THE INFLUENCE OF THERMAL TREATMENT ON SYSTEMS CONSISTING OF POLYMERS AND DISPERSED METALS

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Abstract

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THE INFLUENCE OF THERMAL TREATMENT ON SYSTEMS CONSISTING OF POLYMERS AND DISPERSED METALS

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As we have shown previously (^{1}), a number of systems consisting of organic polymers and highly dispersed metals possess certain electrophysical properties characteristic of semiconductors. In comparison with many organic semiconductors described in the literature ($^{2-8}$), these systems are characterized, first of all, by low values of electrical resistance. Thus, at room temperature the resistances of metal—polymer systems amount to several ohms, and sometimes even tenths of an ohm. The values of the activation energy of conduction, obtained from the course of the curve of the dependence of electrical conductivity on temperature, fluctuate within the range from 0.08 to 0.2 eV.

By varying the methods of preparation of some of these compositions, it was possible to obtain systems having a type of conduction either as in p-, or as in n-semiconductors. In this case the sign of conduction was usually determined from the thermoelectromotive force. In those cases where the Hall effect was measured, the sign of conduction of the specimen was the same as according to the thermoelectromotive force. In what follows we shall conventionally speak of p- and n-type conduction on the basis of measurements of the thermoelectromotive force. It is interesting to note that almost all organic polymers with semiconductor properties described in the literature possess p-type conduction. In view of the differences mentioned above in the properties of polymer—metal systems and organic semiconductors, the ideas developed in the literature concerning the mechanism of conduction of the latter (^{6}, ^{7}) cannot be used without substantial changes for the systems described by us.

The compositions containing powdered iron with a high degree of dispersion were studied most thoroughly. Polymers were introduced into the systems by vibratory grinding of iron powder in a liquid monomer medium, according to the method proposed by V. A. Kargin and N. A. Plate (^{9}, ^{1}). In this way compositions of iron with polyisoprene, polymethyl methacrylate, polystyrene, and polyacrylonitrile were prepared. All these compositions possess n-conduction.

The iron—polyisoprene system was also prepared by depositing the finished polymer from a benzene solution (^{1}). It was shown thereby that if polyisoprene is introduced into the system from solution, the sign of conduction is the same as

Fig. 1 and Fig. 2: plots of the logarithm of electrical conductivity versus temperature.

Figure 1: Fig. 1 and Fig. 2: plots of the logarithm of electrical conductivity versus temperature.

in p-semiconductors. If, however, this system, as was said above, was obtained by polymerization of isoprene during vibratory grinding, then n-conduction is observed. To clarify the question of the structure of the polymer interlayer conducting current, it seemed expedient to study a composition with such a polymer in which the passage of current would be hindered. As such a system, the iron—polyisobutylene composition was chosen. The latter has a specific resistance of about 10^{14} ohm • cm and is a saturated organic compound in which there are no structural features facilitating electron transfer. Proceeding from the enumerated properties of polyisobutylene, it was natural to suppose that

with a considerable content of the latter the system will behave as an insulator.

Polyisobutylene was introduced into the system from a 1% solution in toluene. Samples with different amounts of polymer were studied: 10, 20, and 30%. With a content of 10% polyisobutylene, the specific resistance of the system was about $1 \cdot 10^{-2}$ ohm • cm; at 20% the resistance increased

Fig. 1. Dependence of the logarithm of electrical conductivity on temperature. I —iron-polyisobutylene system; II —iron-polyethylene system.

Fig. 2. Dependence of the logarithm of electrical conductivity on the temperature of polyisobutylene. a —course of the curve with increasing temperature; b —reverse course of the curve.

to $1 \cdot 10^{-1}$ ohm • cm. In both cases the resistance practically does not change with temperature. The sign of the charge carriers, determined from the thermoelectric emf, is in both cases the same as in p-type semiconductors. Apparently, in these systems polyisobutylene does not interact with the surface of the metallic particles, and when the sample is pressed the individual metal particles come into direct contact with one another. This circumstance also explains the fact that, although the specific resistance of the samples increases noticeably upon the introduction of polyisobutylene, nevertheless the temperature dependence of the electrical conductivity of these compositions remains the same as in metals.

A fundamental change in the electrical properties of the system occurs upon introducing 30% polyisobutylene. Under these conditions the resistance of the system increases greatly and becomes greater than $1 \cdot 10^{4}$ ohm. Polyisobutylene envelops the metal particles, and the contact between them is disrupted. However, if this composition is heated in vacuum at 180—200°, it acquires a number of new properties. The specific resistance at room temperature falls to 2–4 ohm • cm.

As can be seen from Fig. 1, the electrical conductivity of such a system decreases with decreasing temperature, which is characteristic of semiconductor-type conductivity. The course of the curve of the dependence of the logarithm of electrical conductivity ($\lg \sigma$) on temperature ($1/T$) resembles that of impurity semiconductors. The curve consists of two straight-line segments with different values of the activation energy (ΔE). In the temperature range from 180 to 0°, the value of ΔE is 0.07 eV; from 0° to −50° it is 0.66 eV. These curves are reversible; the reverse course coincides with the forward one, especially well in the low-temperature region. The sign of the charge carriers in these systems corresponds to that of n-type semiconductors.

Fig. 2 shows the course of the change in the electrical conductivity of pure polyisobutylene in the interval from 30 to 160°. As can be seen, it increases by four orders of magnitude and returns to its former value upon the corresponding lowering of the temperature. This argues in favor of the fact that heat treatment of polyisobutylene in the temperature interval described does not cause any fundamental changes in its structure. Thus, the changes in the electrophysical properties of the iron—polyisobutylene system described above are due to the specific action of powdered iron on the state of the polymer interlayers. The changes that occurred in these interlayers as a result of heating in the presence of iron are retained even at room temperature. The mechanism by which these current-conducting structures arise remains unclear for the present. The experiments described above with the iron—polyisobutylene system show that the appearance of conductivity of the semiconductor type is connected with thermal action on the system. The same conclusion may also be extended to compositions of iron with other polymers, which we mentioned at the beginning of the article and which also possess conductivity of the semiconductor type. Since these systems were obtained by the vibratory-mill method, strong local heating occurred in this process, caused by fracture of the metal or, in any case, by tearing off its surface layers. It should be noted that in our measurements, which were carried out in vacuum, reproducible curves of the temperature dependence of the resistance were obtained only after conditioning the specimens at 200—250°. Thus, even in those cases where the introduction of the polymer into the system was carried out by depositing it from solution, heat treatment in fact also took place.

The iron—polyethylene system was also studied; it was obtained by depositing polyethylene from a solution in ortho-xylene at a temperature of about 140°. The specimens were subjected to prolonged heating in vacuum at 250°. Although the specimens obtained are characterized by a comparatively low resistance (about 14 ohm·cm at room temperature), they do not possess conductivity of the semiconductor type. These properties appear only after repeated grinding and pressing of the specimens, as well as prolonged heating in vacuum. The curve lg σ −1/T (II) has approximately the same course as for the iron—polyisobutylene system (Fig. 1). The comparatively easy restructuring of polyisobutylene upon heating is apparently explained by the presence in the chain of a tertiary carbon atom, which facilitates, at this point, rupture of the chain and formation of new structures.

At present we are carrying out work on the study of the properties of structures arising in our compositions under thermal action. Systems with other transition metals—nickel and cobalt—as well as with a number of metals belonging to other groups are also being investigated.

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