



Soviet-era science, translated into English

PHYSICS

1963

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Abstract

Full Text

PHYSICS

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STUDY OF ELECTRIC CHARGES ARISING DURING DEFORMATION OF POLYMERS

(Presented by Academician V. A. Kargin on May 9, 1962)

Until now, comparatively few studies have been carried out on electric charges produced during deformation of polymers. The first indications of the possible appearance of charges owing to the piezoelectric properties of anisotropic polymer materials were made as early as in ^(1, 2). Subsequently, however, the piezoeffect was little studied, and the very possibility of such an effect was called into question ⁽³⁾. Later, works primarily by Soviet scientists ^(4, 5) showed that the piezoeffect in polymers can occur both in the case of piezoelectric structures—for example, wood—and in the case of an artificially created electrical anisotropy, an electret state. In the latter case the piezoeffect may arise for two reasons: 1) owing to a change in the polarization vector during deformation (“true piezoeffect”); 2) owing to a change in the distances between the electrodes and the surface of the specimen. The occurrence of electrical polarization under the action of a mechanical field was indicated in ⁽⁶⁾.

We investigated the appearance of electric charges during deformation both of polar polymers—polymethyl methacrylate (PMMA), polyvinyl chloride (PVC)—and of nonpolar polymers—polystyrene (PS), polypropylene (PP), and polyethylene (PE). All polymers were taken in powder form, with the exception of PMMA, which was taken in the form of disks cut from organic glass. The powders were pressed into tablets 10 mm in diameter and 10 mm high at room temperature under a pressure of 1.5 tons. The tablets were then placed between the heated plates of a press and were gradually flattened over 3 h at a temperature of 110°. At the end of the process the samples were compressed at this temperature under a pressure of 100 atm and left in this state until the press cooled to 50°. The resulting plates, approximately 1 mm thick, were tested for the presence of electric charge by the lifting-electrode method ⁽⁷⁾. The distribution of charges over the surface of the specimens was also investigated by means of an instrument with a dynamic capacitor. In this procedure the voltage on the capacitor was determined with an MVL-3 voltmeter; it was proportional to the surface charge density. The specimens were compressed between copper foil, ebonite plates, or acetate film in order to study the influence of the facing on the electric charges produced. In all cases a facing of the same material was placed on both sides of the specimen. PVC specimens were tested both in pure

Fig. 1. Dependence of the surface charge density on the storage time of specimens. 1 –PVC; 2 –PVC 100 parts by weight, DBP 10 parts by weight; 3 –PVC 100 parts by weight, DBP 20 parts by weight; 4 –PMMA; 5 –PS; 6 –PP; 7 –PE.

Figure 1: Fig. 1. Dependence of the surface charge density on the storage time of specimens. 1 –PVC; 2 –PVC 100 parts by weight, DBP 10 parts by weight; 3 –PVC 100 parts by weight, DBP 20 parts by weight; 4 –PMMA; 5 –PS; 6 –PP; 7 –PE.

form (without addition of softeners) and with addition of the plasticizer dibutyl phthalate (DBP). The change in the magnitude of polarization as a function of the storage time of the specimens is shown in Fig. 1.

When the specimens are deformed, causing the material to flow mainly in the radial direction, an electrical polarization arises that is not connected with transfer of electrons or ions from the material of the facings into the polymer—the case considered in ⁽⁸⁾.

Washing the specimens with ether or other electrically conducting solvents removes surface charges formed on the surface for a number of accidental reasons, owing to contact of the specimen with the substrate.

or with other objects (tribocharges), but it does not remove the polarization that arose during deformation. After washing with ether, the magnitude of the charge of one sign on one surface of the specimen corresponds to a charge of the opposite sign and of approximately the same magnitude on the opposite surface of the specimen.

The polarization obtained slowly decreases with time. The rate of decay of the charges is somewhat less than the rate of decay of charges on electrets obtained from the same polymers by the usual method, by applying an external electric field ⁽⁹⁾. The half-decay period of the charge of PVC is approximately 10 days, and for PMMA it is more than a month. The introduction of plasticizers sharply accelerates the process of charge decay (Fig. 1).

The absence of a cooling regime under pressure—removal of the specimens from an uncooled press—reduces the magnitude of the polarization. Preparation of specimens directly from powders usually reduces the magnitude of the polarization in comparison with the polarization of specimens prepared from tablets. The magnitude of the surface charge density ranges from zero to 12 CGSE units. Study of the distribution of the surface charge density over the surface of the specimens (Fig. 2) shows that in all cases regions are formed on one surface with different magnitude and sign of charge, but a charge of one sign at a definite point of the surface corresponds to a charge of the opposite sign and of the same magnitude at the corresponding point on the other surface of the specimen.

Fig. 1. Dependence of the surface charge density on the storage time of

specimens. 1 –PVC; 2 –PVC 100 parts by weight, DBP 10 parts by weight; 3 –PVC 100 parts by weight, DBP 20 parts by weight; 4 –PMMA; 5 –PS; 6 –PP; 7 –PE.

Polarization occurs with any facing; the order of magnitude of the surface charges is approximately the same for all facings.

During deformation of PMMA disks, the molecules of the latter are oriented in the radial direction, owing to which, when the specimen is placed between crossed polaroids, a black cross can be seen which does not change its position upon rotation of the specimen. After heating the specimens without pressure, the latter lose their charges, the radial orientation disappears—the black cross visible in polarized light when viewing PMMA specimens disappears, and shrinkage occurs.

The effect of deformation on the magnitude of the charges formed was investigated. PMMA specimens in the form of cubes $10 \times 10 \times 10$ mm were compressed. As can be seen from Fig. 3, the magnitude of the charge increases sharply with the degree of compression. The cubes were cut from sheet organic glass, the sides of which were marked. After deformation, on one side of the PMMA sheet the total sign of the charge was positive (on 9 specimens out of 10), and on the other it was negative. Such reproduction of the sign of the charge is evidently due to a kind of mechanical memory caused by the technology of manufacturing sheet PMMA.

Thus, on the basis of the data obtained, we may conclude that, as a result of mechanical action on a polymeric material, simultaneously with orientation there occurs polarization in a direction perpendicular to the plane of orientation. Such polarization

is due in polar polymers, possibly, to the fact that, when polymer molecules are oriented in accordance with the direction of the deforming force, the dipoles—polar groupings—are oriented in the perpendicular direction^{6,10}. Cooling in the compressed state leads to the fact that the polymer molecules do not have time to become disoriented, and we can measure the resulting electric polarization. Factors that accelerate the disorientation of dipoles (cooling without pressure, introduction of plasticizers) accelerate the decay of electric polarization. The presence of a predominant direction of polarization in specimens as a whole is evidently caused in many experiments by the inhomogeneity of application of the mechanical load and by the large magnitude of the deformation, and leads to the conclusion that large magnitudes of polarization can be obtained mechanically, and that “mechanoelectrets” can be created with their subsequent use as ordinary electrets. The appearance of electric charges of the type described above is evidently possible in many cases of technological operations and mechanical processing of polymers, including when polymers are attached to metals or other materials.

Fig. 2. Distribution of the surface charge density over the surface of a PMMA specimen (in units of the MVL-3 scale)

On the basis of the data obtained, the following conclusions may be drawn:

1. As a result of the action of a mechanical field on polymeric materials, simultaneously with mechanical orientation, electric polarization of the electret type also arises.
2. Factors contributing to the preservation of a mechanically oriented structure also contribute to the preservation of electric polarization, and conversely.
3. Artificially induced asymmetry in the application of a mechanical field can lead to the production of “mechanoelectrets” —electrets obtained without polarization in an electric field.

Fig. 3. Dependence of the magnitude of the charge Q on the degree of compression: h is the height of the PMMA cube after deformation; initial height 10 mm

4. The piezoelectricity of polymeric materials may be due to polarization of the type described, since every electret is at the same time also a piezoelectric ¹¹.

Moscow Institute of Fine Chemical Technology
named after M. V. Lomonosov

Received
3 V 1962

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