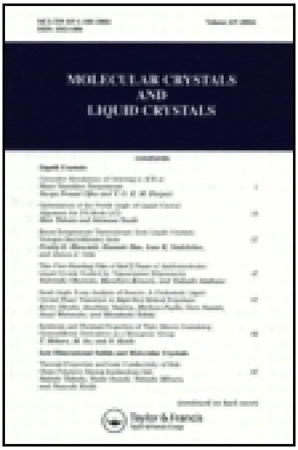

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Highly Conductive Copper Phthalocyanine-Carbon Plack Mixtures

Marek Kulesza [a] , Maria Zabkowska [a] & Witold Waciawek [b]

[a] Institute of Physics, Pedagogical University, 42200, Czestochowa, Poland

[b] Institute of Chemistry, Pedagogical University, 45052, Opole, Poland

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HIGHLY CONDUCTIVE COPPER PHTHALOCYANINE-CARBON BLACK MIXTURES

MAREK KULESZA, MARIA ZABKOWSKA
Institute of Physics, Pedagogical University,
42200 Częstochowa, Poland
WITOLD WACŁAWEK
Institute of Chemistry, Pedagogical University
45052 Opole, Poland

Abstract Data on electrical behaviour of copper phthalocyanine-carbon black mixtures are presented. For some samples the transition between semiconducting and metallic states is observed. The conductivity of the mixtures is found to be dependent on carbon black grain size.

INTRODUCTION

There are several methods to obtain highly conducting organic materials. In our laboratory we have investigated phthalocyanines doped with iodine. However in most cases the samples were thermally unstable due to iodine desorption. Another possibility we have found mixing phthalocyanines with different kinds of carbon blacks.[1] There is much of experimental data on mixtures of carbon black with crystalline polymers.[2-3] Usualy they have a positive temperature coefficient of resistance (PTC) over a limited range of temperature. It means that the electrical resistance of a mixture increases very rapidly with a rise in temperature. The phenomenon is fairly general, it exist e.g. for mixtures of carbon black with ice and with sulphur.[4] For our mixtures metallic behaviour has been observed in spite of the fact that both copper phthalocyanine and carbon black have thermally activated conductivities.

EXPERIMENTAL

Copper phthalocyanine produced by Wola Krzysztoporska Works (Poland), and carbon black HAF, SRF and PM-15 have been used for this investigations. The samples (10%, 15%, 20%, 25% and 30% wt of carbon black) have been prepared at pressure of 380 MPa to make pellets of 10 mm in diameter. Mixtures have been prepared by grinding the components of known percentage in agate mortar. On pellet surfaces silver, copper or indium electrodes have been evaporated in vacuum. Silver paint (DAG 1415, Acheson) has been used as contacting agent. All the samples studied were heated in vacuum before performing the electrical measurements. The electrical conductivity and thermoelectric power have been measured as a function of temperature. The sample electrical conductivity has been calculated performing a precise measurements of voltage drop on it.

RESULTS AND DISCUSSION

The electrical conductivities of copper phthalocyanine carbon black mixtures differing in grain size of carbon black shows Figure 1. In Table I the carbon black particle size are gathered. As one can see from Figure 1. the electrical conductivity increases when carbon black grain size decreases - this behaviour indicates the importance of copper phthalocyanine - carbon black interface for the conduction process mechanism. The similar relation has been reported[5] for a mixture of nickel and polyethylene powders. For some samples we have observed semiconductor - metal transition Figure 2. The transition temperature is

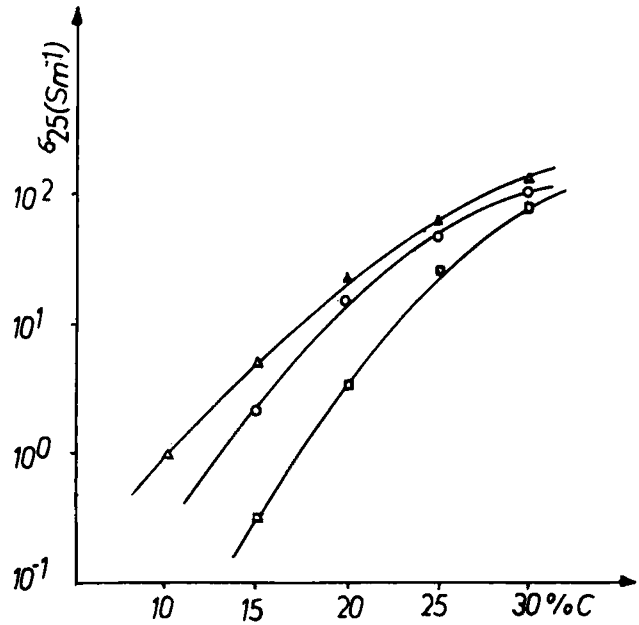

FIGURE 1 Variation of conductivities with carbon black content in weight % of the HAF (Δ), SRF (o) and PM-15 (□).

TABLE I Carbon black particle size

Kind of carbon black	Particle size (nm)
HAF	26-28
SRF	60-80
PM-15	200-300

dependent on the amount and kind of carbon black used in the mixture. For 10% wt of HAF carbon black transition temperature is 350 K - Figure 2. For the 20% wt SRF - 405 K and for the 20% wt PM-15 - 415 K. In samples 20% wt

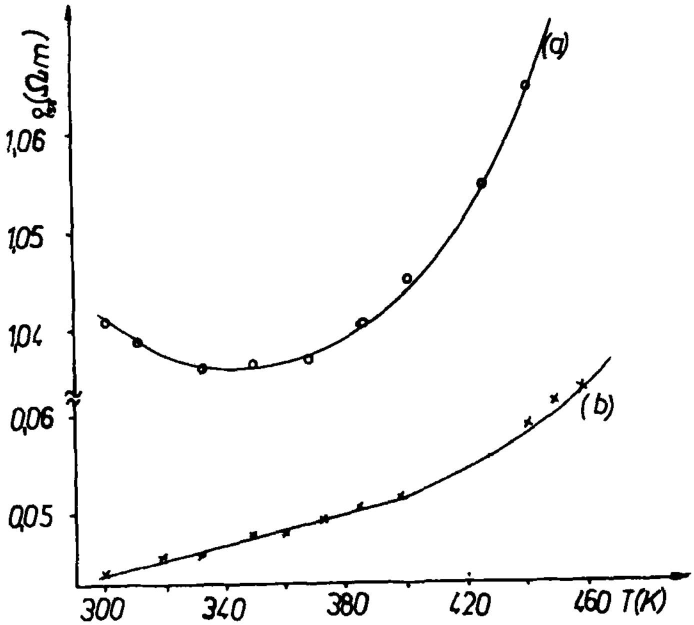

FIGURE 2 Variation of resistivity with temperature of (a) 10% wt HAF carbon black, (b) 20% HAF carbon black.

HAF - Figure 2. 30% wt PM-15 and 30% wt SRF metallic conductivity have been observed in the whole temperature range used 150 to 480 K. Kinds of electrodes (Ag, Au, In) and paints (silver, platinium) used have not influenced the conductivity behaviour studied. For the samples up to 10% wt of carbon black the dependence of ε' and ε" on frequency[6] agreed with the Jonscher's universal dielectric response theory[7] and that behaviour is characteristic for a system with high densities of low-mobility charge carriers in which transport of charge carriers takes place by hopping. It is confirmed by the Hall effect data for high conducting samples studied here. For them the Hall voltage we have not detected. It means that the density of carriers in the mixtures is very high and their mobilities are much less than 0,1 $cm^2V^{-1}s^{-1}$. All the low-resistivity samples have had the linear current-voltage characteristics for the fields a few Vm^{-1}, hence we can treat them as comprising the carbon black particles touching one another. So it seems that the intergrain breaks between the carbon black particles are not the factor controlling conduction.

In our previous work[6] the loss curves, obtained by plotting log ε'' against log f for copper phthalocyanine carbon black mixtures up to 10% wt carbon black, were found to spread over many decades of frequency without any clear maximum. At higher concentrations of carbon black the experimental curves approached a stright line indicating the existence of conducting paths[8] in our samples. That observations give some evidences on charge carriers transport mechanism in studied samples but do not explain it fully, e.g. it does not explain the nature of the metallic conductivity, which depends on the interaction between carbon black and phthalocyanine grains. The development of physical models to explain the observed phenomena is not easy even with a help of the theories[2-4] of PTC existed for crystalline polymers - carbon black mixtures. We hope that further experiments will make it possible to solve the problem.

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