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INFLUENCE OF PRESSURE ON THE ELECTRICAL CONDUCTIVITY OF POLYESTER POLYMER-CARBON BLACK COMPOSITIONS*

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The influence of pressure on the electrical conductivity has been investigated for a hardened polyester resin and its compositions with acetylene carbon black. A decrease of electrical conductivity with a rise in pressure has been ascertained for undoped polymer and non-conductive compositions, while for conductive compositions the electrical conductivity increases. This points to ions in the first and electrons (or holes) in the second case as predominant charge-carriers in the conduction process.

1. *Introduction*

Some electrical properties of polyester polymer-acetylene carbon black compositions have been described earlier [1–6]. These properties have been discovered by investigations of: the dependence of electrical conductivity on the carbon black concentration [1], temperature [2] and current-voltage [3] characteristics, EPR signals [3, 5], relaxation processes and dielectric losses [6]. A very small critical carbon black concentration ($c = 0.4$ phr[1]) separates the compositions into two parts: conductive ($c \geqslant 0.4$ phr) and non-conductive ($c < 0.4$ phr). The investigations performed up to now show that the transport of charge carriers in conductive compositions takes place not only by carbon black aggregates but also by fragments of polymer. The chemical polymer-carbon black bonds are an important factor in this mechanism. Such a view point is different from the generally accepted one [7] for other polymer-carbon black compositions in which the electric conduction takes place by carbon black "paths" only. Knowledge of the mechanism of electric conduction of polymers is to a greater part connected with a determination of nature of charge carriers. For a majority of polymers demonstrating very low electrical conductivity the charge carrier nature and the relation between the ion and electron current is not clear.

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[1] phr means parts by weight of carbon black per hundred parts of polyester resin.

Essential information about this relation may be obtained from investigations of electrical conductivity-pressure dependences. Interesting results can be found in the paper by Saito and co-workers [8], where the influence of pressure on the electrical conductivity was described for various polymers. The negative pressure coefficient of conductivity shows that ions are the predominant charge carriers in these polymers.

The positive pressure coefficient of electrical conductivity which points to the electronic character of conductivity was observed in semiconductor polymers [9], aromatic crystals [10] and inorganic glasses [11].

2. *Materials and apparatus*

For investigations, samples of polyester polymer Polimal 190 and its compositions with acetylene carbon black were used. A way to obtain the samples was described in detail in paper [1]. For conductive compositions ($\sigma \geqslant 2 \cdot 10^{-5}\Omega^{-1}\text{cm}^{-1}$) the electrical conductivity — pressure dependence was measured at the hydrostatic pressure up to 10^4 bar. The paraffin oil was the working fluid. The electrical connection between the pressure chamber and the outside part of the measuring system went through quartz and teflon gasket. The investigated samples were disks 8 mm in diameter and about 1.4 mm thick with vacuum evaporated silver electrodes. The samples were connected to the measuring system by a conductive silver-epoxy paste.

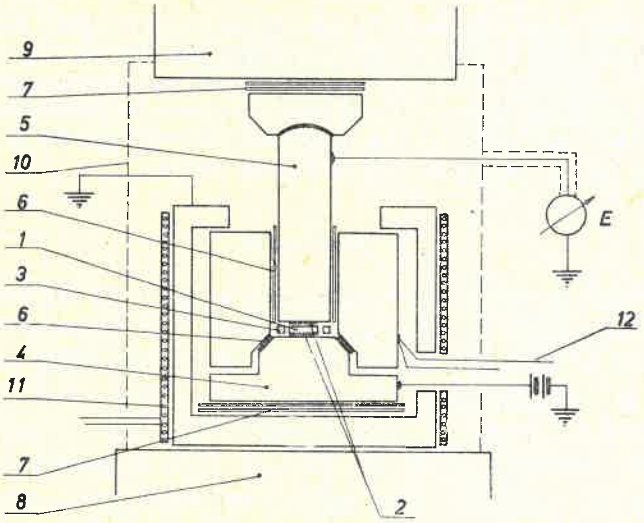

Fig. 1. Schematic design of the pressure chamber: *1* — sample, *2* — electrodes, *3* — polystyrene ring, *4* — anvil plate, *5*—piston, *6* insulating sleeve, *7* — insulating seals, *8, 9* — ram, *10* — electrostatic screen, *11* — heater, *12* — thermocouple

In the case of non-conductive samples ($\sigma = 10^{-13}-10^{-15}\Omega^{-1}\text{cm}^{-1}$) and also for samples described in point 3c a different pressure chamber was used (Fig. 1) and the pressure had a quasi-hydrostatic character. The measurements of electrical conductivity of conductive samples were carried out by the use of a resistance bridge, however, for non-conductive samples by the use of an electrometer, type V-219, at a constant outside voltage of $U = 100$ V.

3. *Results*

a. Conductive compositions

The electrical conductivity-pressure dependences are shown in Fig. 2 for compositions in which the carbon black concentration changes from 0.4 to 5 phr. Because of a great change of electrical conductivity with carbon black concentration [1] (from $2 \cdot 10^{-5}$ to $5 \cdot 10^{-2}\ \Omega^{-1}\mathrm{cm}^{-1}$), in Fig. 2 the relative changes are presented. In all cases an increase of electrical conductivity has been observed. The lower is the carbon black concentration, the higher are the relative increases in the electrical conductivity of compositions.

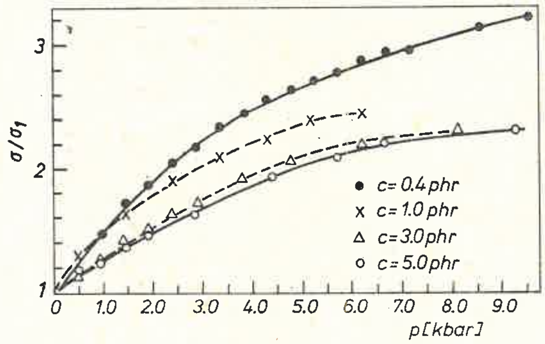

Fig. 2. Relative changes in electrical conductivity vs. pressure for conductive compositions

b. Non-conductive compositions

Compositions with a carbon black concentration of $c \leqslant 0.35$ phr are non-conductive ($\sigma = 10^{-13} - 10^{-15}\ \Omega^{-1}\mathrm{cm}^{-1}$). The influence of pressure on the electrical conductivity of these compositions is shown in Fig. 3. There is shown the dependence of $\sigma = f(p)$ for undoped polyester polymer and compositions with carbon black concentration of $c = 0.35$ phr.

For samples of the undoped polymer as the pressure increases up to $2 \cdot 10^3$ bar, the value of electrical conductivity decreases more than two orders of magnitude and the dependence $\ln \sigma = f(p)$ is linear. For compositions ($c = 0.35$ phr) in the same range of pressure the electrical conductivity decreases by about ten times (Fig. 3). During the measurements the background noise was taken into consideration. This background was connected with the piezo-electric effect of sample, polystyrene ring and teflon seals. By careful selection of insulating and separator pressure seals and also by careful sample screening a reduction of background noise has been achieved. The background current was from one to three orders of magnitude lower than the sample current measured.

It was also ascertained that the change in electrical conductivity of the polystyrene ring was negligibly small in comparison with the electrical conductivity of investigated samples. For a series of samples, changes in electrical conductivity were investigated by repeatedly

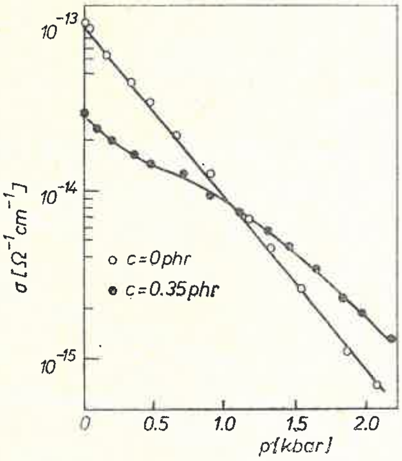

Fig. 3. The electrical conductivity — pressure dependence for non-conductive compositions

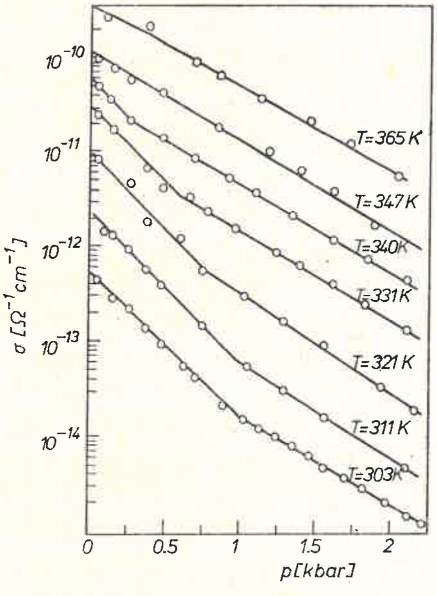

Fig. 4. The influence of temperature on the electrical conductivity — pressure dependence (c = 0phr)

increasing and decreasing the pressure. In all cases an insignificant hysteresis was observed, which disappeared after several repeated changes of pressure.

From the measurements of electrical conductivity-pressure dependence for various temperatures (Fig. 4) it follows that the character of $\sigma = f(p)$ dependence is independent of temperature. For non-conductive samples both for $T < T_g$ and $T > T_g$ a decrease in electrical conductivity with an increase in pressure has been observed (the value of the glass temperature T_g at atmospheric pressure amounts to $T_g \cong 323$ K). The changes in the slope of the line in Fig. 4 are a result of the non-uniform distribution of initial stresses within samples during the following cycles of compression. At low values the pressure does not have a quasi-hydrostatic character. When the temperature increases, the differences in elasticity between the sample and the polystyrene ring decrease and the pressure becomes quickly quasi-hydrostatic.

c. Compositions with mixed electric conduction

Under appropriate polymerization conditions [2], compositions can be obtained whose electric conduction, depending on temperature, has a metallic or thermally stimulated character. Up to some temperature the electrical conductivity of these compositions decreases and then for higher temperatures it increases (see the corner of Fig. 5). This complicated course of $\sigma = f(T)$ dependence can be explained by the contribution of ions and holes to the conduction process and also by the fact that the two components change differently with temperature.

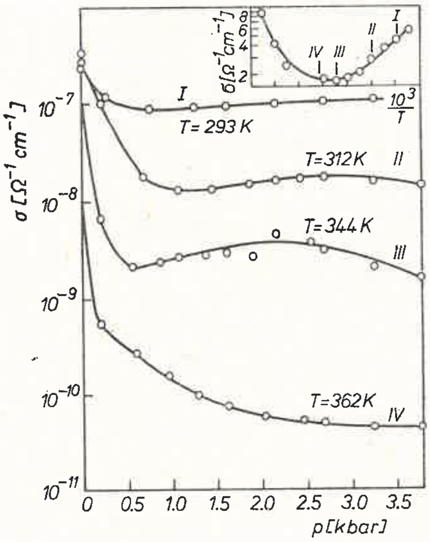

Fig. 5. The electrical conductivity — pressure dependence for samples with mixed electric conduction (in the corner of figure the electrical conductivity — temperature dependence is shown)

In an effort to verify this hypothesis the electrical conductivity-pressure dependence has been investigated for the following temperatures: 293, 312, 344 and 362 K. The results of the measurements are presented in Fig. 5. The initial run of curves ($p < 0.5$ kbar) is connected with the above-mentioned non-uniform distribution of initial stresses. The run of curves for higher pressure ($p > 0.5$ kbar), when the pressure is quasi-hydrostatic, markedly depends on temperature and, therefore, also on nature of electrical conductivity.

At the temperature of 293 K, in the range of pressure 0.5 — 3.5 kbar, there occurs an insignificant increase in electrical conductivity. The same composition behaves differently at 362 K. Here, a decrease in electrical conductivity has been observed in the whole pressure range.

5. *Discussion and conclusions*

The increase in electrical conductivity with an increase in pressure, for conductive compositions (Fig. 2), confirms the electronic character of conductivity. The positive sign of the Seebeck coefficient for these compositions [4] shows that holes are excess charges.

The low carbon black concentration, completely isotropic in samples and other properties of investigated compositions [1–6] suggest an absence of "continuous carbon black paths" and the conduction takes place through conductive polymer-carbon black structures. As a result of radical polymerization and presence of free radicals on the carbon black surface, the carbon black particles have been built-in to the polymer structure as non-touching agglomerates. The conduction process goes on as well through carbon black and polymer fragments. The chemical bonds between polymer macromolecules and carbon black are important factors here.

On the whole, the pressure can: modify electrical properties of a polymer, influence the polymer-carbon black bonds and change the electrical conductivity inside carbon black aggregates. The observed increase in electrical conductivity of conductive compositions is connected mainly with the changes inside carbon black aggregates and conductive polymer-carbon black structures. But it is difficult to differentiate those two factors in our experiments. From Fig. 2 it can be seen explicitly, that independently of the carbon black concentration in compositions, at a pressure of $7 \cdot 10^3 - 8 \cdot 10^3$ bar, changes in electrical conductivity are negligible.

It has been shown by Voet [12], who investigated the changes of electrical conductivity and the specific volume of various carbon blacks under pressure, that transport of charge carriers among carbon black molecules is connected with the tunnelling effect. The contact-resistance is an exponential function of mutual distance among carbon black particles. The diminution of this distance with an increase in pressure is a principal reason of increasing the electrical conductivity.

For non-conductive compositions and the undoped polymer the situation is different. The observed (Fig. 3) decrease in electrical conductivity with an increase in pressure shows that in these cases the ionic conduction is a predominant one. The activation energy of the undoped polyester polymer (calculated from the formula $\sigma = \sigma_0 \exp(-W/kT)$ and data in Fig. 4) is independent of the pressure. This means that the pre-exponential factor σ_0 changes under pressure and the decrease in electrical conductivity may be connected with the diminishing of jump frequency of ions between the equilibrium positions.

We can formulate this reasoning starting from the free volume theory adapted to ionic conductivity in polymers [13]. In accordance with this theory, the electrical conductivity depends on the frequency transition of an ion from one equilibrium position to another:

$$f = \nu \cdot \alpha \cdot P_h \cdot P_j,$$

where ν — the vibrational frequency of the trapped ion, α — a correlation factor ($0 < \alpha < 1$), P_h — the probablity of finding a hole produced by the redistribution of the free volume, P_j — the probability of jumping into the hole.

The pressure effects mainly the value P_h in that with an increase in pressure, the holes partly disappear or their dimensions become lower than the ions dimensions. In both cases the value of P_h decreases, indirectly σ_0 and the electrical conductivity also decrease. The lower changes in electrical conductivity for the non-conductive compositions (Fig. 3) show that part of the free volume is occupied by carbon black particles.

In compositions, for which the results of measurements are presented in Fig. 5, the transport of ions and holes is simultaneous and the electrical conductivity is an additive value. For lower temperatures the hole component dominates and the electrical conductivity increases under pressure (the curve I, above 0.5 kbar). For higher temperatures (the curve IV) the electrical conductivity decreases under pressure — it shows that the ion component dominates here.

According to the above mentioned remarks, the measurements of $\sigma = f(p)$ shown in Fig. 5 confirm a mixed character of electric conduction postulated in the work [2].

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