

Electrical resistivity of the iodine-doped poly(ethylene—co-vinyl acetate)

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Electrical resistivity of iodine-doped copolymers of vinyl acetate has been studied. A remarkable decrease in the electrical resistivity of poly(ethylene—co-vinyl acetate) caused by admixture of iodine is reported.

Было исследовано электрическое сопротивление иодом модифицированных сополимеров винил ацетата. Здесь описано значительное понижение электрического сопротивления поли(этилен—со-винил ацетата), причиной которого является примешивание иода.

Recently organic conductors have been studied extensively especially on the basis of polymers having in the chain a system of conjugated double bonds. Resistivity of such polymers can be markedly decreased by doping substances with which the polymers form donor-acceptor complexes. Extremely low resistivities were obtained for polyacetylene by various electron-acceptor substances like I₂, Br₂, IBr, AsF₅, AgClO₄ [1—3]. Polymers doped with the mentioned electron acceptors are assumed to form complexes similar to π complexes being formed in halogenation of olefin or complexes of carbonium ion with halogen [3]. Halogens react also with other substances, such as poly(sulfur nitride), poly(vinyl carbazole), etc. giving conductive complexes [4, 5].

Experimental

The following commercial copolymers were used for sample preparation: poly(ethylene—co-vinyl acetate), trade mark Levapren (Bayer A.G.); poly(ethylene—co-propylene), trade mark Dutral (Montecatini Edison, SPA); poly(vinyl acetate) and poly(vinyl acetate—co-ethyl acrylate) (Duslo Šafa, CSSR).

Iodine was mixed with polymers on a laboratory roll-mill at room temperature. The due quantity of crystalline iodine was added to the calendered polymer. During mixing iodine was dissolved in polymer which was manifested by the optical homogeneity of sample. The

samples (1 mm thick plates) for measuring the electrical resistivity were prepared by moulding at 50°C. The measuring electrodes were formed by pressing aluminium foils on both sides of the plates. The third electrode (for excluding of the surface currents) was presented by a moulding form. The measurement was done in the iron cage with regulation of temperature. The resistivity was determined by measurement of the current (or electric tension) using a picoampere-meter Fikus FC 403.

Results and discussion

Experimental results show that doping of iodine into poly(ethylene—co-vinyl acetate) markedly decreases its electrical resistivity. Fig. 1 shows graphical dependences of $\log \rho/\Omega \text{ cm}$ against iodine content in poly(ethylene—co-vinyl acetate) of various composition at room temperature.

The resistivity decreases as the iodine increases and reaches the values till 10^5 times lower than that of a polymer without admixture of iodine. The lowest resistivity was obtained for doped polymer with 40 mass % of vinyl acetate. The resistivity of copolymer is markedly affected even by low iodine content to 1 mass %.

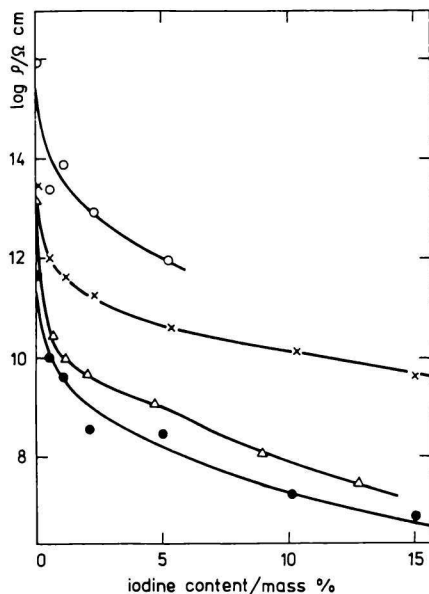


Fig. 1. Graphical dependence of \log of resistivity/ $\Omega \text{ cm}$ against the numerical value of iodine content in poly(ethylene—co-vinyl acetate) containing 90 mass % (x), 40 mass % (●), 33 mass % (Δ), and 8.5 mass % (○) of vinyl acetate.

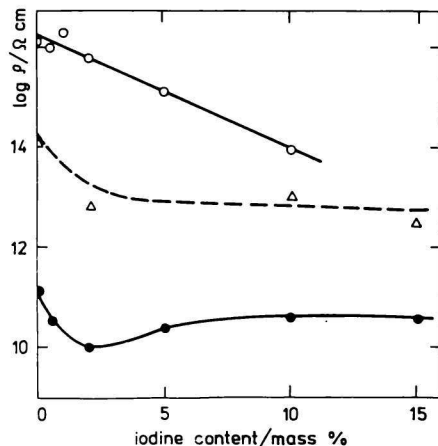


Fig. 2. Graphical dependence of \log of resistivity/ $\Omega \text{ cm}$ against the numerical value of iodine content in poly(vinyl acetate) (○), poly(ethylene—co-propylene) (Δ), and poly(vinyl acetate—co-ethyl acrylate) (●).

Poly(vinyl acetate) [6] and its copolymers [7—9] form in aqueous solution I_2 —KI coloured iodine complexes with light absorbance of a found 530 nm. The structure of the formed complex is not known [7]. The amount of the bound iodine for poly(vinyl acetate) and the results of the study of the complex with vinyl acetate copolymer show that the complex is formed only when the polymer chain contains vinyl acetate sequences longer than the critical length (12—17 monomeric units of vinyl acetate) [7]. We cannot assume sufficiently high concentration of vinyl acetate sequences of supercritical length for statistical poly(ethylene—co-vinyl acetate); with the increasing ethylene content the probability of their occurrence still lowers. The observed marked decline in the resistivity of doped copolymers cannot be assigned only to complex formation of the mentioned type.

The resistivity of poly(vinyl acetate—co-ethyl acrylate) containing 80 mass % of vinyl acetate (Fig. 2) decreases with iodine content over one decade in the range of small iodine concentrations. The polymer is thus saturated even with a small amount of iodine; a little change in resistivity could be attributed to the formation of a stoichiometric complex. The resistivity of the doped poly(vinyl acetate) is high and its change with iodine content is relatively small (Fig. 2). The resistivity of nonpolar poly(ethylene—co-propylene) does not vary with iodine content, either. Results on this copolymer as well as on poly(ethylene—co-vinyl acetate) with a small amount of vinyl acetate are probably influenced by low iodine solubility in a polymer matrix.

Fig. 3 shows graphical dependences of $\log \rho / \Omega \text{ cm}$ against K/T for poly(ethylene—co-vinyl acetate) (40 mass % vinyl acetate) and various iodine

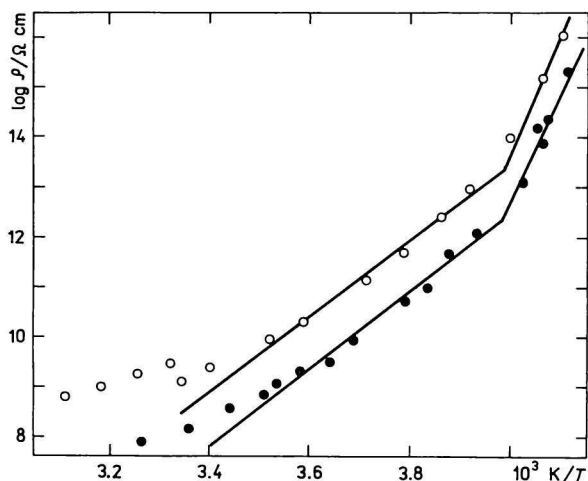


Fig. 3. Graphical dependence of \log of resistivity/ $\Omega \text{ cm}$ against K/T for poly(ethylene—co-vinyl acetate) (40 mass % of vinyl acetate) with 1 mass % (○) and 5 mass % (●) of iodine content.

contents. The curves are linear over the low temperature region with a break at 13.5°C. Similar dependence was also found for other organic semiconductors and the break corresponds to the glass transition temperature [10, 11]. The change of the iodine content is seen as a shift of the curves on the scale of $\log \rho/\Omega \text{ cm}$. A decrease in the resistivity with temperature is slower at higher temperature than in the range close above T_g : this is probably connected with the thermal instability of the complex iodine—polymer. The change in resistivity around T_g shows that the resistivity of the system is closely connected with a release of molecular motions or with diffusion processes in the polymer matrix.

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