ELECTRICAL PROPERTIES OF A DIELECTRIC WITH A VARIABLE NUMBER OF RELAXATORS

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Abstract

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ELECTRICAL PROPERTIES OF A DIELECTRIC WITH A VARIABLE NUMBER OF RELAXATORS

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It is known that if polarization is associated with the orientation of dipoles or is caused by the transfer of ions from one equilibrium position to another, then it is established not instantaneously after a change in the field, but over a certain time. Such polarization is called relaxation polarization. Ions or dipoles whose motion leads to relaxation polarization will be called relaxators.

Various assumptions are made concerning the dependence of the magnitude of relaxation polarization on the time of its establishment. In particular, it is assumed that after the field is switched off the relaxation polarization P disappears with time according to the law:

$$P = P_0 e^{-t/\tau}, \tag{1}$$

where P_0 is the relaxation polarization before the field is switched off; t is the time counted from the moment the field is switched off, and τ is the relaxation time.

If the field in the dielectric varies sinusoidally with time with angular frequency ω, then, owing to relaxation of the polarization, the dielectric permittivity at this frequency ε may turn out to be lower than that which the dielectric would have in a constant field.

Regardless of the nature of the polarization, if equality (1) is fulfilled, then

$$\varepsilon = \varepsilon_0 + \frac{\varepsilon_s - \varepsilon_0}{1 + (\omega\tau)^2} = \varepsilon_0 + \frac{4\pi\chi}{1 + (\omega\tau)^2}, \tag{2}$$

$$\operatorname{tg}\delta = \frac{(\varepsilon_s - \varepsilon_0)\omega\tau}{\varepsilon_s + \varepsilon_0(\omega\tau)^2} = \frac{4\pi\chi\omega\tau}{4\pi\chi + [1 + (\omega\tau)^2]\varepsilon_0}, \tag{3}$$

where ε_s is the static dielectric permittivity; ε_0 is the dielectric permittivity at high frequency, when relaxation polarization does not arise, and χ is the static relaxation electric susceptibility.

The dependence of $\operatorname{tg}\delta$ on ω has a maximum at a frequency determined from the condition

$$(\omega\tau)^2 = \frac{\varepsilon_s}{\varepsilon_0}. \tag{4}$$

The maximum value of the tangent of the dielectric loss angle is equal to:

$$\operatorname{tg}\delta_{\max} = \frac{\varepsilon_s - \varepsilon_0}{2\varepsilon_s}\sqrt{\frac{\varepsilon_s}{\varepsilon_0}}. \tag{5}$$

It is assumed that the relaxation time τ depends exponentially on temperature, i.e.,

$$\tau = \tau_0 e^{V/kT}, \tag{6}$$

where τ_0 is the relaxation time at a very high temperature, V is the activation energy, $kT \gg V$.

Usually, in investigating dielectric losses it is assumed that the number of relaxators does not depend on temperature. Under this assumption, the theory predicts a temperature maximum of $\operatorname{tg}\delta$ at τ and temperature determined from conditions (4) and (6). In the case of low temperatures and high frequencies such that $\omega\tau \gg \varepsilon_s/\varepsilon_0$, the following approximate equalities are valid:

$$\varepsilon - \varepsilon_0 = \frac{\varepsilon_s - \varepsilon_0}{(\omega\tau_0)^2} e^{-2V/kT} = \frac{4\pi\chi}{(\omega\tau_0)^2} e^{-2V/kT}, \tag{7}$$

$$\operatorname{tg}\delta = \frac{\varepsilon_s - \varepsilon_0}{\varepsilon_0}\,\frac{1}{\omega\tau_0}\,e^{-V/kT}, \tag{8}$$

$$\frac{\varepsilon - \varepsilon_0}{\operatorname{tg}\delta} = \frac{\varepsilon_0}{\omega\tau_0} e^{-V/kT}. \tag{9}$$

Extensive experimental material shows that the temperature maximum of $\operatorname{tg}\delta$ predicted by the theory is in a number of cases not observed ([1],[2]). This contradiction between theory and experiment arises because of the simplifying assumption that the number of relaxators is independent of temperature. Experimental data indicate an increase in the number of relaxators with increasing temperature ([3]). In the case of dipolar dielectrics, the increase in the number of relaxators, according to Debye' s statement, is explained by the fact that with increasing temperature the number of dipoles that can rotate through large angles increases. At low temperatures these dipoles are in a "frozen" state, and only elastic rotations of the dipoles through small angles are possible.

Skanavi assumes that in a number of dielectrics in which relaxation polarization is associated with the motion of ions, the number of relaxing ions increases with increasing temperature ([1]). At low temperature the ions are in a fixed state, from which they can be freed when the dielectric is heated. The action of the field on a fixed ion leads only to its elastic displacement about the position of fixation. To free an ion from the fixed state it is necessary to supply it with an energy U, which we shall call the excitation energy of the relaxator. The freed ion enters a potential well that is separated from a neighboring potential well of the same depth by a potential barrier of height V, and from the other potential wells by higher barriers. The transition of the ion from one potential well to another and back can lead to the occurrence of relaxation polarization when the dielectric is placed in an electric field.

Let us consider the case when the number of relaxators increases with temperature. Let us first suppose that the dependence of the relaxation polarization P in a constant field on the temperature T is determined by the formula

$$P = P_0 e^{-U/kT}, \tag{10}$$

where U is the excitation energy of the relaxator, and P_0 is a constant. In what follows we shall replace equation (10) by a more perfect one. From (10) it follows that:

$$\chi = \chi_0 e^{-U/kT}, \tag{11}$$

where χ_0 is a constant.

In the case $U = 0$, χ does not depend on temperature, and formulas (7)–(9) are obtained. Formulas (1)–(3), (6) remain valid also when $U \neq 0$.

If $U \neq 0$, $\omega\tau > 1$, and $\omega\tau > 4\pi\chi/\varepsilon_0$, then, using relations (2), (3), and (6), we obtain:

$$\varepsilon - \varepsilon_0 = \frac{4\pi\chi_0}{(\omega\tau_0)^2} e^{-(U+2V)/kT}, \tag{12}$$

$$\operatorname{tg}\delta = \frac{4\pi\chi_0}{\varepsilon_0\omega\tau_0} e^{-(U+V)/kT}, \tag{13}$$

$$\frac{\varepsilon - \varepsilon_0}{\operatorname{tg}\delta} = \frac{\varepsilon_0}{\omega\tau_0} e^{-V/RT}. \tag{14}$$

Comparing the activation energies of the quantities $\varepsilon - \varepsilon_0$, $\operatorname{tg}\delta$, and $(\varepsilon - \varepsilon_0)/\operatorname{tg}\delta$, and taking into account (7)–(9) and (12)–(14), one can decide whether the number of relaxators changes with temperature. If the activation energies of $(\varepsilon - \varepsilon_0)/\operatorname{tg}\delta$ and $\operatorname{tg}\delta$ are equal to one another, and the activation energy of

$\varepsilon - \varepsilon_0$ is twice as large, then the number of relaxators does not change with temperature. If the ratio of the activation energies of $\varepsilon - \varepsilon_0$ and $\operatorname{tg}\delta$ is less than two, and the activation energy of $\operatorname{tg}\delta$ is greater than the activation energy of the ratio $(\varepsilon - \varepsilon_0)/\operatorname{tg}\delta$, then the number of relaxators increases with temperature. Regardless of whether the number of relaxators changes with temperature or not, the temperature dependence of the ratio $(\varepsilon - \varepsilon_0)/\operatorname{tg}\delta$ can be used to determine V. In comparison with experiment it is necessary that the conditions $\omega\tau > 1$ and $\omega\tau > 4\pi\chi/\varepsilon_0$ be satisfied.

In the case $U \neq 0$, as in the case $U = 0$, $\operatorname{tg}\delta$ has a frequency maximum of losses, which is determined by equations (4) and (5), where ε_s is the static dielectric permittivity at the temperature of measurement.

The temperature dependence of $\operatorname{tg}\delta$ is determined by formulas (3), (6), and (11). If a constant frequency is specified, then in the temperature behavior of $\operatorname{tg}\delta$ a maximum is found at a relaxation time and temperature determined from the condition:

$$\frac{\varepsilon_s/\varepsilon_0 - \gamma}{1+\gamma} = (\omega\tau)^2, \tag{15}$$

where ε_s is the static dielectric permittivity at the temperature of the maximum and $\gamma = U/V$.

The magnitude of the maximum of $\operatorname{tg}\delta$ is equal to:

$$\operatorname{tg}\delta_{\max} = \frac{\varepsilon_s - \varepsilon_0}{2\varepsilon_s + \gamma(\varepsilon_s - \varepsilon_0)} \sqrt{(1+\gamma)\frac{\varepsilon_s - \gamma\varepsilon_0}{\varepsilon_0}}. \tag{16}$$

Expressions (15) and (16) differ from (4) and (5) and reduce to them when $U = 0$ and, consequently, $\gamma = 0$.

Comparing (15) and (4), we see that, in the case where the number of relaxators increases with temperature, the temperature maximum of $\operatorname{tg}\delta$ is observed at a higher temperature than if the number of relaxators did not change with temperature. At large γ, the maximum of $\operatorname{tg}\delta$ is located in the region of very high temperatures. If $\gamma > 1 + 4\pi\chi_0/\varepsilon_0$, then the temperature maximum of $\operatorname{tg}\delta$ will be absent altogether. This condition for the absence of a temperature maximum of $\operatorname{tg}\delta$ is a stringent one. For the maximum of $\operatorname{tg}\delta$ to be absent, it is sufficient that $\gamma > \varepsilon_{sn}/\varepsilon_0$, where ε_{sn} is the largest value of the static dielectric permittivity in the temperature interval in which thermal destruction of the dielectric does not occur.

Proceeding from the shift of the maximum of $\operatorname{tg}\delta$ with increasing temperature, the activation energy V, entering into the expression for the relaxation time τ, was previously determined. It was assumed that

$$\tau = \tau_0 e^{V/kT}, \quad \omega\tau = \text{const}. \tag{17}$$

The formulas obtained above, in particular (15), make it possible to illuminate this question in a new way. If the quantity $1-\gamma$ can be neglected in comparison with $4\pi\chi/\varepsilon_0$, then formula (15) is simplified and takes the form:

$$\frac{1}{1+\gamma}\frac{4\pi\chi}{\varepsilon_0} = (\omega\tau)^2. \tag{18}$$

Hence, taking (11) into account, we obtain:

$$\omega\tau = \text{const} \cdot e^{-U/2kT} \tag{19}$$

or

$$\omega e^{(V+\frac{1}{2}U)/kT} = \text{const}. \tag{20}$$

In this case the activation energy, determined from the shifts of the maximum of $\operatorname{tg}\delta$ with increasing temperature, is equal to $V+\frac{1}{2}U$, i.e., somewhat greater than V. If γ is approximately equal to $\varepsilon_{\text{sn}}/\varepsilon_0$, then the activation energy determined from the shifts of the maximum of $\operatorname{tg}\delta$ with increasing temperature, under the assumption that formulas (17) are valid, may turn out to be considerably greater than V.

According to relations (10) and (11), both the static dielectric permittivity ε_s and $\operatorname{tg}\delta_{\max}$ must increase with increasing temperature. Such an increase will be observed in those cases where the number of excited relaxators is small in comparison with the number of fixed ones. Experimental data show that an increase of $\operatorname{tg}\delta_{\max}$ with temperature does occur ([4,5]).

Formulas (10) and (11) assume that the majority of ions are fixed, and that the number of free ions is small. In the more general case, the numbers of fixed ions n_1 and free ions n_2 are determined by the formulas:

$$n_1 = n\frac{g_1}{g_1 + g_2 e^{-U/kT}}, \qquad n_2 = n\frac{g_2 e^{-U/kT}}{g_1 + g_2 e^{-U/kT}}, \tag{21}$$

where $n = n_1+n_2$ is the total number of ions, g_1 and g_2 are the statistical weights of the fixed and free states, and U is the excitation energy of the relaxator. Assuming that the relaxation electric susceptibility $\varkappa$ is proportional to the number of relaxators and inversely proportional to the temperature, i.e.,

$$\varkappa = \frac{a}{T}n_2, \tag{22}$$

where a is a constant, we obtain:

$$\varkappa = \frac{\varkappa_0' e^{-U/kT}}{(g + e^{-U/kT})T}, \tag{23}$$

where $g = g_1/g_2$, $\varkappa$ is a constant. This formula becomes (11) if the factor $e^{-U/kT}$ is small compared with g, and the temperature dependence $\varkappa_0'/T$ may be neglected in comparison with the temperature dependence of the exponential factor.

As a result of substituting (23) into (2) and (3), an expression is obtained for the dielectric permittivity and $\operatorname{tg}\delta$. A more detailed study of the properties of a dielectric with a variable number of relaxators makes it possible to find small effects that can be detected experimentally.

The behavior of a dielectric with a variable number of relaxators is determined by the character of the dependence of the number of relaxators on temperature. In some cases an increase in the number of relaxators with increasing temperature may lead: (a) to an increase of the dielectric permittivity with increasing temperature, (b) to the absence of a maximum of $\operatorname{tg}\delta$ in the temperature dependence of $\operatorname{tg}\delta$, (c) to an increase of the maximum of $\operatorname{tg}\delta$ in the temperature dependence of $\operatorname{tg}\delta$ with increasing frequency.

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Note: Figure translations are in progress. See original paper for figures.