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Abstract

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ON THE THERMODYNAMIC FEATURES OF THE DEFORMATION OF CHLORINATED GUTTA-PERCHA IN THE HIGH-ELASTIC STATE

From the kinetic theory of high-elastic deformation of polymers it follows ($^{1-3}$) that the reversible deformation of a polymer in the high-elastic state is determined primarily by the change in entropy S upon stretching. The change in internal energy E that occurs in this process is usually small (if crystallization does not take place). The thermodynamic foundations of these phenomena have been analyzed in sufficient detail, and it is known that the experimental fact confirming these ideas is the sign of the temperature coefficient of the modulus of high-elastic deformation. As was first shown by Ferry and Meyer (^{1}), and subsequently studied by Guth and Bartenev (^{2,3}), the deformation of a polymeric substance in the high-elastic state is indeed characterized by a positive sign of the temperature coefficient of the modulus, i.e., with increasing temperature the stress required to maintain a given degree of extension increases. Let us recall that for the elastic deformation of solids the observed dependence has the opposite character—with increasing temperature the magnitude of the modulus decreases, which indicates a substantial change in the internal energy E occurring during deformation of such bodies. These regularities may be written in the form

$$(\partial E/\partial l)_T = f - T(\partial f/\partial T)_l, \tag{1}$$

$$(\partial S/\partial l)_T = -(\partial f/\partial T)_l, \tag{2}$$

where $(\partial E/\partial l)_T$ and $(\partial S/\partial l)_T$ are the changes, respectively, in internal energy and entropy per unit volume per unit extension; f is the nominal stress per unit cross section; $(\partial f/\partial T)_l$ is the temperature dependence of the stress at a constant degree of extension. Thus, by studying the regularities of polymer deformation at different temperatures, one can draw important conclusions about the nature of the deformation and its thermodynamic features. In the present work data are presented concerning the mechanical behavior of the linear polymer *trans*-1,4-polyisoprene—gutta-percha—the regularity of whose chain

Figure 1

Figure 1: Figure 1

Figure 2

Figure 2: Figure 2

structure was disturbed by introducing chlorine atoms at the double bonds. As it turned out, a slight disruption of the regularity in the structure of the gutta-percha macromolecules can substantially alter the mechanical behavior of the polymer within the limits of the high-elastic state.

The specimens for the study consisted of purified gutta-percha, chlorinated at the double bond at 60° in a dilute solution of carbon tetrachloride with a solution of chlorine. The resulting specimens of chlorogutta-percha, containing different amounts of chlorine, were subjected, in the form of films, to cold vulcanization with sulfur monochloride according to the method described in ([4]). The vulcanized specimens were stretched on a Polanyi-type dynamometer at a rate of 1 mm/min at temperatures of 60, 85, 100, and 120°.

Investigation of the structure of the chlorinated unvulcanized specimens showed ([7]) that, upon the introduction of chlorine up to a content of 16%

(which corresponds to the inclusion of a pair of chlorine atoms for every 6 monomer units) no noticeable change occurs in the X-ray scattering pattern, and only a slight "swelling" of the crystal lattice of the original gutta-percha is observed, by 1.8% on average. The melting temperatures of the indicated samples, determined from the disappearance of birefringence in films in polarized light, decrease in proportion to the number of introduced chlorine atoms and agree well with the theoretically predicted values (Fig. 1), calculated from Flory' s equation for crystallizing linear copolymers of irregular structure [5]

$$\frac{1}{T_\mathrm{m}} - \frac{1}{T_\mathrm{m}^0} = -\frac{R}{\Delta H} \ln x_A,$$

where T_m is the melting temperature of the copolymer; T_m^0 is the melting temperature of the pure crystalline homopolymer (in the present case, gutta-percha); ΔH is the molar heat of fusion of gutta-percha, equal to 2030 cal [6];

Fig. 1. Dependence of the melting temperature of gutta-percha on the content of chlorinated units x_B. 1 –experimental data; 2 –theoretical curve calculated from Flory' s equation

Fig. 2. Dependences of the nominal stress on temperature for vulcanized samples of gutta-percha and chlorogutta-percha. 1 –gutta-percha, 2.9% S; 2 –chlorogutta-percha, 7% Cl; 3 –same, 9% Cl; 4 –same, 14.3% Cl (the sulfur content in all chlorinated gutta-percha samples is 2%)

x_A is the mole fraction of units of regular structure, i.e., unchlorinated gutta-percha units.

A certain deviation of the melting temperatures from the theory is associated with the nonequilibrium conditions for determining the melting point for samples

with a noticeable degree of irregularity—at chlorine contents above 8-10%. All these data give grounds for regarding samples of chlorogutta-percha as statistical copolymers of regular units of trans-1,4-polyisoprene and 2-methyl-2,3-dichlorobutadiene, the latter playing the role of "disturbing" units. Above the melting temperature, all these samples, including pure gutta-percha, in the vulcanized state pass into a highly elastic state characteristic of polymers with flexible chains of the polydiene type.

However, a study of the mechanical properties of chlorogutta-percha in the highly elastic state revealed a sharp difference between these samples and pure gutta-percha. Fig. 2 gives data on the dependence of stress at certain constant degrees of extension on temperature for samples of the original gutta-percha containing 2.9% sulfur. These dependences were obtained directly from stress-strain curves recorded at various temperatures. It had first been specially established that, under the stretching conditions adopted by us (low deformation rate, 1 mm/min, and high temperature, 60, 80, 120°), relaxation processes proceed very rapidly, and the magnitude of the stress at a fixed degree of deformation does not change with time. This made it possible, directly in the course of stretching, to record equilibrium stress values for a given degree of elongation. The data obtained agree well with the classical results of Gough (2) on the study of the deformation of vulcanized natural-rubber samples in the highly elastic state, which is characterized by a positive sign of the temperature coefficient of the modulus.

Fig. 3. Change in internal energy and entropy upon stretching gutta-percha and chlorogutta-percha above the melting temperature:
1 —vulcanized gutta-percha, 2.9% S;
2 —vulcanized chlorogutta-percha, 2% S, 7% Cl

Fig. 4. Dependence of deformation on temperature:
1 —gutta-percha; 2 —chlorogutta-percha, 6.5% Cl; 3 —the same, 13.5% Cl

Graphical treatment of these data using equations (1) and (2) made it possible to estimate the change in internal energy and entropy upon stretching. As follows from Fig. 3, indeed, the deformation of pure gutta-percha above the melting temperature is determined almost entirely by the change in entropy. The course of the negative change in entropy upon

during stretching practically coincides with the experimental stretching curve (Fig. 3, f_1), while the change in E is constant and close to zero for all investigated degrees of deformation.

The dependences of the modulus on temperature for chlorinated gutta-percha above the melting point, shown in Fig. 2, have an entirely different form. In an analogous temperature interval, specimens with approximately the same density of the vulcanization network, but containing respectively 7 and 14.3% chlorine, exhibit a negative temperature behavior of the modulus of reversible high-elastic deformation, which is characteristic of solids undergoing deformation with a considerable change in the internal energy of the system. A graphical solution of equations (1) and (2) for a specimen containing 7.9% chlorine gives the curves of the changes in E and S of the system upon deformation, shown in Fig. 3.

It follows from these data that, upon stretching chlorinated gutta-percha by 100%, there occurs, first, a considerable increase in the internal energy of the system and, second, this process proceeds with a positive change in entropy, whereas upon stretching rubber the entropy usually decreases. Thus, pure gutta-percha and its chlorinated analogs behave differently upon deformation in the high-elastic state. Despite the close similarity of their structure and properties within the crystalline state, above the melting point the presence of chlorine atoms in individual units of the polyisoprene chains leads to a sharp change in the mechanical behavior of this polymer. Judging from preliminary data, chlorination does not produce a substantial change in the flexibility of gutta-percha chains: the glass-transition temperatures, determined by the thermomechanical method, rise only slightly, from -55° for pure gutta-percha to -35° for chlorinated gutta-percha containing 13.5% chlorine (Fig. 4).

The results obtained can be explained if it is assumed that in specimens of chlorinated gutta-percha above the melting point there exist certain structures, apparently of a supramolecular character, which impoverish the conformational set of macromolecules and lower the entropy of the system in the unstretched state. Upon stretching to 100% elongation, such structures are destroyed, with a change in internal energy and an increase in entropy. It is possible that it is precisely the units containing chlorine atoms that are a kind of nodes contributing to the stability of such formations.

Further study of the nature of the phenomenon described is currently continuing intensively.

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named after M. V. Lomonosov

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