and other physical methods

Dilatometry. The measurement of the volume or linear size is a traditional and reliable means of detecting glass transition of elastomers, proposed by Wood and Bekkedahl as