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Strain effect on electrical resistivity of thermoexpanded graphite/polyvinylchloride plastisol composite

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The mechanical properties and electrical resistivity of a composite material consisting of polyvinylchloride plastisol material matrix and thermoexpanded graphite filler has been investigated. The percolation threshold has been determined to be $\theta_c = 0.04$ vol. parts graphite. During the material tension, its specific electrical resistivity ρ increases linearly in the filler concentration range $0.04 < \theta < 0.60$. A model has been proposed for the processes characterizing the system conductivity, which is based on the peculiarities of intergrain contacts in the composite material. Guidelines are given on possible usage of the new obtained material in strain gauges suitable for service at increased humidity and in corrosive media.

Исследованы механические характеристики и электросопротивление композиционного материала, матрица которого состоит из поливинилхлоридного пластизоля, а наполнителем служит терморасширенный графит. Установлено, что для рассмотренной системы порог перколяции $\theta_c = 0{,}04$ об. частей терморасширенного графита. При растяжении материала его удельное электросопротивление ρ в диапазоне концентраций $0{,}04 < \theta < 0{,}6$ линейно возрастает. Предложена модель процессов, характеризующих электропроводность рассмотренной системы, которая опирается на особенности межгранульных контактов в композиционном материале. Даны рекомендации по возможному использованию нового полученного материала для тензодатчиков, работающих в условиях повышенной влажности и в агрессивных средах.

A possible usage direction of thermoexpanded graphite (TEG) is the manufacturing of composite materials (CM) with various polymer matrices, having electrophysical properties not worse than similar polymer CMs reinforced with metals. For CMs with TEG filler, a low specific mass, increased stability in various corrosive media, and lower prime cost are distinctive features. To date, some electrical properties of TEG/polyethylene, TEG/organosilicon lacquer, and TEG/fluoroplast CMs have been investigated. Since the polyvinylchloride plastisol (PVCP) is more stable against plastic strains, it would be reasonable to investigate the mechanical characteristics of such a CM with various filler concentrations and also to consider the changes of electrical resistance parameters within a wide strain range. The purpose of this work is to prepared the TEG-PVCP CM, to study the correlations of stress-strain and electrical resistance-strain dependences for the CM with various filler concentrations. Novelty of this work consists in preparation and study of the new composite functional materials.

The CM samples were made from the following components: TEG with bulk density of 1.8 to 2 kg/m^3 and vermiform particle length of 1 to 4 mm; PVCP matrix containing polyvinyl chloride, ester plasticizer, and

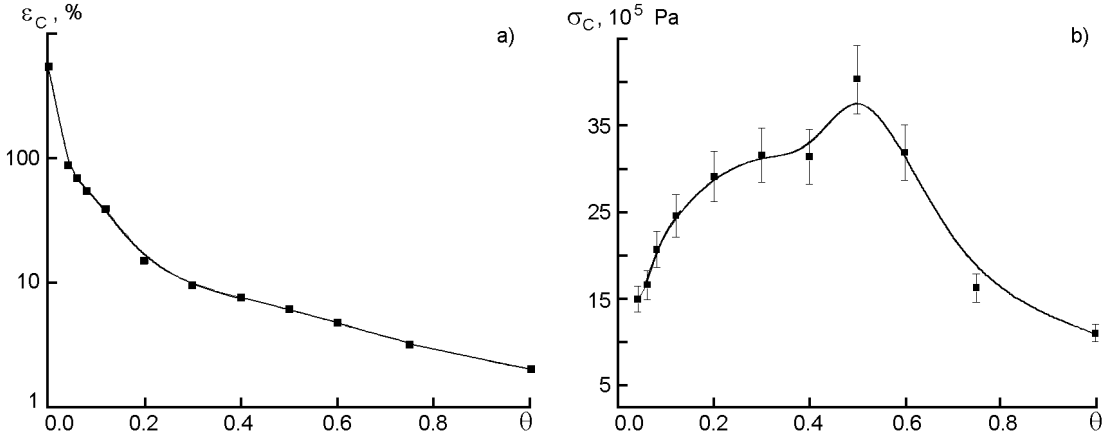

Fig. 1. Concentration dependence of critical strain (a) and critical stress (b).

organometallic stabilizer. The powder mixture was compacted by hot pressing at 175°C and pressure 10^7 Pa. When calculating the concentration in volume parts, θ, the following density values of components were taken: for TEG, $2.0 \cdot 10^3$ kg/m^3, for PVCP, $1.35 \cdot 10^3$ kg/m^3. The specific electrical resistance of the samples, ρ, was measured by standard four-probe method using direct current. The dependences of tensile strength (σ_c) on the relative strain (ε) were determined using a modified tearing machine and standard specimens. The specimens were linearly stretched with the speed 2.96 %/min (the gripper movement speed 0.8 mm/min) up to failure, and changes of electrical resistance and cross-section area of the specimens were measured at the increasing of stretching force applied to the tearing machine grippers.

The consideration of electrical resistance dependences on the filler (TEG) concentration in the CM has shown that the percolation threshold θ_c, in terms of the percolation theory [4], for the CM is equal to 0.04 vol. parts. As the concentration increases ($\theta > \theta_c$), the specific electrical resistance (ρ) decreases sharply from $9.92 \cdot 10^2$ down to 1.0 Ω·cm at TEG content in volume parts θ near 0.12, and then goes down smoothly to $2.81 \cdot 10^{-2}$ Ω·cm for samples pressed of pure TEG. Near the percolation threshold, ($\theta \geq \theta_c$), separate TEG clusters associate and form a continuous infinite cluster of TEG particles through the whole sample. The electrical current passes in this case the cluster skeleton in the CM. The ρ(θ) dependence for materials of this class [1–3] can be described analytically by the classical expression of percolation theory for three-dimensional conducting network with blocked sites: $\rho_{CM}(\theta) \sim \rho_{TEG}(\theta - \theta_c)^{-t}$, where ρ_{CM} and ρ_{TEG} are specific electrical resistance of the CM and TEG, respectively; $t = 1.7$, the critical index. A drawback of that model application to CM of the class under consideration is its formality. The model does not take into account the interaction between the polymer and filler, contact and dimensional phenomena in the field of low TEG concentration and is somewhat approximated in the high TEG concentration region.

Fig. 1 presents the concentration dependences of the failure strain ε_c and stress σ_c for the samples. As is seen, the ε_c value for pure PVCP samples is 550 % while for those pressed from pure TEG, 2 %. As θ increases up to 0.2, ε_c decreases sharply down to 15 % and then it decreases more smoothly. Introduction of TEG into PVCP decreases the CM stability against strain, but, up to a certain concentration ($\theta \sim 0.4$), it raises its tensile strength. This fact can be explained as follows: for samples with low TEG concentration, the material strength is defined by the polymer matrix. Thus, the Poisson coefficient ν is found to be the same in the directions perpendicular and parallel to the pressing axis up to $\theta \sim 0.08$. At this concentration, the relative narrowing of the CM in the directions perpendicular and parallel to the pressing axis becomes different, and at the further increase of concentration, this difference becomes more evident. As the concentration attains $\theta > \theta_c$, at which the continuous infinite cluster appeared ($\theta_c \sim 0.12$), the strength is defined both by that of polymer matrix as well as that of the filling material. At $\theta \sim$

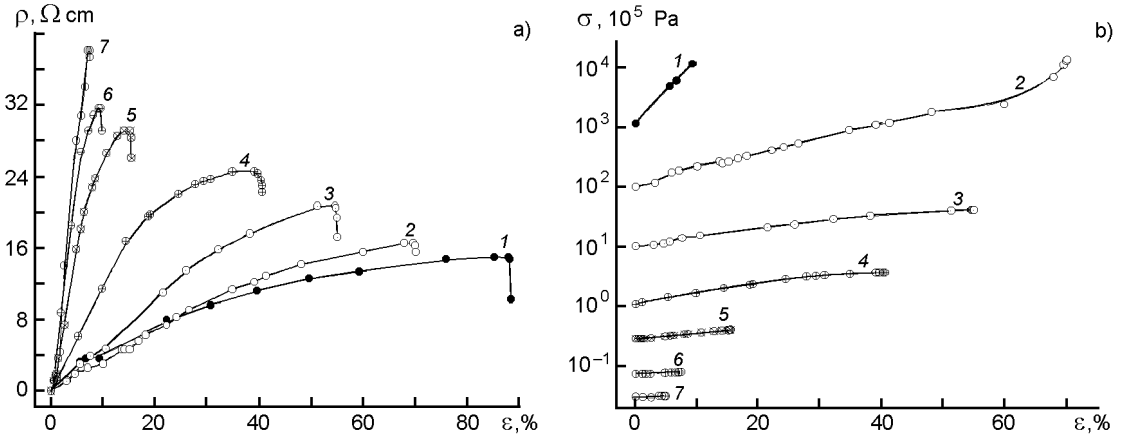

Fig. 2. Dependences of mechanical stress (a) and electric resistance (b) on strain for various filler concentrations (volume parts): 0.04 (*1*), 0.06 (*2*), 0.08 (*3*), 0.12 (*4*), 0.2 (*5*), 0.3 (*6*), 0.4 (*7*).

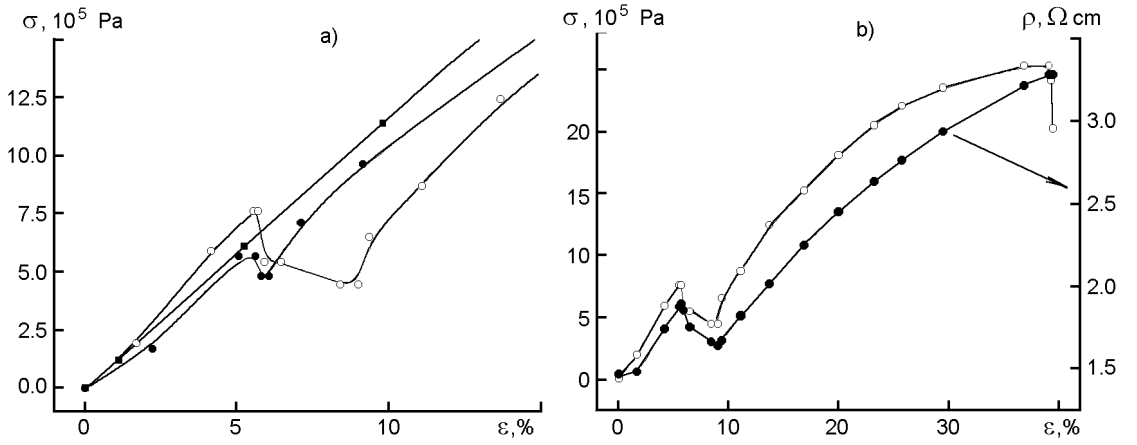

Fig. 3. (a) The stress-strain curve fragments for various samples with θ = 0.12; (b) correlation of the stress-strain and electric resistance-strain curves for a sample with θ = 0.12.

0.4, maximum σ_c value is attained. At the further increase of TEG concentration, the character of the CM strain changes from elastic-plastic to fragile, $\nu = 0$ in parallel and perpendicular directions to the pressing axis, and its mechanical strength goes down. In this concentration area, it is just the TEG matrix that contributes mainly to the CM strength. Fig. 2a illustrates the family of -strain curves stress for the CM at θ varying from 0.04 to 0.4.

The ρ(ε) measurements done in parallel to σ(ε) ones has shown (Fig. 2b) that the specific electrical resistance ρ of material depends linearly on the strain. The dependence can be described analytically as $\rho = \rho_0 + k\varepsilon$, where ρ_0 is the specific resistance of unstrained material; k, a proportionality factor which depends on TEG concentration. At $\theta > 0.6$, $k = 0$. At $\theta = 0.04$, ρ grows indefinitely after even a small strain, that is caused presumably by breakdown of contact bonds between TEG particles. At relatively high filler concentrations (θ ~ 0.06), nonlinear sections appear in the ρ(ε) dependence in the high strain region; that can be caused by dimensional effects of electrical resistance, when the distance between TEG particles is close to the free path length charge carriers. At $\theta > 0.07$, the linear character of dependence is restored.

At concentrations exceeding that necessary for infinite cluster formation ($\theta \geq 0.12$), a maximum similar to the fluidity tooth for metals [5] appears in σ(ε) curves for some samples (Fig. 3a). It is possible to explain the appearance of tooth of fluidity in the framework of the following model. Due to straining, two extreme cases are possible in a certain volume: the TEG particles arranged parallel or perpendicular

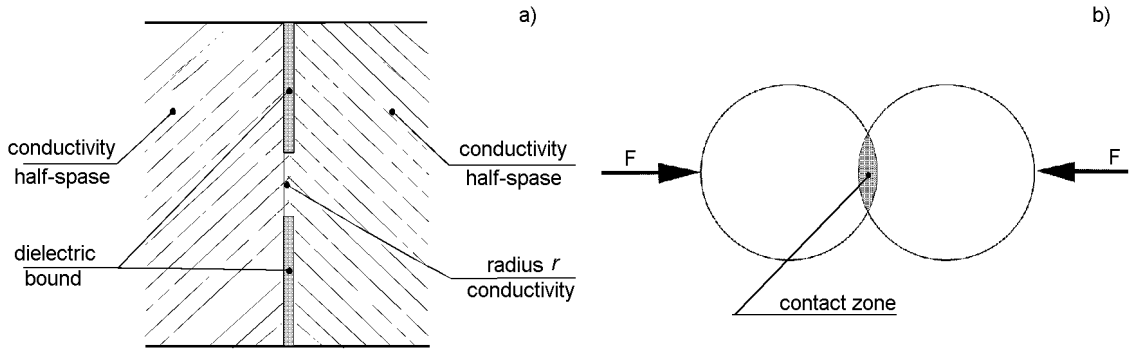

Fig. 4. Model concept of the intergrain contact.

to the matrix stretching axis. In the first case, the material acquires an additional strength due to the face that the strain is a shear one. At a certain stress, the dense contact between particles is broken off (top of the tooth). A further straining results in a—reduced stress, since the material strength in this volume is defined by the polymer matrix only. In the second case, the cohesion strength of particles lower than in the first one. It is just the polymer matrix that contributes mainly to the composite strength, so the fluidity tooth is absent. The tooth height can be supposed to depend on the size of areas where the particles are parallel. The maximum appearance in the $\sigma(\varepsilon)$ curve is accompanied by a maximum in the $\rho(\varepsilon)$ one (Fig. 3b). This is explained by that cross-section narrowing of the material results in a compaction of particles at initial stages of deformation.

The CM electrical resistance changes can be described using the following model. At any concentration $\theta > \theta_c$, the kinetic properties of the material are defined mainly by properties of intergrain contacts (electric current passes the infinite cluster). Each such contact represents a micro-narrowing in the conductive circuit. Such a contact can be presented by a bridge disk of radius r in a non-conductinve boundary dividing two conductve half-spaces (Fig. 4a). At $r > \lambda$, where λ is the electron free path, the resistance of contact (Haln resistance) is defined by the expression $R = \rho/2r$, where ρ is the specific resistance of a conductive half-space. At $r << \lambda$, there is an additional dispersion of current on the disk boundaries. The contact resistance R (Sharvin resistance) is defined as $R = (\rho/2r)(\lambda/2r)^{-1}$.

For an arbitrary relation r and λ, the resistance is

$$R\frac{r}{\lambda} = \frac{\rho\lambda}{4r^2}\left[1 + \frac{4}{\pi}\frac{r}{\lambda}\mathrm{arctg}\frac{r}{\lambda}\right].$$

At a change of pressure, the contact response to compression can be estimated from solution of the elasticity theory problem [6] for spheres being squeezed by external force F (Fig. 4b). The effective pressure $P = F(\pi D^2/4)^{-1}$, where D is the contact zone diameter. The radius r for elastic deformations

$$r = \alpha\frac{D}{2}P^{1/3}, \quad \alpha = \left[\frac{3(1-\nu^2)}{4E}\right]^{1/3},$$

where E is the Youngs modulus; ν, the Poisson factor. If there is a certain some initial pressure P_0 in the polymer, then

$$r(P) = \alpha\frac{D}{2}(P + P_0)^{1/3} = \alpha P_0^{1/3}\frac{D}{2}\left(1 + \frac{P}{P_0}\right)^{1/3}.$$

It follows from the above formulas: at $r >> \lambda$, $R(P) \sim \alpha(1 + P/P_0)^{-1/3}$, at $r << \lambda$, $R(P) \sim \alpha\ (1 + P/P_0)^{-2/3}$.

Taking into account Eq.(7) we get: at $r >> \lambda$, $R(r) \sim \alpha(1 + r^3/r_0^3)^{-1/3}$; at $r < \lambda$, $R(r) \sim \alpha\ (1 + r^3/r_0^3)^{-2/3}$.

So, as r increases, the resistance should decrease and at the CM stretching, to go down, as it was observed in experiment. The specific electrical resistance of the TEG/PVCP composite material depends linearly on strain in the TEG concentration range from 0.04 to 0.6 vol. parts. This dependence can be used in practice for manufacturing of the CM strain gauges for service under high humidity and aggressive media. Besides of the strain gauges, the CM are potentially suitable for microphone membranes, DC/AC converters, sensors of automatics, etc. CM magnetoresistors changing electrical resistance in a magnetic field are

known [7]. By analogy, the CM described in the work can be called dilatoresistors.

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Вплив деформації на електроопір композиційного материалу терморозширений графіт/полівінілхлоридний пластизоль

Д.Ю.Караман, В.С.Копань, С.Л.Рево

Досліджено механічні характеристики та електроопір композиційного матеріалу, матриця якого складається з полівінілхлоридного пластизолю, а в якості наповнювача використовується терморозширений графіт. Встановлено, що для розглядуваної системи поріг перколяції $\theta_c = 0{,}04$ об. част. графіту. При розтязі матеріалу його питомий опір ρ у діапазоні концентрацій $0{,}04 < \theta < 0{,}6$ лінійно зростає. Запропоновано модель процесів, що характеризує електропровідність системи, що спирається на особливості міжгранульних контактів в композиційномуматеріалі. Дано рекомендації з можливого використання нового отриманого матеріалу для тензодатчиків, що здатні працювати в умовах підвищеної вологості та в агресивних середовищах.