



Mullins effect in polymer large deformation strain gauges

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Abstract

The possibility of making strain gauges with high sensitivity to changes in mechanical stress based on hard elastic films of isotactic polypropylene, with thixotropic polymer softening during cyclic deformation (Patrikeev-Mullins effect) and the “dry crazing” effect, is studied. Three options of rigid elastic film preparation using isotactic polypropylene for successive deposition of an adhesive layer of a solution of macromolecular compounds and an electrically conductive layer of a graphite dispersion are proposed. The optimal order of operations for manufacturing electrical sensors with high sensitivity to changes in mechanical stress has been established, including preliminary cyclic deformation in the air to form open micropores as a result of “dry crazing”. A mathematical model has been developed, which predicts the mechanical stress and/or the change in mechanical stress of film strain gauges based on the change in the electrical resistance of the conductive layer in the 6–35% strain range with up to 700 relative strain sensitivity.

Keywords Mullins effect · Dry crazing · Strain gauge · Polypropylene · Conductive layer

Introduction

Reversible tensile strains of polymer films, sheets, or fibers, reaching several hundred percent elongation, which can be repeated many times without destruction, are characteristic of spatially cross-linked high-molecular compounds – thermoplastics, which are in a highly elastic state. Known thermoplastic high-molecular compounds belong to the group of soft elastomers, which are easily deformed with little mechanical stress, i.e. have a small initial modulus (M_0) and a monotonically increasing tensile stress up to a relative elongation of 10%, 50%, 100%, and 200% ($M_0 < M_{10} < M_{50} < M_{100} < M_{200}$). As a rule, these materials are isotropic, incompressible, and do not change their density when stretched.

At the end of the twentieth century, anisotropic fibers and films with anomalous deformation properties were obtained by melt extrusion of crystallizing thermoplastics with a high degree of spin draw and its subsequent isometric annealing, called rigid elastics [1–4]. The anomaly of the mechanical properties of rigid elastics consists of a high modulus of elasticity at the beginning of stretching, M_0 , and a negligible increase in stress upon subsequent stretching to a certain elongation limit, which can be more than a hundred percent. Anisotropic materials made of rigid elastics, when stretched along the direction of preferred orientation, are reversibly deformed to significant elongation without necking. The elasticity of thermoplastic materials is achieved due to certain features of the macromolecules' structure, which determine a high degree of crystallinity and the following conditions for the production of films by slot extrusion of the melt [5]:

- a rapid flow of the extrudate through the slot die;
- the ability of the polymer to crystallize with the formation of a system of parallel lamellae;
- unidirectional orientation of the lamellae structure;
- contact uniform cooling of the film after spinneret drawing on a metal cylinder with temperature control.

Isotactic polypropylene meets these requirements. Hard-elastic “spring” films made from polypropylene were first

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obtained and comprehensively studied. It has been established that during melt extrusion with accelerated spinneret drawing, polypropylene crystallization nuclei are located along the orientation direction, while crystallites grow in a perpendicular direction. The supramolecular structure of a hard elastic “spring” film has a central rod, which is formed by extremely elongated fibrillar elements, on which parallel folded lamellae are formed perpendicular to the stretching direction [2].

When the films are stretched, the lamellae move in the direction of mechanical stress, and the space between them can be filled with a liquid substance in contact with the surface due to atmospheric pressure and wetting forces. A new porous composite material is formed with a huge developed interfacial surface stabilized by an adsorption-active liquid [3]. The properties of a liquid solution or dispersion in contact with the surface of a deformed rigid elastic film determine the composite material's surface properties. If the liquid or dispersion is electrically conductive, then the composite material will be electrically conductive.

To assess the possibility of obtaining electrically conductive materials based on polymers in a rigid elastic state and the prospects for their practical applications, one should compare different production technologies and quantitative data of the electrical resistance change in polymer composites (the GF coefficient) during deformation presented in review papers [6, 7]. The composition of ingredients, production methods, and the ability to change the electrical conductivity of materials during deformation determine various options and areas of their practical applications, for example, as indicators of the destruction of power parts made of glass and organic plastics, strain gauges in shock absorbers, gauges of local deformations in sports and medicine, elements of flexible electronics, robotics, aviation, and mechanical engineering, as well as in systems for automatic servicing of air passengers during baggage handling [8].

The article [9] proposes an original method for in situ polymerization of polyurethane foam with the simultaneous production of a polymer with electrically conductive fillers. A porous composite electrically conductive material is obtained by coating the surface of foam bubbles with silver nanoparticles during the synthesis of polyurethane foam from 3,4-ethylene dioxithiophene. This material is proposed to be used for the production of flexible bending and compression strain gauges for detecting small human movements. Flexible pressure sensors have an ultra-high sensitivity to mechanical stress during compression and bending of about 3 kPa^{-1} [9].

To increase the electrical conductivity of elastic polymeric dielectrics, the processes of the screen, inkjet, and aerosol inkjet printing of sensors of various shapes using electrically conductive liquid compositions (inks) are used. These conductive polymer prints on films with a specific

electrical conductivity of up to $1,000 \text{ } \Omega/\text{cm}$ provide monitoring of the deformation and failure of rigid composites and have been proposed as indicators of failure of glass-reinforced plastics in aircraft construction [10].

The combination of the aerosol deposition of electrically conductive compositions on polymer films in an active solvent (plasticizer), followed by film deformation and drying, makes it possible to obtain stable electrically conductive materials with high sensitivity to repeated stretching. In [11], multi-walled carbon nanotubes (MWCNTs-ODA) modified with *n*-octadecylamine in tetrahydrofuran were deposited on the surface of a pre-stretched elastic film made of (ethylene-butylene)-*b*-polystyrene (SEBS) copolymer. Tetrahydrofuran is a solvent and plasticizer for styrene copolymers. The authors systematically studied the structure and properties of sensors and the amount of deformation of an elastic polymer film at the time of aerosol application. It is shown that if the pretension strain was less than 50%, then the nanotubes do not cover the film with a dense layer and the resulting layered composite has low electrical conductivity. With an increase in the pretension strain to 100% and contraction after the deposition of an aerosol, densely accumulated clusters with optimal electrical conductivity were formed on the surface.

A tensile strain sensor based on electrically conductive elastic composites formed in an arbitrary form (with the desired geometry) by screen printing was obtained from a mixture of silver-coated polystyrene spheres (PS@Ag) and liquid polydimethylsiloxane (PDMS) [12]. In the 0–10% strain range, it has a high strain sensitivity. For example, at 10–60% strain, the calibration factor GF is equal to 6, and at 60–80% strain, it increases to 78.6.

A simple method has been developed for obtaining an electrically conductive material (web) coated with carbon nanotubes (CNTs) by microdissolving the surface layer of polyester fibers using polyester fabric as an example. The microdissolved layer of a macromolecular substance becomes sticky and acts as an adhesive agent for creating a strong immobilization of CNTs on the surface of the filaments [13]. A similar method of CNT immobilization on the surface of a flexible polymer film by the sticky adhesion of solid particles is implemented in [14] by successive deposition of liquid PDMS on the surface of a rigid polymer substrate and deposition of single-walled carbon nanotubes (SWCNT). PDMS is used as a viscous adhesive to firmly immobilize nanotubes on the film surface.

A set of hybrid composite materials based on a polypropylene matrix with a binary filler mixture of multi-walled CNTs and clay particles was obtained and characterized [15]. The authors found a synergistic effect of viscoelastic response to the stretching of polypropylene materials containing binary filler (CNTs and clay). The synergistic effect may be due to the additional so-called “cold” crystallization of polypropylene on the surface of active fillers [16].

The choice of polymeric materials for sensors of large tensile strains and the method of connecting electrically conductive substances with solid elastomers is a very difficult technological task complicated by the manifestation of the Patrikeev-Mullins effect [17–20]. The Patrikeev-Mullins effect consists of a significant (more than 50–80%) reduction in the modulus ($M_0 \gg M_{10} \leq M_{50} \leq M_{100}$) and mechanical stress in the material during repeated stretching following the first cycle of reversible deformation. This effect violates the unambiguous relationship between the electrical conductivity of the material and mechanical stress, which is necessary for the correct use of strain gauges.

Until now, the Patrikeev-Mullins effect has been the object of intensive theoretical and experimental research. In scientific publications devoted to the problems of mechanics and structure of deformed materials of organic [17, 18] and inorganic nature [21–25], there is no consensus on the nature of this phenomenon.

It is known that the Patrikeev-Mullins effect negatively affects the performance of technical parts, for example, anti-vibration systems made of silicone rubber. The compliance of anti-vibration machine parts changes significantly after the first deformation cycles. To partially eliminate the negative effect (75%), a procedure of three loading/unloading cycles of parts is applied before they are installed. To achieve 95% accuracy in stabilizing the deformation properties of elastic materials, it is proposed to carry out seven loading and unloading cycles [26].

The manifestation of the effect during the deformation of hard elastic films made of crystallizing thermoplastics, including films with high internal stresses and “shape memory”, has a number of structural features [20, 27–32] that complicate mathematical modeling, prediction, and practical use of the mechanical properties of layered film composites obtained by cyclic deformation in contact with liquid dispersions.

To mathematically describe the deformation of elastomers, molecular models of the nonlinear elasticity of polymer networks have been developed [33]. The mathematical description of the deformation of solid amorphous and crystalline polymers takes into account two mechanisms of localized deformations: shear compliance and crazing. Depending on the sensitivity of the polymers to crack formation, crack nucleation occurs at the beginning of film stretching at low elongations during elastic deformation [34].

Modeling methods are used to describe the processes of mixing dissimilar ingredients to prepare polymer composites and predict their electrical properties [35–37]. This study uses mathematical modeling for the quantitative description of layered strain gauges with the Patrikeev-Mullins effect in a gas and liquid medium, ensuring their high sensitivity to changes in mechanical stress at large strains.

Materials and methods

A hard-elastic film of isotactic polypropylene (3 g/10 min melt flow index and 77–79% degree of crystallinity) was used as a substrate for strain gauges, which was obtained by the slot extrusion of the melt with 6–8-fold spunbond drawing at the time of extrusion, followed by isometric heat treatment by processing the extrudate in a roll at 140 ± 5 °C. Film thickness after heat treatment is 0.34 ± 0.05 mm. The tensile strength of the film is 55 ± 5.4 MPa, and the failure strain is $600 \pm 15\%$.

As an adhesive for fixing the electrically conductive dispersion of graphite on the polymer film, a solution of an ethylene-vinyl acetate copolymer in *o*-xylene, commercially available in an aerosol can, Tesa 60150 brand (solution #1) and/or a solution of a styrene-butadiene-isoprene copolymer in commercially produced styrene was used, along with the aerosol Krylon 7777-SuperQuickGripSprayAdhesive, USA (solution #2). As an electrically conductive dispersion, we used a dispersion of graphite with polytetrafluoroethylene (PTFE) in propanol-2 of industrial production in an aerosol package, GRAPHIT 33/200 brand.

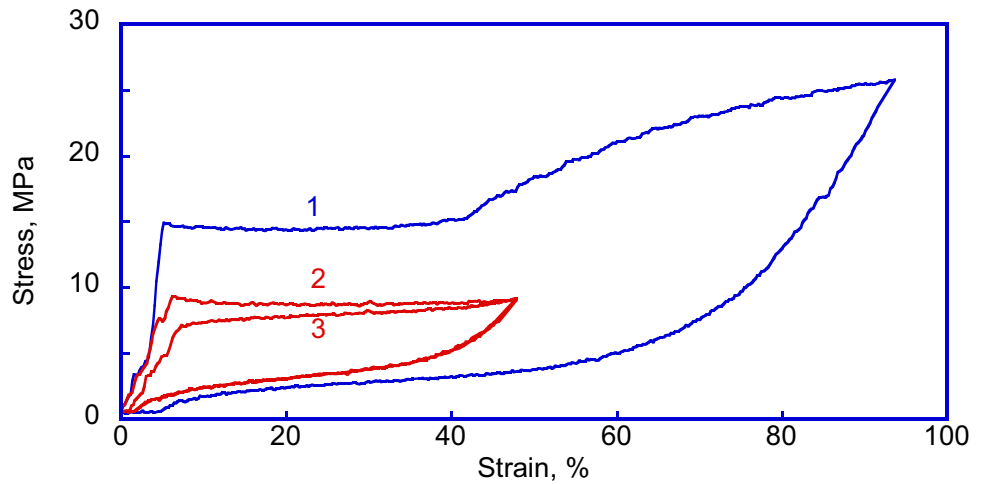
The deformation of a hard elastic polypropylene film and the successive application of solutions of macromolecular compounds and dispersions were carried out using three options in the following order.

Option 1. A hard-elastic film of isotactic polypropylene is initially stretched in the air to a 50% relative strain to form an open porous structure with a maximum volume of pores and voids [22]. Then an adhesive is applied to the stretched film in a stressed state—solution #1 of a high molecular compound in a volatile solvent and an electrically conductive dispersion of graphite by spraying from an aerosol can. The film was reduced to its original size and dried to constant weight. After drying, copper foil electrodes are applied to the film and a bridge circuit is assembled to measure the resistance of the strain gauge during stretching.

Option 2. The second type of strain gauge was obtained as follows. A solution of a high molecular weight compound in a volatile solvent was applied to a hard elastic film of isotactic polypropylene from an aerosol package of adhesive #2. The film with a liquid layer spontaneously contracted and dried to a constant weight.

Option 3. The third option was carried out as follows. A hard elastic film of isotactic polypropylene was cyclically deformed by 100% in the air (curve 1 in Fig. 1) to form open micropores and thixotropic softening of the structure, i.e., to implement the Patrikeev-Mullins effect. After repeated cyclic deformation, a solution of a high molecular compound #1 in a volatile solvent and an electrically conductive graphite dispersion were applied to the film in a stressed state at 50% strain by spraying from an aerosol package. The film was reduced to its original size and dried to constant weight.

Fig. 1 Stress–strain curves of cyclic hard elastic polypropylene film stretching (1) and layered film strain gauges according to preparation options 2 and 3, respectively



Unitless strain gauge factor GF is calculated as:

$$GF = \frac{\Delta R/R_0}{\Delta l/l_0} \quad (1)$$

Here, R_0 is the initial resistance of the strain sensor, ΔR is the relative change in resistance during deformation, l_0 is the initial length of the sensor, and Δl is the specimen elongation. The sensor strain sensitivity to mechanical stress Q is calculated as:

$$Q = \frac{\Delta R/R_0}{\Delta \sigma} [\text{Pa}^{-1}] \quad (2)$$

Here, R_0 is the initial resistance of the sensors, ΔR is the change in resistance during deformation, and $\Delta \sigma$ is the increase in stress, respectively.

The dimensionless coefficient of strain gauge sensitivity to mechanical stress (ΘF) by analogy with the strain gauge sensitivity coefficient to strain under tension (GF) is calculated as:

$$\Theta F = \frac{\Delta R/R_0}{\Delta \sigma/\sigma} \quad (3)$$

Here, R_0 is the initial resistance of the sensors, ΔR is the change in resistance during deformation, σ is the initial stress value, and $\Delta \sigma$ is the increase in stress, respectively.

Results and discussion

In the study of the optical properties and transparency of hard elastic polypropylene films, the loosening of the structure and the formation of many open micropores and voids exposed to the environment were established [3, 20]. Under cyclic tensile and compressive deformations of films, the voids repeatedly open and close. In

this case, the Patrikeev-Mullins effect manifests itself, high reversibility of deformation is ensured, and the pliability of the polymer changes significantly. The opening of micropores on the surface of films can be used to introduce substances from the environment into the bulk of the polymer and, in particular, adhesive compositions for fixing the electrically conductive layer. However, when a polymer is exposed to an active wetting liquid, a significant change in its mechanical properties is possible, which negatively affects its elasticity and reduces reversible deformation (Fig. 2).

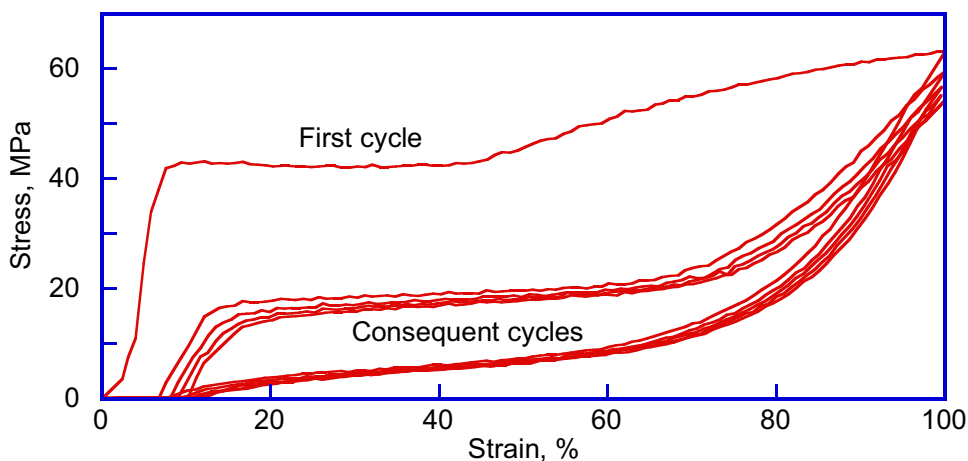
To quantify the possible effects of liquid adhesive compositions on the deformation properties of films, we studied the dependence of changes in the mechanical properties of layered composites on the deformation history of films and the order of operations for applying adhesive solutions of macromolecular compounds and liquid compositions containing electrically conductive particles. The investigated samples of layered composites—polymer sensors of large deformations consist of several thin layers of polymer composites, inextricably linked by adhesion forces (Fig. 3).

Layers of adhesives and an electrically conductive composition of graphite are typical plastic materials with a rheology characteristic of a viscous fluid. To describe the stereometry of plastic deformation of a layer of an electrically conductive composition containing graphite, we consider the scheme of stretching to the degree of elongation λ of an elementary volume of material of constant density (incompressible and not loosening) in form of a cube with a side equal to 1 (Fig. 4).

$$v = \text{const} = 1 \text{ m}^3 = h \times b \times l = S_0 \times l \quad (4)$$

$$S_0 = 1 \times 1 = 1 \text{ m}^2 \quad (5)$$

Fig. 2 Cyclic stress–strain curves of a film of hard elastic polypropylene in the air before applying solutions and aerosol according to preparation option 3



$$\lambda = \frac{l_\lambda}{l_0}; \tag{6}$$

$$S_\lambda = n_i \times b_i \tag{7}$$

$$l_\lambda = l_0 \times \lambda = \lambda \tag{8}$$

$$S_\lambda = \frac{v}{l_\lambda} = \frac{1}{\lambda} \tag{9}$$

Since the electrical resistance of the conductor, R is determined by the electrical conductivity ρ , length l , and cross-sectional size S_λ , then the dependence of the electrical resistance of the layer on the degree of elongation of the film sensor λ will have the form:

$$R = \frac{\rho}{S} \tag{10}$$

$$R_\lambda = \rho \times \frac{\lambda}{1/\lambda} \rho \lambda^2 \tag{11}$$

To determine the mechanical characteristics of the substrate polymeric materials with the Patrikeev-Mullins effect, a standard test of a hard-elastic film of isotactic polypropylene in the form of tapes for tension at a constant speed of 200 mm/min was used in Fig. 2. The most adequate trend equations for the mathematical description of the dependence of stress on the films' strain in various ranges were obtained in the characteristic areas of tension and contraction in Fig. 5.

To approximate the experimental data, we used the equations of the trend lines: a straight line (Eq. 12) and a second-order polynomial (Eq. 13) of the following forms:

$$\sigma = k\varepsilon_1 + b_1 \tag{12}$$

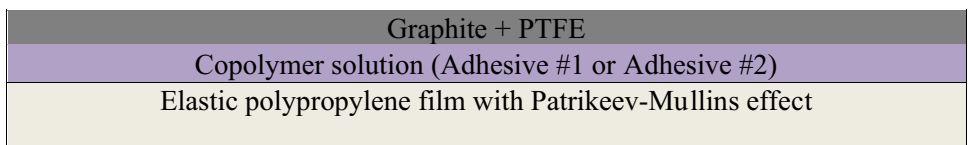
$$\sigma = k_2\varepsilon_2^2 + b_2 \tag{13}$$

Here, k_1 is the modulus of quasi-elasticity of the film, and k_2 , b_1 , and b_2 are constants.

The quantitative characteristics of film sensors obtained by various options for applying layers of macromolecular compounds and graphite dispersion are presented in Table 1. In options 1 and 3 with the stage of preliminary deformation of the film in air, the Patrikeev-Mullins effect is realized by the mechanism of “dry crazing” of the polymer crystal structure, and option 2 is realized by the mechanism of “crazing of the polymer structure in contact with the liquid”. The peculiarity of “crazing in contact with a liquid” is the absorption of a solution of a high-molecular compound by a polypropylene film and local softening (plasticization) of the fibrillar structure of the polymer by the solvent. The polypropylene film prepared for testing the electrical conductivity of the strain gauge according to option 2 has the modulus of quasi-elasticity with a minus sign in the linear stretch section from 6% to 35% and it is not advisable to use it as strain gauge substrates.

Of greatest interest is the option of mechanical preparation of films before applying a layer of an electrically conductive composition, as a result of which the linear dependence of stress on strain has a coefficient $k > 0$. For

Fig. 3 The layout of layers in polymer large deformation strain gauges



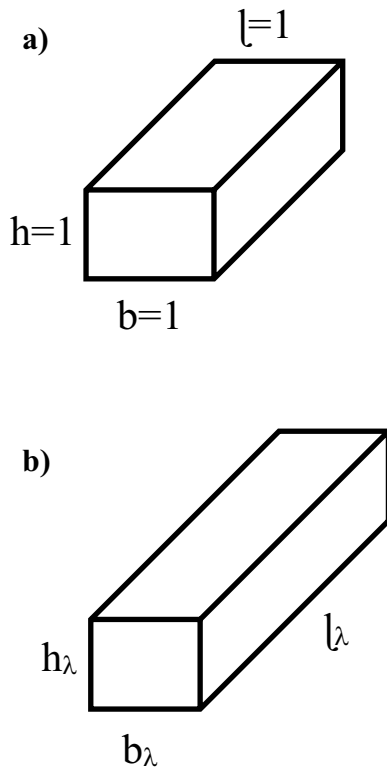


Fig. 4 Schematics of sample **a** before and **b** after deformation

example, in options of mechanical modification of the structure of films 1 and 3, including the stage of preliminary stretching of the film in air and application of a copolymer solution in a stressed state, the range of subsequent deformations is about 35% with a 0.0128-0.019 film modulus of quasi-elasticity.

To determine the specific electrical conductivity of a polymer composition containing a dispersion of graphite (ρ),

necessary for constructing a mathematical model of specific strain gauges, the resistance of the composition layer on a pliable base was measured in the 0–60% strain range in Fig. 6. The specific electrical conductivity of the layered version of the polymer composition “polypropylene—filler”, obtained by applying graphite to the film, exceeds the electrical conductivity of the composition obtained by mixing the polymer melt with nanotubes [37].

Mathematical model of a polymer layered sensor

To obtain an analytical expression for the dependence of the resistance of the composite layer $\Delta R/R_0$ on the mechanical stress in the substrate of a strain gauge made of a modified hard elastic polymer film, we consider the dependence of the stress σ on the relative elongation ϵ (Fig. 7) and the change (relative increase) in the electrical resistance of the deformable electrically conductive layer $\Delta R/R_0$, rigidly associated with a deformable dielectric (Fig. 8). In this case, the purpose of the transformations is from two functional dependencies $\sigma = f(\epsilon)$ and $\Delta R/R_0 = F(\epsilon)$ to obtain $\sigma = \sigma(R) = \sigma(\epsilon^{-1}(R))$, where $\epsilon^{-1}(R)$ is the function inverse to $R(\epsilon)$. The most important thing, in this case, is the establishment of the $\epsilon = \epsilon(R)$ dependence, since the inversion of the functional dependence requires the fulfillment of certain conditions such as monotonicity, convexity, etc. In accordance with the available experimental data (Fig. 5), we will assume that the dependence $\sigma(\epsilon)$ is linear in a certain range of ϵ .

At the same time, it is obvious that $\sigma(\epsilon) = k(\epsilon - \epsilon_0) + \sigma_0$, $\sigma(\epsilon) = k\epsilon - k\epsilon_0 + \sigma_0$ and $k = \frac{\sigma_1 - \sigma_0}{\epsilon_1 - \epsilon_0}$, $\epsilon_0 \leq \epsilon \leq \epsilon_1$. The theoretical dependence $\Delta R/R_0 = F(\epsilon)$ is approximated by a quadratic function based on the calculation of the resistance

Fig. 5 Engineering stress–strain curves of characteristic sections of the cyclic deformation of the film sensor (Option 1) with the Patrikeev-Mullins effect

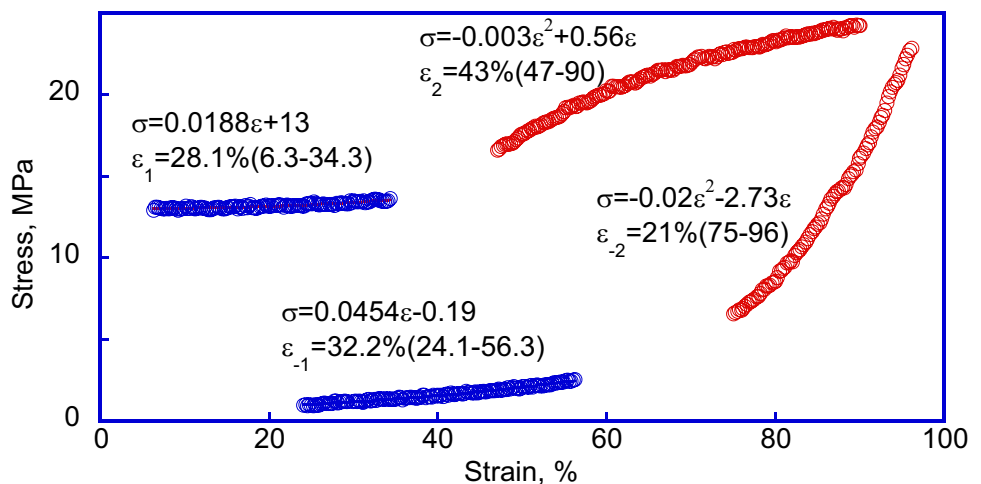


Table 1 Schematics of a polymer film preparation and applying a, b, and c layers. Options 1, 2, and 3 of the polypropylene film deformation before applying the adhesive (solutions of macromolecular com-

pounds) and the layer of electrically conductive composition (graphite dispersion)

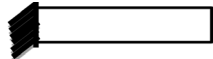
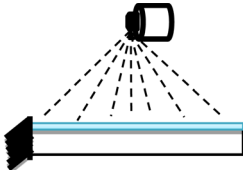
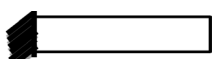
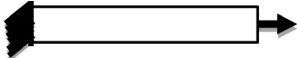

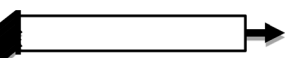
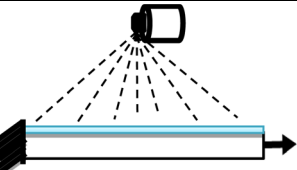

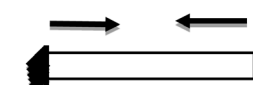
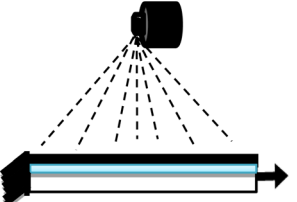
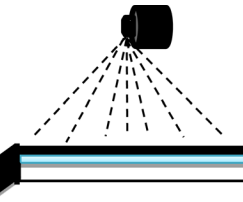
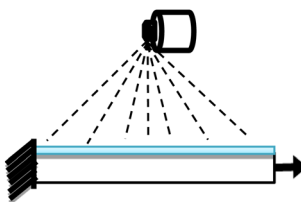


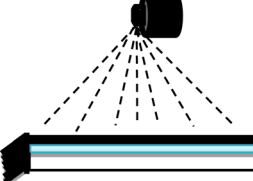



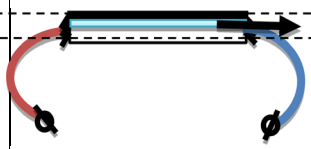
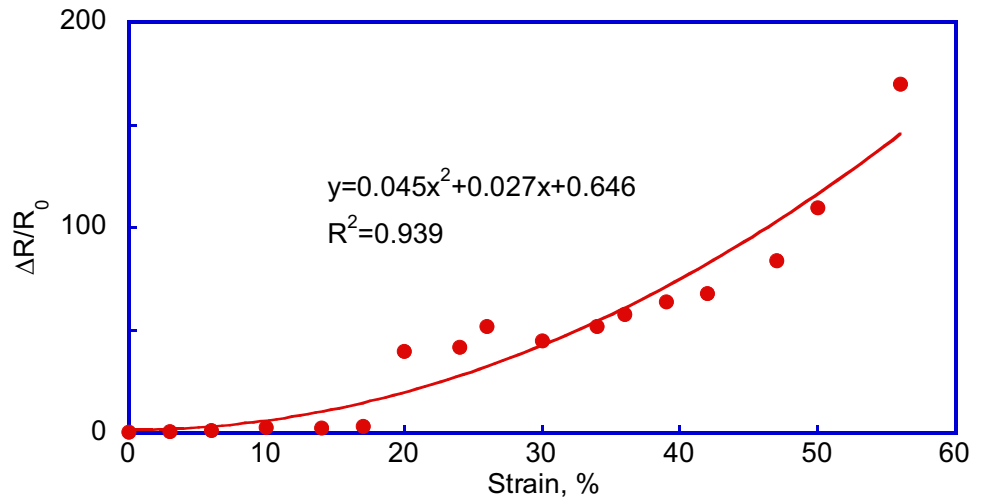
Stage #	1 st Option (Dry crazing)	2 nd Option (Crazing in liquid)	3 rd Option (Dry crazing)
1			
2			
3			
4			
5			
6			
7			
Strain range	28-52%	33.5-55.5%	34.5-55.5%
Modulus of quasi-elasticity, k_1	0.019-0.045	-0.0014-0.0478	0.0128-0.048

Fig. 6 Relative change in the electrical resistance of the composition layer with a graphite dispersion on a polymer substrate under tension



of an elementary volume of a conductive substance during plastic deformation without changing its density.

Let us assume that $R(\epsilon) = a\epsilon^2 + b\epsilon + c$, and find the coefficients a, b, c . The figure shows that

$$\begin{cases} a\epsilon_0^2 + b\epsilon_0 + c = R_0, \\ a\epsilon_1^2 + b\epsilon_1 + c = R_1, \\ a\epsilon_2^2 + b\epsilon_2 + c = R_2. \end{cases} \quad (14)$$

The coefficients a, b , and c are found as a solution to this system of linear algebraic equations. For example, according to Cramer's formulas:

$$\Delta = \begin{vmatrix} \epsilon_0^2 & \epsilon_0 & 1 \\ \epsilon_1^2 & \epsilon_1 & 1 \\ \epsilon_2^2 & \epsilon_2 & 1 \end{vmatrix}, a = \frac{1}{\Delta} \cdot \begin{vmatrix} R_0 & \epsilon_0 & 1 \\ R_1 & \epsilon_1 & 1 \\ R_2 & \epsilon_2 & 1 \end{vmatrix}, \quad (15)$$

$$b = \frac{1}{\Delta} \cdot \begin{vmatrix} \epsilon_0^2 & R_0 & 1 \\ \epsilon_1^2 & R_1 & 1 \\ \epsilon_2^2 & R_2 & 1 \end{vmatrix}, c = \frac{1}{\Delta} \cdot \begin{vmatrix} \epsilon_0^2 & \epsilon_0 & R_1 \\ \epsilon_1^2 & \epsilon_1 & R_2 \\ \epsilon_2^2 & \epsilon_2 & R_3 \end{vmatrix}$$

From the equation, $a\epsilon^2 + b\epsilon + (c - R) = 0$ one can get the dependence

$$\epsilon(R) = \frac{-b + \sqrt{b^2 - 4a(c - R)}}{2a} = -\frac{b}{2a} + \sqrt{\frac{b^2}{4a^2} - \frac{c - R}{a}} \quad (16)$$

We do not take into account the second root of the quadratic equation, since it leads to a dependence devoid of physical meaning, in which case $\epsilon \rightarrow -\infty$ when $R \rightarrow +\infty$.

Using the empirically found parameters of the electrical resistance of a polymer composition containing a graphite dispersion and the coefficient of quasi-elasticity of a polypropylene film prepared for testing according to option 1 and using the MathCad computer program, we build a graph of the theoretical dependence of the form $(\Delta R/R_0)(\sigma) \equiv r(\sigma) = 1.0888\sigma^2 - 13.27\sigma + 30.539$.

The red dots on the plot of $\Delta R/R_0(\sigma)$ show the results of empirical testing of the sensor layout made according to option 2 following the patent description [22] (Table 2 and Fig. 9). A polypropylene film is stretched

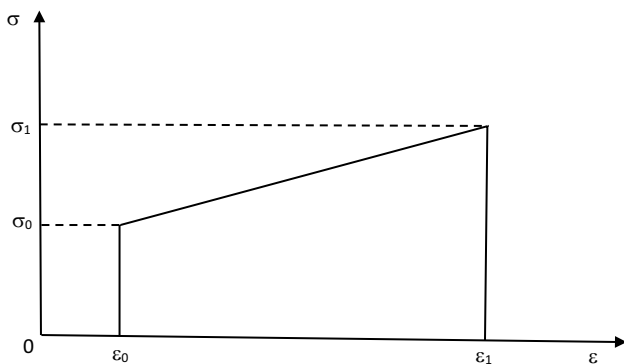


Fig. 7 Schematics of a fragment of the stress–strain dependence graph $\sigma(\epsilon)$

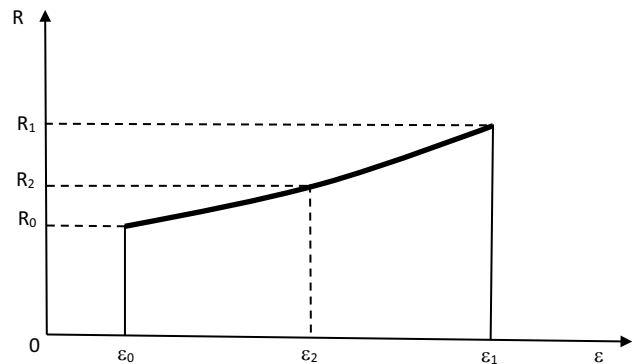


Fig. 8 Fragment of the graph of the relative change in electrical resistance dependence on the strain $(\Delta R/R_0)(\epsilon)$

Table 2 Measured resistance of the sensor (Ydata) dependence on the voltage (Xdata)

xdata :=)	ydata :=)
8.66		0.24	
9		0.33	
13.5		48.44	
15		77.88	
19		154.55	
20.5		263.44	
25		394.55	

in the air to a relative elongation of 50%, and then an adhesive and an electrically conductive dispersion of graphite are applied to it in a stressed state by spraying from an aerosol can.

To calculate the dimensionless strain gauge factor of the sensor to mechanical stress (ΘF) in a certain range at different elongation, as indicated above, we apply the formula (3):

$$\Theta F = \frac{\Delta R/R_0}{\Delta \sigma/\sigma}$$

Since $\Delta \left(\frac{R}{R_0}\right) \approx \frac{d(R/R_0)}{d\sigma} \cdot \Delta \sigma$, we get

$$\Theta F = \frac{\frac{d(R/R_0)}{d\sigma} \cdot \Delta \sigma}{\Delta \sigma} \cdot \sigma = \sigma \cdot \frac{d(R/R_0)}{d\sigma} = \theta \cdot \sigma \tag{17}$$

Since for a particular sensor design, a practically significant stress range is $\sigma = 15\text{--}25$ MPa, and the sensitivity Θ monotonically increases from $78/15 = 5.2 \text{ MPa}^{-1}$ to $378/25 = 15.12 \text{ MPa}^{-1}$ in Fig. 9, it is advisable to use the average value of the dimensionless coefficient of strain sensitivity of the sensor to mechanical stress ΘF .

Table 3 Tensile calibration coefficients

Tensile calibration coefficients						
Strain range, %	6–35			35–60		
	Manufacturing option	1	2	3	1	2
Modulus of quasi-elasticity k_1 , MPa	0.019	-0.0014	0.0128	0.172	0.22	0.18
Strain calibration coefficient GF	1.5	1.5	1.5	3.5	3.5	3.5
Strain sensitivity QF, MPa^{-1}	79	-1071	117	20	16	19
Calibration factor ΘF	450	-8568	702	140	112	133

In this example of the sensor according to option 1, but without pre-stretching of the film, the average value of the dimensionless strain sensitivity coefficient ΘF is close to a constant value—the tangent of the slope of the section of the graph of the function, which is equal to 450 ($300 \cdot 15 \text{ MPa} / 10 \text{ MPa} = 450$).

For sensor versions 1, 2, and 3, the calibration coefficients are given in Tables 3 and 4, indicating the direction of movement of the test machine (film stretching and contraction) of the ranges of cyclic deformation, in which an approximate linear approximation (Figs. 7 and 8) of the functions $\sigma = f(\epsilon)$ and $\Delta R/R_0 = F(\epsilon)$.

In the case of a sensor obtained according to option 1, the non-linearity of the dependence of the strain gauge coefficient ΘF on voltage is described as:

Since $\Delta \left(\frac{R}{R_0}\right) \approx \frac{d(R/R_0)}{d\sigma} \cdot \Delta \sigma$, then we arrive to

$$\Theta F = \frac{\frac{d(R/R_0)}{d\sigma} \cdot \Delta \sigma}{\Delta \sigma} \cdot \sigma = \sigma \cdot \frac{d(R/R_0)}{d\sigma} \tag{18}$$

Since $\frac{d(R/R_0)(\sigma)}{d\sigma} = 2.1776 \cdot \sigma - 13.27$, we finally get

$$\Theta F = 2.1776 \cdot \sigma^2 - 13.27\sigma \tag{19}$$

Fig. 9 Graph of the theoretical dependence of the electrical signal of the sensor on the mechanical stress

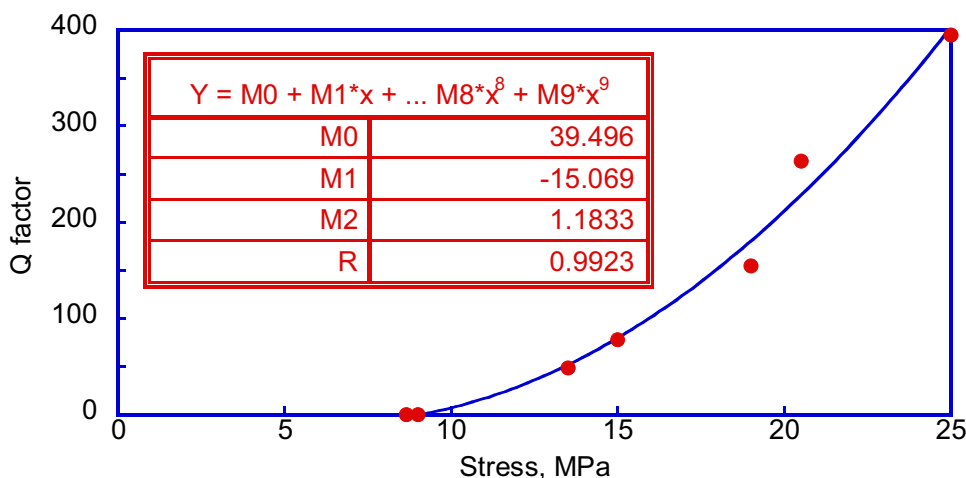


Table 4 Contraction calibration coefficients

Strain range, %	Contraction calibration coefficients					
	60–25			25–6		
Manufacturing option	1	2	3	1	2	3
Modulus of quasi-elasticity k_1 , MPa	0.95	0.89	0.86	0.045	0.047	0.048
Strain calibration coefficient GF	1	1	1	0.2	0.2	0.2
Strain sensitivity QF, MPa^{-1}	1	1.1	1.2	4.4	4.3	4.2
Calibration factor ΘF	7	7.7	8.4	17.6	17.2	16.8

Conclusions

Based on the example of rigid elastic films of isotactic polypropylene, aerosols of solutions of macromolecular compounds in volatile solvents, and graphite dispersion, a new method for obtaining electrical strain gauges with high sensitivity to changes in mechanical stress is shown. The super high sensitivity of electrical sensors to changes in mechanical stress in a certain 6–35% strain range is due to the implementation of structural rearrangements of “dry crazing” and the Patrikeev-Mullins effect in hard-elastic films of isotactic polypropylene. A comparison of three options of hard isotactic polypropylene elastic films preparation for an adhesive layer application of a solution of macromolecular compounds shows the advantage of “dry crazing” of the polymer over “crazing” of the polymer in contact with a liquid. A mathematical model for the strain gauges is proposed, which predicts the mechanical stress and/or the change in mechanical stress in the film from the change in the resistance of the electrically conductive layer.

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Declarations

Competing interests The authors declare no competing interests or conflicts of interest.

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