Within the limits of experimental accuracy, the data obtained agree with those of [6] (at atmospheric pressure) and with calculated values obtained from the thermal equation.

NOTATION

C_p, isobaric specific heat, J/kg·deg K; v, specific volume of material studied, m^3/kg; V, volume of material studied heated by internal heat source, m^3; $b = \Delta t/\Delta\tau$, heating rate at specified temperature, deg K/sec; W, inner heater power, W; W', correction for thermal loss, W; C_1, ballast heat capacity of measurement cell at given temperature, J/deg K; e, emf; t, temperature °C; T, thermodynamic temperature, °K; R, universal gas constant, J/kg·deg K; P, pressure, MPa; τ, time, sec.

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APPARATUS AND METHOD TO DETERMINE THE ANISOTROPIC STATE OF ORIENTED POLYMER MATERIALS BY MEANS OF THERMOPHYSICAL PARAMETERS

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A method and apparatus are proposed for the determination of the heat-conduction anisotropy of oriented film materials. Experimental results on realization of the method are presented.

The technological processes to obtain film materials are related to the action of high temperature, pressure, and shear stress on polymer systems [1], which is accompanied by strain and orientation of the structural elements contributing to the origination of an anisotropic oriented state [2].

However, in a number of cases such a state results in obtaining oriented film materials with unstable physicomechanical properties and high shrinkage. These phenomena are associated with the incompleteness of the relaxation processes [3] in such systems and the origination of significant internal stresses [4].

In this connection, the development of methods to determine the degree of film orientation as a function of different technological factors is of great practical value.

The degree of polymer film orientation is usually estimated by the value of their birefringence [5] and by an acoustic method [6]. However, the results obtained by these methods do not always uniquely characterize the degree of orientation of the structural elements.

It is shown in this paper that a very promising method, which permits the determination of the degree of film material orientation as a function of different technological factors,

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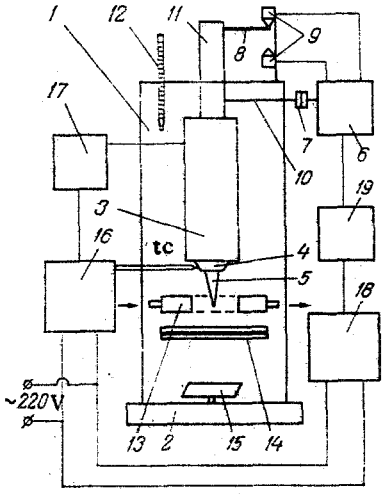

Fig. 1. Diagram of the apparatus to determine the anisotropic state of oriented polymer materials.

is the method of determining the heat-conduction anisotropy. Its crux is to measure the ratio between the heat conduction in two mutually perpendicular directions. This method has been used earlier to study the anisotropic properties of block polymers which differ significantly in structure and properties from film materials [7]; the measurement in two mutually perpendicular directions was here realized in different specimens.

We proposed a method and construction of an instrument to study the anisotropic state of oriented, comparatively thin (50-200 μm) polymer films from one test.

Underlying the construction of the instrument is a method with a point heat source, which permits measurement of the heat-conduction anisotropy in one specimen [8]. A characteristic feature of this method is the fact that the melted domain takes on the shape of an ellipse under the effect of a point heat source perpendicular to the plane of the anisotropic specimen because of the dissimilar heat propagation velocities in the two mutually perpendicular directions. The anisotropy of the material is estimated by the relationship of the thermophysical characteristics in these directions, and can be defined as the ratio of the magnitudes of the principal axes of the ellipse [9].

The diagram of the experimental apparatus is represented in Fig. 1. The instrument consists of an assembled metal housing 1 with six side windows, four of which (the upper) are closed by shutters. The housing is mounted on the base 2 with two adjuster bolts and a level. Within the housing is a heating element 3 of 100-W power provided with a 10-mm-diameter copper rod 4, in the lower part of which are a conical needle 5 and a calked-in Chromel–Copel thermocouple (tc) with 0.2-mm thermoelectrode diameter. The point heat source is fixed relative to the specimen by using a DSDR-2 reversing electric motor with the gear 6, clutch 7, spring, a thrust bearing set in ebonite, a spring grip 8, whose upper and lower position is constrained by microswitches 9, a shaft 10 with a gear seated rigidly on it, a micromodular rack mounted on the moving rod 11 of the heating element. The temperature in the chamber was measured by thermometer 12. A ring-type refrigerator 13, whose base is a protective shield against radiative heat fluxes in the specimen, is used to cool the specimen. A cassette unit 14 for the specimens and a flat mirror reflector 15 are in the lower part of the instrument.

The method of conducting the experiment is the following. Prepared 50-200-μm-thick 10 × 15 mm specimens are set in the holder on the cassette unit support (if specimens of less thickness are used in the experiment, then thin-layered coatings of a melting thermal indicator are deposited on them). Then a cooling agent (water) is delivered to the refrigerator and the heating element is connected by a "network" tumbler through the electronic potentiometer ÉPR-09 16 and the laboratory LATR autotransformer 17. The presence of the LATR in the circuit permits setting and maintaining the heating element temperature to a high degree of accuracy. The temperature is checked by the thermocouple connected to the potentiometer, on whose scale the given test temperature is set. Upon reaching this temperature, which exceeds the melting point of the specimen under investigation by about 10-12°C, the specimen is inserted into the working zone of the instrument, and the "start" button of the control module 18 (Fig. 2) through the step-down transformer TBS-3 19 connects an electric motor, which delivers the heating element with the needle to the specimen at a 2 rpm rate from up to down through a clutch and a micromodular rack toothing. The time of specimen contact with the

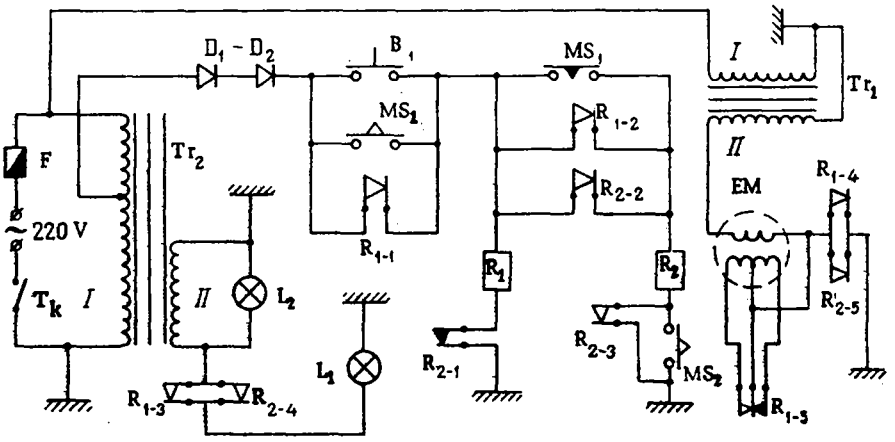

Fig. 2. Electrical circuit diagram of the control module: Tr_1) TVS-24 reducing transformer to supply the DSDR-2 electric motor; Tr_2) power autotransformer for control-module supply; EM) DSDR-2 electric motor; R_1, R_2) dc RPN-22 relays to switch the direction of electric motor rotation; R_{1-1}, R_{1-2}, R_{1-3}, R_{1-4}, R_{1-5} and R_{2-1}, R_{2-2}, R_{2-3}, R_{2-4}, R_{2-5}) relay contacts of R_1 and R_2, respectively; D_1, D_2) D7D rectifier diodes; T_k) TM-2 tumbler for switching the control module; MS_1, MS_2) upper and lower MP-5 microswitches to switch electric motor rotation; B_1) electric motor "start" button; L_1, L_2) 6.3 V signal lamps for the connection of the control module and electric motor, respectively; F) 1-A fuse.

needle is 3 sec. Then the lower microswitch closes and the electric motor is automatically switched to the reverse path. The heating element with the needle, having been moved to the initial position, closes the upper microswitch, here disconnecting the electric motor. The specimen is later removed from the working zone of the instrument, removed from the holder, and the results obtained are counted. The test duration is 10 min. The error in measuring the heat-conduction anisotropy did not exceed 2.5%.

The simplicity of the method, the adequate accuracy, and the possibility of determining the anisotropy for different polymer materials in one specimen in one test in a comparatively brief time interval permit its being recommended to estimate and study the degree of orientation of polymer films, coatings, and other materials in laboratory or factory practice, as well as for the technological control of production.

The kinetics of drawing PETF (polyethylene terephthalate) specimens was studied by using the method described.

The dependence of the heat-conduction anisotropy of films obtained from amorphous PETF specimens on the degree of uniaxial tension is represented in Fig. 3 (curve 1).

It is seen that an intense rise in the anisotropy of the film heat conduction is observed as the degree of drawing increases. The most abrupt rise in the heat-conduction anisotropy is here detected for small degrees of drawing (K = 1.5-2.0). As the drawing increases further to K = 2.5-3.5, the anisotropy in the film heat conduction does not change substantially.

It would be interesting to clarify the influence of additional orientation (additional drawing), used for a more significant increase in the physicomechanical properties of prestrained materials [10], on the heat-conduction anisotropy of PETF films. To this end, the polyethylene terephthalate specimens, prestrained to K = 2.0 and held for 1 month at room temperature in the free state, were repeatedly subjected to uniaxial tension (K_{fin} = 5.0) under conditions analogous to the initial film orientation process. It is seen from Fig. 3 (curve 2) that the heat-conduction anisotropy rises as the degree of additional drawing of the PETF films increases, and grows by 10-13% in the final stage of additional orientation as compared with the uniaxially oriented films without additional drawing.

The apparatus was also used to study the influence of different technological modes to obtain film materials on the degree of their orientation.

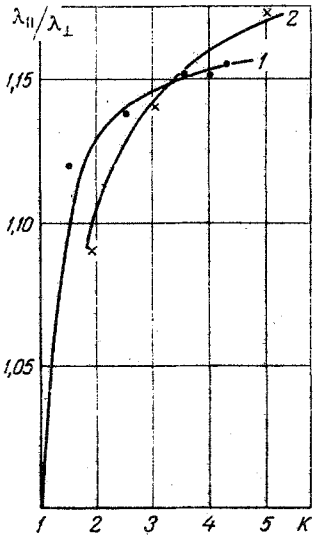

Fig. 3

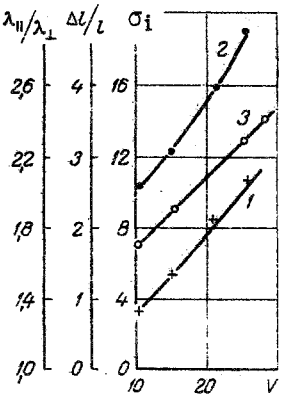

Fig. 4

Fig. 3. Dependence of the change in heat-conduction anisotropy ($\lambda_{\parallel}/\lambda_{\perp}$) on the degree of uniaxial tension (K) of PETF specimens (curve 1) and those stretched preliminarily to K = 2.0 and held in the free state (curve 2).

Fig. 4. Change in the heat-conduction anisotropy $\lambda_{\parallel}/\lambda_{\perp}$, (1), internal stresses σ_i, kgf/cm^2 (2), and shrinkage $\Delta l/l$, % (3), as a function of the rate of obtaining the polyethylene films V, m/sec.

Data on the change in heat-conduction anisotropy, internal stresses, and shrinkage as a function of the rate of obtaining polyethylene films on an extrusion machine are presented in Fig. 4. The internal stresses were estimated by a polarization optics method [11]. As is seen from the figure, the degree of orientation grows abruptly as the rate of obtaining the films increases. A direct interconnection exists here between the degree of orientation and the internal stresses. The incompleteness of the relaxation processes, which causes the abrupt growth of internal stresses with the increase in orientation, results in obtaining material with unstable physicomechanical properties and considerable shrinkage during exploitation.

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