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Abstract

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SYNTHESIS OF SEMICONDUCTING COMPOSITE MATERIALS BY THE METHOD OF RADIATION GAS-PHASE GRAFT POLYMERIZATION

The preparation of polymeric materials possessing semiconducting properties is one of the important problems of contemporary macromolecular chemistry. Numerous studies have shown by the present time that polymers with a system of conjugated bonds in the chain possess the most interesting electrophysical properties ([1]). Such polymers can be obtained both by their direct synthesis from monomers, for example acetylenic ones ([2]), and by transformations in the chains of ready-made polymers (pyrolysis of polyacrylonitrile) ([3]). However, up to now all known high-molecular-weight organic semiconducting materials have been obtained either in the form of nonthermoplastic and insoluble powders, or in the form of weak fibers and fabrics. Unsatisfactory mechanical properties are one of the reasons hindering not only their application, in particular their use as elements of radio-engineering devices, but even the investigation of these materials.

In the present work the task was set of obtaining organic polymeric semiconducting materials possessing high mechanical strength. In doing so we proceeded from the assumption that composite materials, for example fibers consisting of two components, one of which possesses the necessary complex of electrophysical properties while the other serves as a substrate determining the mechanical strength of the system, should meet these requirements.

Recently the possibility was shown of obtaining this kind of composite materials by irradiating solid "substrates" in the presence of vinyl, olefinic, and acetylenic monomers present in the gaseous or vapor state ([4–7]); the new polymer chains formed under such conditions prove to be chemically bonded to the surface of the substrate ("grafted" to it). By this method grafted materials were obtained both on the basis of polymeric substrates (fibers, films) and on the basis of mineral powders—peculiar mineral-organic products that can combine the properties of the grafted polymer and the properties of the original inorganic substance.

It was natural to suppose that the method developed in these studies could also be applied to solving the problem posed in the present work: obtaining mechanically strong semiconducting materials. For this purpose we carried out

Figure 1

Figure 1: Figure 1

experiments on radiation gas-phase graft polymerization of acetylenic monomers and acrylonitrile on glass fiber, which was to play the role of a strong substrate. In addition, owing to its high thermal stability, glass fiber made it possible to carry out the thermal treatment of the grafted fibers necessary for imparting the required electrophysical properties to them.

The radiation source was an electron accelerator (voltage 800 kV, dose rate 10^5 rad/sec). Irradiation was carried out in the absence of air in a glass two-chamber apparatus ([4]), which made it possible to thermostat the glass fiber separately and, separately, the liquid monomer, whose temperature determined the vapor pressure in the system. As the substrate, use was made of–

fibers made of ordinary alkali-free glass fiber, consisting of 1000 monofilaments 6-7 μ thick. Before the experiments the fibers were treated with benzene and alcohol to remove the size.

Fig. 1. Dependence of electrical conductivity on temperature for pyrolyzed polyacrylonitrile on glass fiber: 1 –without preliminary conditioning in vacuum; 2 –after conditioning in vacuum (heating at 200°)

As a result of the experiments carried out, the possibility was established of obtaining combined mineral-organic fibers possessing semiconductor properties (8).

Thus, for example, when glass fiber was irradiated at a temperature of 150° in the presence of phenylacetylene (vapor pressure 400 mm Hg, dose 2000 Mrad), a grafted fiber was obtained containing about 14 wt. % grafted polyphenylacetylene. Investigation of the electrical conductivity of the fiber showed that with increasing temperature it rises sharply, and at a temperature of 300° its specific electrical conductivity is $1.3 \cdot 10^{-5}\ \Omega^{-1}\,\mathrm{cm}^{-1}$.

When glass fiber was irradiated at a temperature of 80° in the presence of acrylonitrile vapor (200 mm Hg, dose 2000 Mrad), 12% polyacrylonitrile was grafted. The sample was heated in a nitrogen atmosphere to a temperature of 500° in order to impart semiconductor properties to the grafted polyacrylonitrile (3). Fig. 1 shows the dependence of the specific conductivity of the resulting combined fiber on temperature. The measurements $\sigma = \sigma(T)$ were carried out in vacuum (10^{-5} mm Hg). As can be seen from the figure, the fiber obtained possesses semiconductor properties; heating it in vacuum leads to an increase in conductivity and a decrease in activation energy. The magnitude of the specific electrical conductivity of the combined fiber obtained and its dependence on temperature correspond to the established regularities characterizing the electrical properties of pyrolyzed polyacrylonitrile (1,3). The increase in conductivity and the change in its temperature dependence upon heating the fiber in vacuum are

apparently connected with desorption of oxygen (9). The mechanical strength of the combined semiconductor fibers is 40–50 kg/mm^2.

Thus, the fundamental possibility has been shown of obtaining, by the method of radiation gas-phase graft polymerization, combined semiconductor fibers possessing high mechanical strength. At present, experiments are being carried out to obtain by this method new semiconductor fibers using other monomers and substrates, and to study their electrical and mechanical properties in greater detail.

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CITED LITERATURE

1. V. A. Kargin, A. V. Topchiev et al., *Journal of the All-Union Chemical Society named after D. I. Mendeleev*, **5**, no. 5, 507 (1960).

2. A. A. Berlin, M. N. Cherkashin et al., *High-Molecular Compounds*, **1**, 1817 (1959).

3. A. V. Topchiev, M. A. Geiderikh et al., *Doklady AN*, **128**, 312 (1959).

4. B. L. Shchetinin, S. R. Rafikov et al., *Proceedings of the 1st Conference on Radiation Chemistry*, Publishing House of the Academy of Sciences of the USSR, 1962, p. 497.

5. E. V. Egorov, P. D. Novikov et al., *Doklady AN*, **146**, 1360 (1962).

6. A. V. Vlasov, N. V. Mikhailov et al., *Chemical Fibers*, no. 6, 24 (1963).

7. A. V. Vlasov, P. Ya. Glazunov et al., *Doklady AN*, **144**, 382 (1962).

8. A. V. Vlasov, B. L. Shchetinin et al., USSR Author' s Certificate No. 158979, priority of November 9, 1962, *Bulletin of Inventions and Trademarks*, no. 23, 1963.

9. I. M. Kustanovich, I. I. Patalakh, L. S. Polak, *Kinetics and Catalysis*, **4**, no. 1, 167 (1963).

Note: Figure translations are in progress. See original paper for figures.