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Study of dispersive mobility in polyimide by surface voltage decay measurements

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ABSTRACT

In order to study charge trapping and transport in polyimide, we have submitted samples of Kapton HN to corona charging and measured its surface potential decay with an electrostatic voltmeter. We propose a two terms mobility to explain the experimental data: a non-dispersive contribution based on Toomer and Lewis model added to a dispersive process, which is associated with the disordered structure of the material. The non-dispersive model alone did not fit well to the data for short times, but our assumption makes the theoretical expression fit successfully to the experimental data. Some important parameters related to the charge transport properties of the material are determined and discussed.

1. Introduction

The use of polyimide (PI) has become widespread in aerospace industry because of its high performances as thermal and electrical insulators. Due to its properties, this material is used as a thermal blanket to prevent artificial satellite systems from wide temperature oscillations. Satellites in space environment are exposed to intense radiations (energetic electrons, ions, X-rays,...) that charge its surface electrically. Polyimide, as it happens in other insulating materials, becomes charged electrically when it is subjected to radiation, so that spontaneous discharges may arise that can lead to malfunctions of the sensitive systems on board [1–4]. In order to improve its mechanical and electrical properties, some studies on PI have been carried out, which propose new synthesis processes [5], fabrication of composites with carbon nanotubes [6] and with silica [7].

There have been registered a few cases where normal operation of board electronics have been interrupted due to spacecraft charging [8]. Understanding and controlling the processes that lead to space charge formation and relaxation in this material are, thus, relevant in order to improve the performance of such blankets. The aim of this paper is to study the space charge relaxation in polyimide, in order to characterize the microscopic processes that contribute to the mobility of the carriers.

Surface potential decay experiments are widely used to study charge transport in polymers [9–15]. In these experiments a film of polymer is submitted to a discharge from a needle and the ions produced are injected on the surface of the film. Electrons or holes move towards the rear electrode due to their own electric field in order to reach electrical equilibrium. Several authors have proposed models to describe these processes [16–20]. Carriers in this situation do not move with the proper mobility of the band, but their mobility is modulated by the presence of traps and by the influence of other carriers. That is why an effective mobility

$$\mu_{\rm eff}(t) = \mu_0\eta(t) \tag{1}$$

has to be considered, where μ_0 is the proper mobility in the band and $\eta(t)$ is the ratio of carriers contributing to the process at a time t.

2. Theory

In the case of amorphous materials, discrete trapping levels or bands of trapping levels appear at the bottom of the conduction band (traps for electrons) and the top of the valence band (traps for holes). Carrier mobility is affected by the presence of such trapping levels. Electrons near the bottom of the conduction band move

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between extended states by hopping. Such process requires no thermal activation and leads to relatively high mobilities of about $10\ \mathrm{cm^2\,V^{-1}\,s^{-1}}$. If the electron is captured by a trap, its mobility becomes orders of magnitude smaller (analogous process may happen for holes at the top of the valence band). Electron captured by a shallow trap needs thermal energy to perform a thermally activated hopping process, resulting in mobilities of about $10^{-3}\ \mathrm{cm^2\,V^{-1}\,s^{-1}}$. Carriers located in deep traps experience very long capture time and their mobility becomes very small ($10^{-10}\ \mathrm{cm^2\,V^{-1}\,s^{-1}}$ to $10^{-17}\ \mathrm{cm^2\,V^{-1}\,s^{-1}}$). Therefore, a sharp variation of the mobility is expected at levels close to both, the bottom of the conduction band and the top of the valence band, which determines the mobility edges, resulting in a trap modulated mobility [21–23].

The distances between various neighboring trapping sites have some variations about a mean value and even a distribution in trapping energy levels may happen. As transition times which determine the kinetics of the process sensitively depend on these differences in distance and energy, they will suffer a wide statistical dispersion, which results in a mobility that shows a power time dependence in the time domain (dispersive mobility) [24]. This dispersive behavior is reflected by a sublinear frequency dependence in frequency domain measurements of the conductivity [25].

We shall consider that charge transport through the sample is due to two contributions in order to explain the surface potential decay observed in PI. One contribution is associated with a non-dispersive transport process and the other with a dispersive transport process. Charges travelling through the sample may become trapped, so that only a fraction of them contributes to mobility. This lowers the density of carriers of the leading charges' line, so that there are less charges competing for the traps and the effective correlation diminishes, that is why we can expect the dispersive term to be more important for short times. Taking this into account, we can write the effective mobility as

$$\mu_{\mathrm{eff}}(t) = \mu_{\mathrm{N}}(t) + \mu_{\mathrm{D}}(t) = \mu_0(\eta_{\mathrm{N}}(t) + \eta_{\mathrm{D}}(t)) \tag{2}$$

where subindex N refers to the non-dispersive process and D to the dispersive one.

2.1. Non-dispersive mobility

In the case of non-dispersive transport, we consider that charges are injected into the bulk immediately after the corona injection. The band structure can provide several kinds of traps for the charge carriers with different energetic depths. The initial charge spreads into the different traps, a_i being the portion of the initial charge trapped in the state $i = 1\ldots n$, with $\sum_{i=1}^{n} a_i = 1$. Charges drift through the sample hopping from one localized state to another, r_{ri} being the probability per unit time of a charge to release from a trapping level i and r_{ti} the probability per unit time to be retrapped at trapping level i. In this case the function $\eta(t)$ has the form [26]:

$$\eta_N(t) = LT^{-1}\left[\frac{1}{s}\frac{1}{1+\sum_{i=1}^{n}\frac{r_{\mathrm{ti}}}{s+r_{\mathrm{ri}}}a_i}\right] \tag{3}$$

where LT refers to the Laplace transform of the function and s is the reciprocal time.

In order to ensure our assumption that all charges are injected instantaneously, we have applied a high enough electric field to the needle. In this case charges do not fall into surface traps from where they jump to the bulk, but they are injected directly into the bulk, where the dynamics of charge transport occurs by hopping between localized trapping centers. In our study we consider the simplest case: we assume that the existence of one trapping level thermally connected and that thermally disconnected levels are filled. Therefore, Eq. (3) can be written as

$$\eta_{\mathrm{N}}(t) = LT^{-1}\left[\frac{1}{s}\frac{1}{1+\frac{r_{\mathrm{t}}}{s+r_{\mathrm{r}}}}\right] \tag{4}$$

Transformation of Eq. (4) to time domain leads to

$$\eta_{\mathrm{N}}(t) = \frac{r_{\mathrm{r}} + r_{\mathrm{t}}\ \mathrm{e}^{-Rt}}{R} \quad (R = r_{\mathrm{r}} + r_{\mathrm{t}}) \tag{5}$$

This expression was previously found by Toomer and Lewis, who considered the dynamics of the hopping transport, and defined [18]

$$\mu_{\mathrm{eff}}(n_{\mathrm{f}} + n_{\mathrm{t}}) = \mu_0 n_{\mathrm{f}} \tag{6}$$

where n_{t} refers to trapped charge and n_{f} refers to free charge, the one that contributes to mobility.

When charges get the grounded rear electrode they do not contribute any more to the surface potential that we measure, so the decay behaves differently during the travel of the leading charges than after they have reached the grounded electrode. The time this front of charges takes to get through the sample is the transit time, t_τ. We shall limit our study to $t < t_\tau$. Up to the transit time the derivative of the surface potential can be written [18] as

$$\frac{\mathrm{d}V}{\mathrm{d}t} = -\frac{1}{2}\mu_{\mathrm{eff}}(t)\frac{V_0^2}{d^2} \tag{7}$$

where d is the sample thickness.

2.2. Dispersive mobility

Several authors [24,26–30] have treated dispersive mobility theoretically but, as far as we know, low attention has been paid from the experimental point of view. This behavior has been taken on account by several authors to describe the anomalous transport observed in some photosensitive materials, and it has been extended to different areas successfully, such as fluid dynamics, geology, Brownian motion, as well as to electric transport in insulating materials [30–33].

Scher and Montroll [24] developed a stochastic transport model to explain charge transport in disordered materials. This model is based on the dispersion of the distances between localized sites available for carriers to hop and on the dispersion of the potential barriers between these sites. This distribution in distances and/or energies affects the time a charge needs to hop from one site to another. These charges are supposed to follow a time dependent random walk governed by a waiting-time distribution function $\psi(t)$. The shape of this distribution function will be related to the lack of order of the material. In the reciprocal time domain this function is related to $\eta(t)$ by [24,28]:

$$\mathrm{LT}[\eta(s)] = \frac{s\mathrm{LT}[\psi(s)]}{1-\mathrm{LT}[\psi(s)]} \tag{8}$$

On the one hand, charge transport in a free of traps ordered material is described by a Gaussian distribution function $\psi(t) \propto \mathrm{e}^{-\beta t}$, where there is no dispersion of the charges' packet and the shape of the charges' distribution is maintained. This corresponds to a constant mobility, $\mu \propto \mu_0\delta(t)$. On the other hand, a dispersive transport regime in a potential decay process is characterized [24] by $\psi(t) \propto t^{-1-\alpha}$, which gives a time dependence of mobility

$$\eta(t) \approx LT^{-1}\left[ks^{1-\alpha}\right] \tag{9}$$

where k is a constant and $0 \le \alpha \le 1$. For the initial stage of the discharge, the time derivative of the surface potential is approximately [28]