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A quantitative analysis of the polarization reversal in the 73 mol % vinylidene fluoride–27 mol % trifluorethylene copolymer

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We show that a time-dependent, effective-medium approximation essentially explains the time behavior of the polarization reversals obtained in doped copolymers of vinylidene fluoride and trifluorethylene at 60 °C by Ieda, Fukada, and Wada [*J. Appl. Phys.* **64**, 2026 (1988)], who attributed the observed effects to charge accumulation at the boundaries of the permanently polarized crystallites. Moreover, the results seem to indicate that some hindrance (perhaps of mechanical origin) opposes the action of the switching electric field.

I. INTRODUCTION

A great deal of discussion has been devoted to the importance of internal fields due to space charge development on the stability of the ferroelectricity on polymers such as polyvinylidene fluoride (PVDF) and copolymers of vinylidene fluoride and trifluorethylene (VDF-TrFE).¹ Here we will be concerned with a work by Ieda, Fukada, and Wada² in which a similar effect was clearly shown to be present. These authors worked at 60 °C with the 73 mol % VDF–27 mol % TrFE copolymer, varying the amount of iodine doping in order to increase the conductivity and, consequently, to enhance the charge separation effect. The technique employed was the polarization reversal for increasing waiting times, t_w , after a convenient preparation of the sample by alternating voltage pulses (as will be shown later). They noted that although this process collected the same total charge at each reversal, the process required more time, t_s , for larger waiting times, t_w . They interpreted these results by saying that during the waiting time conductivity charges of the amorphous phase were deposited on the boundaries of the ferroelectric domains, causing the depolarization field to decrease. Since the switching time for the flipping process is electric field dependent,^{3,4} the observed increase of the switching time was explained by the above-mentioned decrease of the depolarization field which would contribute progressively less to the electric field applied in the reverse direction after the waiting time is over. Concerning the influence of doping, the $\log(t_s) \times \log(t_w)$ plots for a constant polarizing electric field were displaced to higher t_s , at constant electric field, for increased doping (see Fig. 9 of Ref. 2 or our Fig. 1 to be shown later).

In this article we will be more quantitative and show that the observed relation between $\log(t_s) \times \log(t_w)$ may be reasonably explained (there is one exception, to be commented upon later, corresponding to $t_w = 1$ s) by a simple effective time dependent^{5,6} medium theory appropriate to the topology of permanently polarized ellipsoidal crystallites embedded in a conducting medium, whose results are

given in the next section. As a consequence of our analysis it will be inferred that there is a hindrance, possibly of mechanical origin, to the dipole reorientation.

II. THEORETICAL RESULTS

We assume a planar capacitor with a dielectric consisting of polarized ellipsoidal crystallites embedded in an amorphous phase, having, respectively, permittivities ϵ_c and ϵ_a . We also assume that at the end of the initialization process (a series of positive, short circuit, and negative applied voltage 1-s-long steps, terminating with a positive bias, see Fig. 2 of Ref. 2) no charge accumulation occurs at the boundaries of crystallites. However, such an accumulation does occur during the larger waiting times, t_w , following the initialization, producing a decrease of their internal electric field. Using a time-dependent, effective-medium approximation, it can be shown that^{5,6} the electric field, E_1 , inside ellipsoidal crystallites (whose axes $\mathbf{a}$ are parallel to the previously applied electric field E_0) is given by

$$E_1 = -\frac{n^{(a)}(1-C_0)P_0}{\epsilon_a - (\epsilon_a - \epsilon_c)n^{(a)}(1-C_0)} \exp\left(-\frac{t_w}{\tau}\right). \quad (1)$$

In Eq. (1), P_0 is the polarization density of the ferroelectric crystallites, C_0 is their volume fraction, and $n^{(a)}$ is the depolarization factor⁷ given by

$$n^{(a)} = \frac{abc}{2} \int_0^\infty \frac{ds}{(s+a^2)R_s}, \quad (2)$$

$$R_s = \sqrt{(s+a^2)(s+b^2)(s+c^2)}, \quad (3)$$

in which b and c are the lengths of the other two ellipsoidal axes. For the sphere, $n^{(a)}$ is $\frac{1}{3}$. Note that the $\mathbf{a}$ on $n^{(a)}$ has nothing to do with the $\mathbf{a}$ of ϵ_a .

Still referring to Eq. (1), τ is the relaxation time equal to

$$\tau = \frac{\epsilon_a - (\epsilon_a - \epsilon_c)(1-C_0)n^{(a)}}{g[1 - (1-C_0)n^{(a)}]}, \quad (4)$$

FIG. 1. The best fitting (full curves) provided by our Eq. (9) [and also Eq. (13)] to the plot in Fig. (9) of Ref. 1 for 1 month (1M) and 1 week (1W) doped samples and for an undoped one (UD) (discrete marks are the measured values). The electric field was kept constant (0.8 MV/cm) while the waiting time, t_w , was varied from 1 to 1000 s. The switching time, t_s , is also in seconds.

g being the conductivity of the amorphous phase. Note that E_1 is decreasingly negative with respect to the previous orienting electric field, which was made null during the waiting time. The electric field E_0 is applied again after t_w with the reversed sense, such that the total field, E_t , inside the crystallites becomes

$$E_t = -\frac{\epsilon_a E_0 + n^{(a)}(1 - C_0)P_0 \exp(-t_w/\tau)}{\epsilon_a - (\epsilon_a - \epsilon_c)(1 - C_0)n^{(a)}}, \quad (5)$$

whose absolute value decreases with t_w . The switching time t_s depends on the electric field via

$$t_s = t_{s_0} \exp\left(\frac{E'_a}{E}\right), \quad (6)$$

where t_{s_0} and E'_a are constants. E in Eq. (6) was first taken as the applied field⁴ but a more refined treatment showed that it should better be taken as the actual field inside the crystallites⁸ [like in Eq. (5), with $t_w=0$]. By a proper change of E'_a , Eq. (6) can be rewritten using Eq. (5) for the modulus of the field inside the crystallites,

$$t_s = t_{s_0} \exp\left(\frac{E_a}{E_0 + A \exp(-t_w/\tau)}\right), \quad (7)$$

with

$$E_a = E'_a(1 - \epsilon_c/\epsilon_a)(1 - C_0)n^{(a)}$$

and

$$A = n^{(a)}(1 - C_0)P_0/\epsilon_a. \quad (8)$$

Taking the log of both sides of Eq. (7) we finally get

$$\log(t_s) = \log(t_{s_0}) + \frac{0.4343}{(E_0/E_a) + (A/E_a)\exp(-t_w/\tau)}. \quad (9)$$

In the next section a correction to Eq. (9) will be proposed on account of the analysis carried out there.

TABLE I. Parameters derived from either Eq. (9) or Eq. (13). See also Fig. 1. $t_{s_0} = 5.0 \times 10^{-8}$ s was chosen from Ref. 2 and used as such in all the cases.

Doping time	$10^2 \times E/E_a^a$	$10^2 \times A/E_a$	τ (s)
1M	7.29	1.75	86
1W	7.76	1.95	129
UD	8.00	2.58	150

^a $E = E_0$ if Eq. (9) is used and $E = E_0 - E_i$ for Eq. (13) (see Sec. III).

III. FITTING

The curves in Fig. 9 of Ref. 2 were fitted with our Eq. (9) for a constant applied field (0.8 MV/cm)⁹ and a varying t_w for different doping; the results are shown in Fig. 1 and Table I. t_{s_0} was chosen equal to 5×10^{-8} ($10^{-7.3}$ s) in all cases.² Except for the $t_w = 1$ s points, that is, for most of the time, Eq. (9) provides a reasonable fitting, producing the values of the parameters E/E_a , A/E_a , and τ as given in Table I in which UD refers to an undoped sample while 1W and 1M refers to samples kept, respectively, one week and one month within a saturated iodine atmosphere at room temperature. The figure seems to be reasonable but an unexpected decreasing trend with doping is observed for E/E_a and A/E_a . As $E_0 = 0.8$ MV/cm, E_a gives for the 1M sample 11 MV/cm (see the following) and $A \approx 0.19$ MV/cm.

From Eq. (4), τ is inversely proportional to the conductivity, g , which ought to increase with the doping time, t_p . Calling g_0 the conductivity of the undoped sample

$$g = g_0 + k t_p \quad (10)$$

or

$$1/\tau = 1/\tau_0 + k' t_p, \quad (11)$$

with k and k' constants. Figure 2 shows that the reciprocal of the conductivity relaxation time is indeed proportional to t_p .

We have also examined Fig. 10 of Ref. 2, which was obtained by varying the applied electric field for fixed waiting times on the 1M sample. According to Eq. (9) we may find that

$$E_0 = \frac{0.4343 E_a}{\log(t_s) + 7.3} - A \exp\left(-\frac{t_w}{\tau}\right). \quad (12)$$

FIG. 2. The inverse of the relaxation time, $1/\tau$, as a function of the doping time. $1/\tau$ is proportional to the conductivity, Eq. (4).

FIG. 3. Plot corresponding to our Eq. (14). The points were taken from Fig. 10 of Ref. 2 and refers to the 1M sample subjected to the specified waiting times (1800, 300, and 1 s denote curves 1, 2, and 3, respectively), for varying electric fields.

Figure 3 shows the straight lines for $E_0 \times 1/[\log(t_s) + 7.3]$ plots corresponding to $t_w = 1800, 300$, and 1 s, corresponding to curves 1, 2, and 3, respectively. The intercept at the ordinate axis for curves 1 and 2 is clearly positive, while a negative one was expected from Eq. (12). One ad hoc way out of this difficulty is to change the denominator in Eq. (7) in such a way that Eq. (9) now reads

$$\log(t_s) = \log(t_{s0}) + \frac{0.4343E_a}{E_0 + A \exp(-t_w/\tau) - E_i}, \quad (13)$$

changing Eq. (12) into

$$E_0 = \frac{0.4343E_a}{\log(t_s) + 7.3} - A \exp\left(-\frac{t_w}{\tau}\right) + E_i, \quad (14)$$

where E_i is a correction to the applied E_0 field. Note that E_i in Eq. (13) does not affect the dependence between $\log(t_s)$ and $\log(t_w)$ as in Eq. (9). For $t_w = 1800$ s ($\tau = 86$ s) the term containing the exponential gives a negligible contribution and the intercept gives directly $E_i \approx 0.20$ MV/cm. From the slopes of the straight lines in Fig. 3 and with the help of Eq. (14), we get for $E_a \approx 8.14$ MV/cm. Practically the same value is obtained when recalculating A by means of Eq. (13) with the data of Table I for the 1M sample. It is also interesting to note that curve 1 corresponding to

$t_w = 1$ s is parallel to the other two and displaced downward as it should be because of the non-negligible contribution from the term in A in Eq. (14). In view of this, it is not clear to us why the points corresponding to $t_w = 1$ s in Fig. 1, especially for the 1M sample, are not fitted by our Eq. (9).

We may speculate that the origin of the correction field E_i could be ascribed to a mechanical hindrance for the orientation of the dipoles leading, ultimately, to a threshold value for the switching electric field (not to be confused with the so-called coercive field).

IV. FINAL COMMENTS

As confirmed more quantitatively here, the method devised in Ref. 2 clearly allows detecting the influence of conductivity charges to the stabilization (in the sense of requiring greater times for turning the dipoles). However, a temperature higher than room temperature was used for that purpose. Such a stabilization effect has been invoked to occur^{1,10} in pure β -phase PVDF at room temperature and therefore it would be interesting to try to correlate this effect with the sample conductivity.

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