

Space - charge - limited conduction in NiCl_2 - doped PMMA films

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SUMMARY:

The effect of weight fraction (1-4%) of NiCl_2 dopant on some parameters characterising the space charge limited conduction (SCLC) in polymethylmethacrylate (PMMA) composites was investigated. The studied parameters are the concentrations of traps, trapped and free charge carriers. It was implied that NiCl_2 acts as an efficient electron acceptor and this was attributed to the formation of $\text{Ni}_{1-x}\text{Cl}_4^{2-}$.

I-INTRODUCTION:

Chutia and Barua investigated the effect of temperature on some parameters of the SCLC for Al/polymer/Al structures, in the case of PMMA (1) and polyvinylacetate (2) films. It is known that (3-5) the doping materials and mechanisms affect notably the electrical conduction of polymers. The present work was devoted to clarify the role of NiCl_2 dopant content on the main parameters characterising the SCLC in Ag/PMMA composite/Ag structure.

II-EXPERIMENTAL:

The studied films were prepared by casting method as follows (6). PMMA material was dissolved in benzene. $\text{NiCl}_2 + 6 \text{H}_2\text{O}$ was dissolved in ethylalcohol, and then added to the polymer solution. After the mixture attained a suitable viscosity it was cast to a glass dish, and kept in a dry atmosphere at 30°C for two weeks. Several thicknesses were available in the range of $20-200 \pm 5$ microns. The electric current was measured by an electrometer (Levell TM98P) of accuracy $\pm 0.2\%$. The films were in the form of discs of 1.6 ± 0.001 cm diameter. Contacts were of highly conductive silver paste with an area of 1 cm^2 . A guard ring was used. The sample was short circuited for about two days, at a constant temperature 30°C , before the dc voltage was applied. The dielectric constant was measured using NF-decameter of frequency range $50-10^6$ Hz at room temperature.

III-RESULTS AND DISCUSSION:

Fig. (1) depicts the current (I)-voltage (V) characteristics at temperature = 293 K for (pure and) doped PMMA films of thickness ≈ 0.2 mm. These plots can be divided into three

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segments, denoted by I, II and III. An ohmic conduction, i.e., $I \propto V$, was indicated in the low voltage segment. In this region the current was controlled by thermally generated carriers and its maximum voltage was denoted by V_{tr} . For the second segment a trap square-law ($I \propto V^2$) was verified and its maximum voltage was denoted by V_{tr1} . At this voltage limit sufficient charges have been injected into the insulator to fill the traps. The current increased sharply, obeying the power dependence $I \propto V^n$ with $n \geq 5.7$ at the third segment. The sharp increase of the current in this region could be attributed to the release of trapped charge carriers. Increasing the voltage higher than the limit of the third segment (>900 V) the film was destructed and a continuous spark was observed.

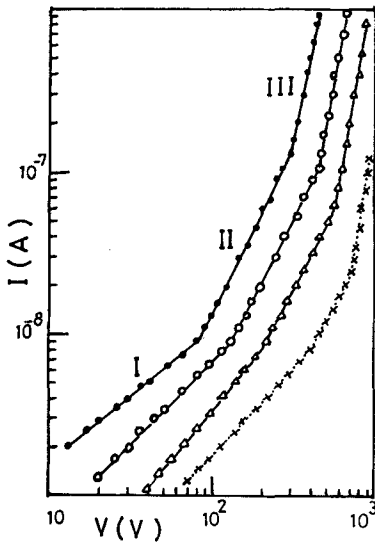


Fig. (1)

The I-V plots of: pure PMMA (x), PMMA doped with (Δ)1, (O)2 and (●) 4 wt.% NiCl₂.

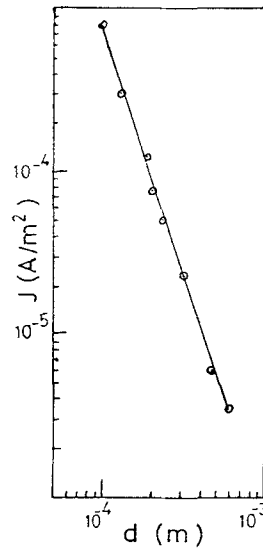


Fig. (2)

Thickness dependence of J for PMMA films in the square law region.

Fig. (2) shows the thickness (d) dependence of the current density (J) in PMMA films in the square law region. A straight line of slope = -2.99 was observed, i.e. $J \propto d^{-3}$.

The results of Figs. (1,2) suggest a space charge limited conduction within the range of V_{tr} to V_{tr1} and the following equation [1] can be verified:

$$J = (9/8) \mu_o \epsilon_o \epsilon \Theta V^2 / d^3, \quad [1]$$

where μ_o is the free carrier mobility, ϵ_o is the permittivity of free space, ϵ is the dielectric constant of the polymer and Θ is the ratio between the free electrons (n_o) in the conduction band to the total electron density ($n_o + n_t$), n_t being the density of trapped electrons. Thus,

$$\Theta = n_o / (n_o + n_t). \quad [2]$$

Experimentally θ is the ratio between the current at the start of the rise to that at the end of the rise in the square-law region (1).

The trap concentration is given by

$$N_t = (2 \epsilon_0 \epsilon / e d^2) V_{tr1}, \quad [3]$$

where e is the electronic charge.

The equilibrium concentration of charge carrier in the conduction band n_0 is defined as

$$n_0 = (\epsilon_0 \epsilon \theta / e d^2) V_{tr}. \quad [4]$$

Using equation 2 and 4 the value of the trapped carrier density n_t can be calculated.

Table (1): The values of ϵ , V_{tr} and V_{tr1} for the studied films.

Sample	ϵ	V_{tr} (Volt)	V_{tr1} (Volt)
PMMA	3.1	400	700
PMMA + 1% NiCl ₂	3.0	215	560
PMMA + 2% NiCl ₂	2.9	130	550
PMMA + 4% NiCl ₂	2.7	80	300

Table (1) lists the value of ϵ , V_{tr} and V_{tr1} for the studied films. The values of the θ , N_t , n_0 and n_t parameters, obtained as explained above, are plotted in Fig. (3) as function of NiCl₂ content. It is clear that all the mentioned parameters decrease as the dopant content increases.

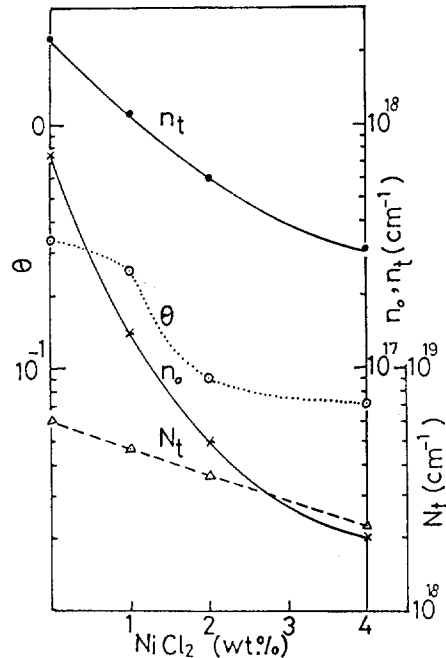


Fig. (3)
The dependence of θ , N_t , n_0 and n_t on NiCl₂ content.

The concentration of free carriers (n_0) descends faster than the trapped carrier concentration (n_t). This implies that the NiCl₂ dopant acts as an efficient electron acceptor which may be attributed to the formation of Ni_{1-x}Cl₄²⁻ (4).

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