Phase Transition in Pyrolyzed Samples of Natural Silk

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Annotation. The article discusses the use of non-recyclable fibrous waste of natural silk as electrically conductive materials for special purposes. The dependence of the electrical conductivity of powdered samples of natural silk on the heat treatment temperature is shown. A phase transition is described, in particular, the "metal-dielectric" transition in pyrolyzed samples of natural silk.

Keywords: natural silk, cocoon, silk industry waste, waste processing, heat treatment, electrical conductivity.

The combination of specific physical, mechanical, chemical, and electrical properties of polymers makes it possible to use these materials in various branches of technology. For the rational use of polymers as dielectrics, semiconductors, or electrically conductive materials, it is necessary to know their electrical properties, understand the patterns of changes in these properties, and understand the patterns of changes in these properties with varying the structure of polymers and operating conditions [1–2].

The dependence of electrical properties on the structure of macromolecules and the supramolecular structure makes it possible to use measurements of electrical properties to study the structural features of polymers. The study of the electrical properties of polymers is one of the most important problems in the physics of polymers and the physics of dielectrics. The practical significance of these studies is associated primarily with the need to create disposable electrical insulating materials and structures for the developing branches of the electric power industry and nanoelectronics [3-4].

In recent years, to solve a number of fundamental and applied problems of physics, as well as to design new devices, organic materials have been increasingly used, which are increasingly being used in non-traditional areas. For example, in semiconductor physics and microelectronics, intensive research is being carried out aimed at expanding the range of semiconductor materials with new properties. One of the varieties of semiconductor materials are organic semiconductors - a wide class of substances that belong to the type of bond and have a noticeable electrical conductivity.

Previously [5], the process of formation of semiconductor pyropolymers based on natural silk was studied and the mechanism of their conductivity was studied. However, the practical use of polymeric materials requires studying the physics of a number of electrophysical processes.

This work is devoted to the investigation of the "metal-dielectric" transition in pyrolyzed samples of natural silk. As is known, in the low-temperature region, pyrolyzed silk samples treated at a heat treatment temperature (HTT) of 900 exhibit an exponentially temperature-dependent hopping conductivity with a variable hop length of the type

$$\sigma = \sigma_0 \exp\left[-(To/T)^{1/2}\right] \qquad (1)$$

on localized states in the region of the parabolic Coulomb quasi-gap near the Fermi level. Let us consider the electrical conductivity of pyrolyzed silk that has undergone heat treatment at HTT > 900°C. As is known [5], no exponential dependence σ(T) is observed here and the conductivity depends on the temperature in a power-law manner

$$\sigma \propto T^{-m} \qquad (2)$$

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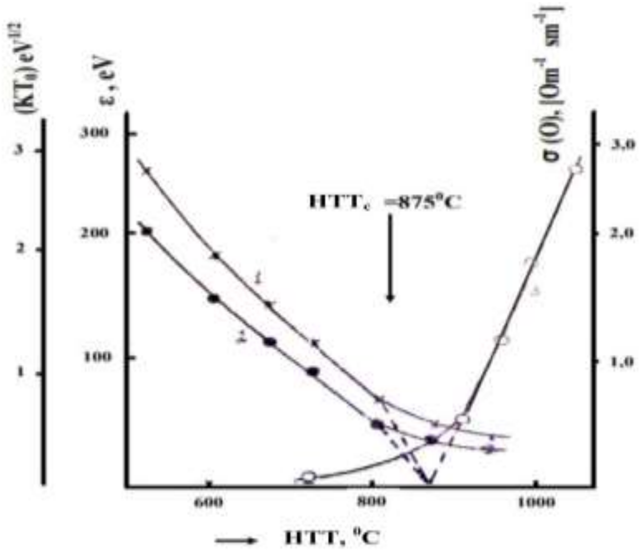
The exponent m included in it continuously decreases from 1.50 at HTT = 900°C to 1.15 at HTT=1100°C. At lower temperatures, dependence (2) weakens and tends to enter the regions б(T) that are weakly dependent on temperature. The value of б(O) was determined by extrapolating the curve of dependence of electrical conductivity on temperature to zero temperature. According to [6-8], dielectric or semiconductor (as in this case) properties are determined by some parameters. In particular, in the case of hopping conduction with a variable hop length, the latter occurs in a narrow zone of width $(kT_o)^{1/2}$. In the case of hopping conduction with a constant hop length, the electrical conductivity is characterized by the activation energy εz. The presence of dependence of type (2) predicts the metallic character of conductivity, the characteristic of which in our case is б(O).

The figure shows the dependence of the parameters $(kT_o)^{1/2}$, б(O) and activation energy ε_3 on the heat treatment temperature.

As can be seen, the linear sections of the dependences б(O), $(kT_o)^{1/2}$, as well as ε3 from the high-temperature part б(T) on the heat treatment temperature are extrapolated to their zero values at the critical value HTT^s = 875 ± 10ºC, where and a metal-dielectric transition occurs in pyrolyzed silk.

The analogy between the nature of the electrical transfer on both sides of the metal-dielectric transition in pyrolyzed silk and in other disordered systems, where the continuity of the transition, on the one hand, and the possibility of its description within the framework of the scaling theory, on the other hand, has been experimentally proven, suggests the possibility of describing the metal-dielectric transition. and pyrolyzed silk in the framework of the theory under consideration.



Picture. Dependence on the
heat treatment temperature of the conductivity parameters of the pyro-silk: 1-activation energy - ε_z; 2 - zone width $(kT_o)^{1/2}$;
3- zero electrical conductivity б(O).

The scaling theory of metal-dielectric transition considers the critical behavior of the properties of a system by analogy with second-order phase transitions in the form of power functions of the coherence length ξ.

For example, in the case of doped semiconductors

$\xi = \xi^* /1 - \frac{n}{nc}/^{\nu_\xi}$,

where ξ* is some constant;

$\nu_\xi \approx h$ is the critical index;

n, n_c are the concentration of uncompensated carriers and its critical value.

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In pyrolyzed silk, the HTT/HTT^s ratio acts as a critical parameter that determines the proximity to the transition. Therefore, for the correlation length and an arbitrary FS function with a critical behavior near the metal-insulator transition, one can write down.

$$F=F^* (1- HTT/HTT^s)^{\nu f} \qquad (3)$$

Note that in the scaling theory of the metal-dielectric transition, expressions of the type (3) with the critical parameter HTT/HTT^S are obtained by passing to the limit at $HTT \to HTT^S$ from some more general expression of the form ($mHTT/HTT^S$), i.e. on the basis of experimental data, the critical parameters of the scaling theory were found, which correspond to the values:

$$\nu_{\sigma_0} = 1,1 \pm 0,2; \qquad \nu_{t_0} = 2,0 \pm 0,1; \qquad \nu_{\varepsilon} = 1,4 \pm 0,2;$$

Thus, on the basis of the studies carried out, a "metal-dielectric" transition was achieved in pyrolyzed silk. It is carried out, in contrast to classical semiconductors, where the transition is achieved by increasing the concentration of donors, changing the heat treatment temperature, which is more controllable. By adjusting the heat treatment temperature, we can obtain samples with desired electrical properties. For these purposes, non-textile waste from the production of natural silk can be successfully used, since the production of electrically conductive polymer composite materials with desired properties is an urgent task. The semiconductor material obtained by this method does not differ in its performance from other electrically conductive materials and can make up for the shortage of this product, which is needed by various industries. The positive side of recycling is also the fact that an additional amount of useful products is obtained for various sectors of the national economy, there is no re-pollution of the environment.

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