

# Semiconductor Properties of Polyamide-6 Containing Dispersed Copper or Zinc Additives

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## Synopsis

It was expected that elemental copper or zinc introduced into polycapraamide would interact with amide groups of the polymer and that the materials would be characterized by semiconductor properties. To prove this theory, resistivity at several temperatures was determined and thermal activation energies calculated. As the metal contents were relatively low, metallic conductivity was avoided. Temperature-resistivity dependence and a negative temperature coefficient of the resistivity prove that polyamide-metal compositions can be classified as semiconductors.

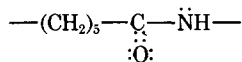
## INTRODUCTION

Recently, an increased interest in electrical properties of some polymers has been observed. Due to these electrical properties, several polymers, among them polymers modified with metal atoms, are classified as organic semiconductors. Well known are polychelates with azoporphyrin rings, poly(phthalocyanines) and poly(tetracyanoethylene), as well as ferrocene, characterized by 0.8 – 1.0 eV activation energy and electrical resistivity less than  $10^{14}$  ohm-cm.<sup>1-3</sup>

Some interest was directed as well to polymers with a straight hydrocarbon chain containing metal additives.

Polyisoprene modified with metallic iron<sup>4</sup> was studied and proven to have a marked semiconductivity. One can expect, thus, that even a double-bond system ( $\pi$  electrons) can interact with electron shells of metal atoms. In poly(methyl methacrylate) containing colloidal dispersed copper, semiconductivity was shown by means of conductivity-versus-temperatures measurements and subsequent calculations of decreased activation energy.<sup>5</sup>

Nonbonding electron pairs existing in amide groups of the polycapraamide chains



are suitable to form coordination bonds with electron acceptors; and this phenomenon is broadly utilized in proposing copper compounds for polyamide antioxidants or plasticizers.

In the case of polycapraamide modified with powdered iron,<sup>6</sup> marked changes in the electrical properties were observed. Polyamides, even in the basic state, are characterized by an interesting electrical behavior: their specific resistance

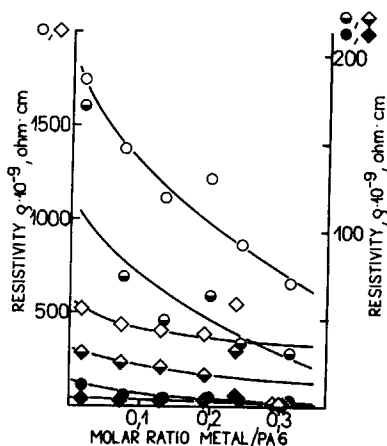


Fig. 1. Dependence of resistivity of the sinters on the molar ratio metal/PA 6: (○) copper at 25°C; (◐) copper at 54°C; (●) copper at 78°C; (◑) zinc at 26°C; (◒) zinc at 48°C; (◓) zinc at 68°C.

under direct current decreases from  $10^{13}$  ohm-cm to  $10^7$  ohm-cm at room temperature and 160–180°C (433–453°K), respectively. This phenomenon is explained on the basis of proton mobility of amide groups.<sup>7</sup> Later works, however, proved the electron character of the polyamide conductivity at increased temperatures.<sup>8</sup>

These observations permit one to postulate a high possibility for added metal to interact with amide groups in the polymer and subsequently change the electrical properties of polyamides.

Copper and zinc were selected for addition to polycaproatamide, PA6, because they should easily form coordination bonds. It was expected that they would influence polyamide properties even if heterogeneous systems resulted. Only electrical measurements could be taken into consideration either because of a lack of optical transmission or the necessity of powdering the samples which destroys metal-polymer interactions.

## EXPERIMENTAL

Monomer-free powdered PA 6 with a degree of polymerization  $P = 250$  and mp 215–217°C (488–490°K) was desiccated *in vacuo* before use.

Metal powders were strained through a 0.078-mm sieve. Copper was warmed with paraformaldehyde up to its evaporation temperature and kept in  $\text{CO}_2$ . Zinc was oxide free and did not require reduction.

Melting of polyamide with metal powders proved unsuitable due to the great differences in density, which caused metal sedimentation; therefore, sintering was employed as an alternate method. It was first stated that PA 6 could be molded 6° below its melting point under 1000 kg/cm<sup>2</sup> pressure. The structure of the resulting material could not be distinguished from the polyamide formed from the melt. An electrically heated mold was used to form six tablets simultaneously. Samples with metal additives were formed under the same conditions. Tablets 6 mm in diameter and 2.9–3.0 mm thick were obtained.

The electrical resistivity of the tablets was determined using an electrometer VA-J-5118 (Ger. Dem. Rep.) with a controlled temperature measuring chamber.

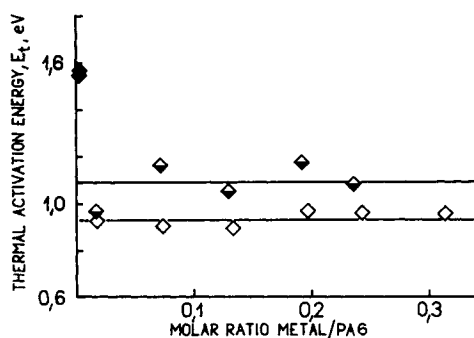


Fig. 2. Thermal activation energy  $E_t$  vs. molar ratio metal/PA 6: ( $\blacklozenge$ ) polycapraamide; ( $\diamond$ ) PA-Cu sinters; ( $\blacklozenge$ ) PA-Zn sinters.

The face surfaces of the tablets were covered with silver paste; tension was applied by means of copper electrodes; and tests were made in a nitrogen atmosphere.

## RESULTS

Experiments were made on samples containing 0.02–0.30 gram-atoms of metal per mole of polyamide (calculated on the basic unit of polycapraamide, MW = 113). This range differs substantially from the one described in reference 6, where up to 60% iron was introduced into polycapraamide, and simple metallic

TABLE I  
Experimental and Calculated Data for PA-Zn Sinters

No.	Composition of sinters		Temp., $1/T \times 10^3$ , $^{\circ}\text{C}$	$1/^{\circ}\text{K}$	$\rho \times 10^{-9}$ , ohm-cm	$\lg \rho$	Thermal activation energy $E_t$ , eV
	% of Zn in sinters	Zn/PA mole ratio					
1	1	0.0175	25	3.36	514.0	11.711	0.964
			48	3.12	30.2	10.480	
			72	2.90	3.04	9.483	
2	4	0.072	26	3.34	430.3	11.634	1.152
			48	3.12	25.0	10.398	
			69	2.93	3.18	9.503	
3	7	0.130	26	3.34	401.0	11.604	1.050
			49	3.11	20.9	10.320	
			68	2.93	3.22	9.508	
4	10	0.192	26	3.34	389.0	11.590	1.172
			48	3.12	18.2	10.260	
			68	2.93	3.07	9.487	
5	12	0.236	26	3.34	542.0	11.734	1.080
			48	3.12	32.3	10.509	
			68	2.93	4.44	9.647	
6	15	0.301	24	3.37	<2.58	9.412	1.083
			Average stand. dev. variance		0.083		
			$s_{n-1}^2$		0.0069		

TABLE II  
Experimental and Calculated Data for PA-Cu Sinters

No.	Composition of sinters		Temp., $1/T \times 10^3$ °C	$1/^\circ\text{K}$	$\rho \times 10^{-9}$ , ohm-cm	$\lg \rho$	Thermal activation energy $E_t$ , eV
	% of Cu in sinters	Cu/PA mole ratio					
1	1	0.018	22	3.38	1740.0	12.241	0.921
			52	3.08	171.0	11.233	
			79	2.84	12.0	10.079	
2	4	0.074	24	3.37	1370.0	12.137	0.902
			54	3.06	73.4	10.866	
			78	2.85	6.56	9.817	
3	7	0.134	24	3.37	1118.0	12.049	0.890
			52	3.08	49.0	10.690	
			79	2.84	5.08	9.706	
4	10	0.198	26	3.34	1210.0	12.083	0.964
			52	3.08	63.2	10.801	
			79	2.84	5.42	9.734	
5	12	0.243	24	3.37	864.0	11.937	0.955
			52	3.08	35.9	10.555	
			78	2.85	2.95	9.470	
6	15	0.314	25	3.36	660.0	11.820	0.952
			53	5.07	29.8	10.474	
			78	2.85	2.25	9.352	
			Average		0.930		
		stand. dev.	0.031				
		variance					
		$s_{n-1}^2$	0.00095				
7	Pure poly-(caproamide)		23	3.38	38800	13.589	1.554
			43	3.16	5000	12.699	
			63	2.98	81.5	10.911	
			82	2.81	4.19	9.622	

conductivity could not be avoided. The results and calculated activation energies  $E_t$  are given in Tables I and II.

Thermal activation energy  $E_t$  was calculated in eV according to

$$\rho = \rho_0 \cdot \exp(E_t/kT)$$

where  $\rho_0$  = standard resistivity, ohm-cm;  $k$  = Boltzman constant,  $8.617 \times 10^{-5}$  eV; and  $T$  = temperature, °K.

## DISCUSSION OF THE RESULTS

The decrease in the electrical resistivity of the sinters, if compared to polyamide, was greater in the case of the PA-zinc system than in the PA-copper system (Fig. 1).

It can thus be concluded that the resistivity of PA-metal sinters is of non-metallic character and that it is not the simple sum of a nonmetallic polyamide and a metallic additive.

The changes in the  $E_t$  and the resistivity of the sinters when compared to polyamide itself prove that there exists a different interaction between the polyamide and copper or zinc (Fig. 2).

It is possible to some extent that electronegative zinc ( $E_{Zn} = -0.76$  V) can substitute for acidic hydrogen atoms in amide groups at the high temperature of molding, while copper can only interact with free electron pairs of nitrogen atoms ( $E_{Cu} = +0.35$  V).

The resistivity of polyamide containing dispersed zinc does not depend on the amount of zinc additive, but on the probability (degree) of the substitution of acidic hydrogen atoms by zinc atoms. Below the melting temperature, only those groups can be substituted which are not crosslinked (bounded) by the hydrogen bonds. It was observed in our case that the substitution takes place with 1% or less of zinc in the sinters. Only part of the zinc reacts with the polyamide and decreases the value of the resistivity and  $E_t$ . The other part remains as a metallic filler dispersed in the polymer matrix and cannot change the resistivity remarkably. That is the reason why the resistivity is almost constant with increasing amounts of zinc in the sinters ( $\rho$  of PA-Zn fluctuates around ca.  $4.6 \times 10^{11} \pm 0.6 \times 10^{11}$  ohm-cm at 22–25°C, around  $2.5 \times 10^{10} \pm 0.7 \times 10^{10}$  ohm-cm at 48–49°C, and around  $3.6 \pm 0.8 \times 10^9$  ohm-cm at 68–72°C for samples 1–5 (Table I). A negative coefficient of resistivity is caused by ionic conductivity and not semiconductivity. The rapid drop of the resistivity at 15% of Zn can be attributed to a combination of metallic and ionic conductivities.

The increase of metal content in PA-Cu sinters causes a marked decrease in resistivity—as much as a fivefold-decrease at 78–79°C (Table II).

Analysis of the basic linear dependence of the resistivity logarithms on the temperature reciprocal  $\lg \rho = f(10^4/T)$  and negative temperature coefficient of the resistivity prove that the above-described polyamide-copper compositions can be classified as semiconductors.

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