*Table 1* Single activation energies for the thermal oxidation of various polyolefins

| Activation energy (kcal/mol) | IPP | APP | IPB | APB | IPP-1 | IPMP (below 150°C) | IPMP (above 150°C) | APMP |
|---|---|---|---|---|---|---|---|---|
| $E_1$ | 21 | 18 | 16 | 18 | 21 | 10 | 10 | 13 |
| $E_5$ | 29 | 29 | 25 | 22 | 26 | 17 | 19 | 27 |
| $E_6$ | 24 | 30 | 22 | 19 | 25 | 23 | 18 | 30 |

IPMP (above and below 150°C) are listed in *Table 1*. In the case of IPP, APP, IPB, and APB, the values of the various kinetic parameters (i.e. $K_1$, $K_2$, $K_3$, $\rho_m$, $A$, $k'$) used to estimate $E_1$ and $E_6$ were refined and recalculated as described elsewhere[9]. From *Table 1*, different values of $E_1$ may be noted which may be attributed to the different nature and identity of the polyolefin chain in the initiation step. It is possible that the values of $E_1$ may be somewhat low for step (1). In the case of low hydrocarbons Russel[10] studied the oxidation of indene and found that the kinetics of the reaction were consistent with the initiation process as in step (1). The activation energy for the reaction was estimated as 25 kcal/mol from the R–H bond energy and the dissociation energy of $H{-}O_2$. Further, by assuming a steric factor of $10^{-3}$ and a collision number of $10^{11}$, $k_1 = 10^8\exp(-25\,000/RT)$. The calculated value of $k_1$ for the indene oxidation at 50°C was found to be in good agreement with the experimental value at 50°C. In the case of the polyolefins, relative to values of $E_1$ (of *Table 1*), it would be noteworthy to consider or take into account the influence of metal catalyst[1]. Polyolefins may contain trace metals as residuals from the Ziegler–Natta catalysis of the olefins. For example, the lower value of $E_5$ for IPB compared with APB was attributed by Stivala, Yo and Reich[5] to the presence of various trace metals in the isotactic poly(butene-1) sample detected from its ash by spectroscopy.

Values of $E_6$ activation energy for the decomposition step of peroxides yielding non-volatile carbonyl products for APP was reported as 27 kcal/mol by Nieman[11] and a value of 21 kcal/mol for IPMP was reported recently by Zitomer and DiEdwardo[12].

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# Non-linear electric behaviour of polymeric materials interpreted through free volume changes

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## INTRODUCTION

The electrical behaviour of polymeric materials has received much attention because some of the properties peculiar to polymers may find useful applications. The change of resistivity with temperature[1], the relationship between the applied electrical field and the resulting current[2,3] and the dielectric rigidity[4] may be considered typical examples of such studies.

The occurrence of non-linear electric phenomena in these materials is generally attributed both to the temperature rise due to the circulating current (especially relevant in the case of an alternating current) and to the direct influence of the applied field. If, as an example, the stress aging phenomenon is considered, i.e. the degradation in time of the electrical characteristics when a field is applied, the process rate, $v$, is assumed to be[5]:

$$v = aT^w \exp(-b/kT) \times \exp\{f(V)[c + (d/kT)]\} \qquad (1)$$

where $a$, $b$, $c$, $d$ and $w$ are material constants, $k$ is Boltzmann's constant, $T$ is the absolute temperature and $f(V)$ is a function of the applied voltage. In equation (1) the effect of temperature is taken into account through an Arrhenius-type dependence and that of the electrical field through the Eyring model.

In this work a possible interpretation of non-linear effects is advanced in terms of 'free volume'. Use will be made of concepts analogous to those already applied in considering nonlinearities in the rheological behaviour of polymeric systems.

## ANALOGY BETWEEN ELECTRICAL AND MECHANICAL BEHAVIOUR

Viscosity and resistivity depend upon temperature in a similar way. This dependence is often written as:

$$\eta = A \exp\left(\frac{E_a}{RT}\right) \qquad (2a)$$

$$\rho = B \exp\left(\frac{E_a}{RT}\right) \qquad (2b)$$

where $\eta$ and $\rho$ are viscosity and resistivity, respectively; $E_a$ is activation energy and $A$ and $B$ are frequency factors.

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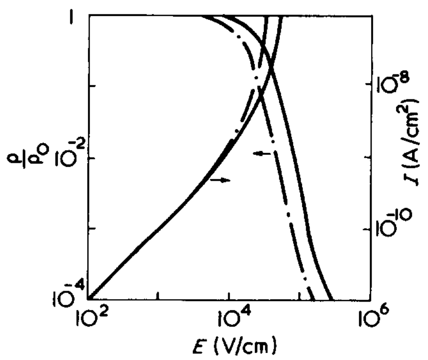

*Figure 1* Dimensionless resistivity and current vs. electric field. ——, $a = 1 \times 10^{-4}$ m$^2$/N; — · —, $a = 3 \times 10^{-4}$ m$^2$/N; $f_0 = 0.1$; $\rho_0 = 10^{13}$ Ω cm; $\epsilon' = 2.5$

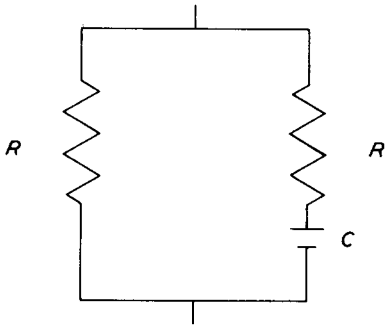

*Figure 2* The circuit used for modelling the material

On the other hand, the dependence of viscosity upon temperature has often been written as[6]:

$$\eta = \eta_0 \exp\left(\frac{1}{f} - \frac{1}{f_0}\right) \tag{3}$$

where the free volume fraction, $f$, is considered to vary linearly with temperature at temperatures near $T_g$:

$$f = f_g + \Delta\alpha(T - T_g) \tag{4}$$

In equation (3), $\eta_0$ is the viscosity corresponding to the free volume fraction $f_0$, i.e. to a reference temperature. In equation (4), $f_g$ is free volume fraction at the glass transition temperature, $T_g$, and $\Delta\alpha$ is the difference in the thermal volume expansion coefficients above and below $T_g$.

An equation similar to equation (3) is here proposed to interpret the dependence of resistivity upon temperature:

$$\rho = \rho_0 \exp\left(\frac{1}{f} - \frac{1}{f_0}\right) \tag{5}$$

Equations (3) and (5) should be quite general: however, their application may be limited in practice. For instance the linear dependence of free volume on temperature (equation 4) is only verified in the range $T_g$ to $T_g$ + 100°C. Other relations which are valid over wider ranges are limited to few polymers[7].

It has often been stated that the ratio $\eta/\rho$ is independent of temperature[8], or equivalently, that the activation energy for the two processes is the same. The experimental results are somewhat uncertain: they certainly indicate similar values of $E_a$, but in some cases discrepancies in the ratio $\eta/\rho$ by as much as a factor of two have been found[9]. It should be appreciated that the assumption that equations (3) and (5) hold simultaneously implies that the activation energies for the two processes are equal.

In the field of polymer rheology, it has recently been proposed[10] that there exists some sort of equivalence between temperature and stress, i.e. that the application of a stress to a polymeric material corresponds to a temperature increase. In particular, the assumption has been made that the free volume changes, not only because of changes in temperature, but also as a consequence of the applied stress through the stored elastic energy:

$$f = f_0 + a\frac{E_\tau}{G} \tag{6}$$

where $f_0$ is the free volume fraction at a given temperature when the sample is stress free, $G$ is the elastic modulus, $E_\tau$ is the stored elastic energy and $a$ is a constant depending on the nature of the polymer, the value of which can be found by best-fitting with some experimental data. Through equation (6) and an equation formally equivalent to equation (3) it is possible to explain the well known viscosity decrease with increasing velocity gradient and many other non-linear effects. It is proposed that a similar approach can be used to explain the dependence of current upon voltage.

In particular, a relationship similar to Ohm's law is considered valid in the case of a resistance changing with the applied voltage.

The main assumption is that at any given temperature we have:

$$\rho = \rho_0 \exp\left(\frac{1}{f} - \frac{1}{f_0}\right) \tag{7}$$

with

$$f = f_0 + aE_E \tag{8}$$

where $a$ is a constant for the material and $E_E$ is the energy stored in the dielectric, given by:

$$E_E = \frac{1}{2}\epsilon'\epsilon_0 E^2 \tag{9}$$

where $\epsilon_0$ is the dielectric constant of a vacuum, $\epsilon'$ is the dielectric constant of the polymer and $E$ the dielectric field strength.

## THEORETICAL PREDICTIONS

We shall consider the case of an amorphous polymer above its glass transition temperature or a molten polymer. Following on from experimental evidence[2,11] the steady state electrical behaviour of the material can be described simply by a single resistance. From equations (7)–(9), the dependence of $\rho$ upon $E$ can easily be calculated, and, applying Ohm's law:

$$i = \frac{E}{\rho} \tag{10}$$

the non-linear dependency of the current upon voltage is derived.

In *Figure 1* the predicted behaviour for both the resistivity and the current is reported as a function of the applied electric field.

Typical values of $f_0$ and $\rho_0$ have been employed in the calculations while the influence of the parameter $a$ is shown. The curves show the qualitative features which are experimentally observed[2,3]

The single resistance model proves inadequate in the interpretation of transient responses. We shall use the model shown in *Figure 2* where a capacitor $C$

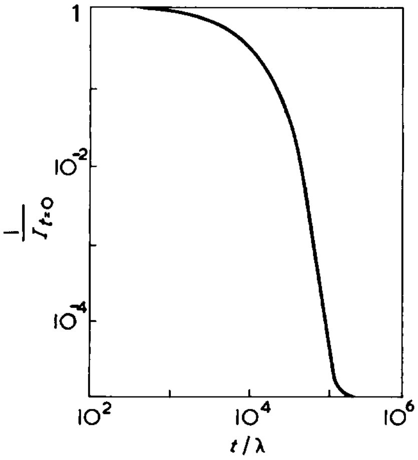

*Figure 3* A generalized plot of current vs. time in dimensionless form $\rho_0/\rho_0' = 10^5$

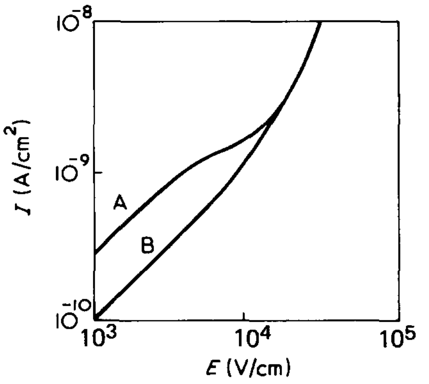

*Figure 4* Current vs. electric field at different values of time. A, $t/\lambda_0 = 11$; B, $t/\lambda_0 = 100$. $a = 1 \times 10^{-4}$ m$^2$/N

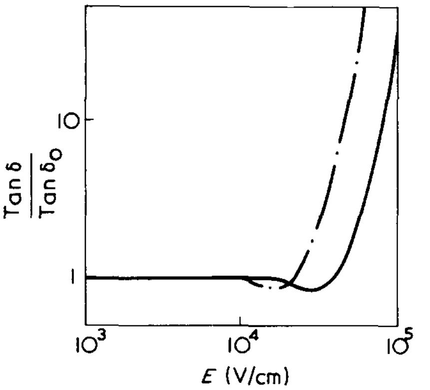

*Figure 5* Dimensionless dissipation factor vs. electric field (r.m.s.). ——, $a = 1 \times 10^{-4}$ m$^2$/N; — · — ·, $a = 3 \times 10^{-4}$ m$^2$/N. Frequency = 50 Hz

and a second resistor $R'$ are added in parallel to the steady state resistor $R$. Such a model accounts for the current decay which is typical of 'real' dielectrics even in the linear range[2,11].

If we include the previously considered variations of $R$ and $R'$ in the model we can easily interpret some non-linear effects.

The equation of the circuit in *Figure 2* is:

$$I = \frac{V}{R} + \frac{V}{R'} \exp\left(-\frac{t}{R'C}\right) \qquad (11)$$

where $V$ is voltage and $t$ is time.

By defining the relaxation time, $\lambda$, as $\lambda = R'C$ equation (11) may be rewritten as:

$$i = \frac{E}{\rho} + \frac{E}{\rho'} \exp\left(-\frac{t}{\lambda}\right) \qquad (12)$$

where $i$ is current density.

In equation (12), $\rho$, $\rho'$ and $\lambda$ depend on $E$ through equations (7), (8) and (9). Of course equation (12) degenerates as expected at steady state as previously considered.

Predictions from equation (12) are reported in *Figure 3* in a generalized form for the same value of $f_0$ used before and for an assumed ratio $\rho_0/\rho'_0$. This ratio has been chosen as being equal to $10^5$ as suggested by the physical meaning of $R$ and $R'$: $R$ is the ohmic resistance of the material, which is, in general, very large, while $R'$ is the loss resistance of the 'real' dielectric and is thus much smaller than $R$.

From a plot such as that in *Figure 3* for assigned values of the electric field, it is possible to obtain the dimensional values of the current as a function of time for any given material, i.e. for assigned values of $\rho_0$, $\epsilon'$ and $a$.

Experimental evidence of non-linear effects are given, for instance, in ref 2, where current–voltage curves are reported for two different values of time. In *Figure 4*, the theoretical predictions are reported in a similar form. The parameter of the curves is the dimensionless time $t/\lambda_0$, with $\lambda_0$ indicating the value of $\lambda$ at zero electric field. The predicted behaviour is qualitatively very similar to that observed experimentally, but for the highest values of the applied field. It must be noticed, however, that such high values of the field are of the order of the dielectric strength.

Considering now the behaviour of these materials when subjected to alternating voltages, we recall, as an example of non-linear effects, the increase of the dissipation factor with the field (r.m.s.)[12].

The phase angle for the model circuit in *Figure 2* is given by:

$$\tan\phi = \frac{\rho/\omega\epsilon'\epsilon_0}{\rho'^2 + (1/\omega^2\epsilon'^2\epsilon_0^2) + \rho\rho'} \qquad (13)$$

where $\omega$ is $2\pi$ x frequency.

In *Figure 5*, predictions from the model for a given value of $\omega$ are reported in the form of dimensionless $\tan\delta$ vs. $E$ ($\delta = 90° - \phi$). In this Figure, $\tan\delta_0$ represents the value of $\tan\delta$ at a very small field.

The theoretical curves closely resemble those experimentally observed, which show a rapid upturn after an initial zone where $\tan\delta$ is essentially constant.

A final comment is necessary with regard to the temperature problem. We have assumed throughout this study that temperature does not change because of electric effects. This is an approximation which is certainly good in the d.c. case while it might be somewhat questionable in the a.c. case, especially at high frequency. However it is easy, at least in principle, to include thermal effects in the model predictions by considering the known dependence of $\rho$ on temperature through free volume (equations 4 and 5).

Finally, it must be noticed that no attempts have been made to compare quantitatively experimental results and model predictions. Our feeling is that for a quantitative description of the transient electric properties of polymeric materials one relaxation time is not enough, and, in fact, it is experimentally known that these materials show in general a distribution of relaxation times. Work is in progress in the direction of extending the single relaxation time model to the case of a spectrum.

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