Dielectric abnormal relaxation in condensed matter

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It has been shown by many experimental data of polymers that the dielectric response function is of a stretched exponential, $\phi(t) = \exp\left[-(t/\tau^*)^{k\beta}\right]$. The parameter β_k is indicated to express a measure of the molecular interaction by the coupling model. Experimental data on β_k support this. However deviation of the experimental complex permittivity from that calculated is common for polymers. The stretched exponential function explained the complex permittivity only in a frequency range log f / f_m ≤1.5 The deviation is in many cases independent of the frequency. No satisfactorily explanation has been given to this phenomenon. Below conventional glass transition temperature a relaxation peak of Debye type can be seen in an ultra-low frequency region.

§ 1. Introduction

The theory of dielectric relaxation gives the complex permittivity ε^* as

$$\frac{\varepsilon^*-\varepsilon_\infty}{\varepsilon_0-\varepsilon_\infty} = \int_0^\infty \exp(i\omega t)[-\frac{d\phi(t)}{dt}]dt, \qquad (1)$$

where ε_0 and ε_∞ are the permittivity at the low- and high-frequency limits, respectively, and $\phi(t)$ is the dielectric response function.[1] The dielectric relaxation has been discussed mostly in terms of the complex permittivity. Empirical representations of the Cole-Cole[2] and Davidson-Cole[3] have been used quite often for the discussion. Havriliak and Negami[4] (HN) presented the following equation which involves both representations:

$$\frac{\varepsilon^*-\varepsilon_0}{\varepsilon_0-\varepsilon_\infty} = \frac{1}{\left[1+(i\omega\tau_{HN})^\beta\right]^\alpha} , \qquad 0<\alpha,\beta\le1 \qquad (2)$$

where τ_{HN} is a relaxation time, and α and β are shape parameters dominating the frequency dependence of the complex permittivity. This corresponds to the Cole-Cole equation when $\alpha=1$ and the Davidson-Cole equation if $\beta=1$. It is established that Eq.(2) gives a good explanation of the complex permittivity of polymers.[4-10] In spite of the great success of Eq.(2), the physical meanings of the parameters α and β are still in despite.[5-9]

Previously Williams and Watts[11] found empirically a response function and it was later pointed out that the function is the Kohlrausch frictional exponential function,[12]

$$\phi(t) = \exp\left[-(t/\tau^*)^{\beta_k}\right], \qquad 0<\beta_k<1 \qquad (3)$$

τ^* is a relaxation time.

Particularly interesting theories have been presented recently for the Kohlrausch function. Ngai et al.[13] have developed a coupling model for condensed matter, where molecular orientation undergoes certainly an interaction with its complex environment and the

environment fluctuates during the orientation. This brings naturally a time-dependent rate constant and β_k is a measure of the interaction. Amorphous polymers are good examples to examine the validity of the theory.

Bendler et al.[14] have also derived the Kohlrausch function by applying the Montroll-Weiss random walk to a defect diffusion model.[15] It was shown that $\varepsilon'(\omega)$ given by the Kohlrausch function is described naturally from the Levy distributions.

Palmer et al.[16] have recently developed a hierarchically constrained dynamics for glassy relaxation and derived the Kohlrausch function under a certain postulate for Ising spins. Over a very wide time range of $\tau_0 \leq t \leq \tau_m$, where τ_0 is a microscopic time ($\sim 10^{-14}$s) and τ_m is the ergodic time, the response function is of the Kohlrausch form if temperature is not much higher than T_g. However, it crosses over to pure exponential behavior of $\exp(-t/\tau_m)$ for $t > \tau_m$. The Kohlrausch function is also derived by the model coupling theory.[17]

§ 2. Dielectric relaxation described by the Kohlrausch function

Micro-Brownian motion of polymer chain is one of the most important subjects in polymer physics. Relaxation phenomena such as viscoelastic relaxation, dielectric relaxation, and NMR relaxation are dominated more or less by such motions. Recent studies on the micro-Brounian motion showed that the response function is the Kohlrausch function for a variety of polymers.

As an example, dielectric dispersion and absorption curves of poly(vinyl acetate)(PVAc)[10] are shown in Fig.1. Bath curves are well explained by Eqs. (1) and (4) in frequency region of $f < 10^2 f_m$, where f_m is the frequency of the maximal absorption. However in the high frequency region of $f > 10^2 f_m$, both curves deviate definitely from the calculated ones. In solution of PVAc in benzene too, the same trend can be seen as is shown in Fig.2. It is quite interesting that the experimental observation is always larger than that calculated in the high frequency region. The difference is almost independent of the frequency. If it comes from another relaxation, such a relaxation is quite abnormal and cannot be interpreted at all. This feature may be universal for all polymers. However it can be observed only by the dielectric relaxation. Other relaxations such as viscoelastic relaxation have never shown such an abnormal behavior observed by the dielectric measurement.

§ 3. Kohrausch function and coupling model

The coupling model have shown that β_k is a parameter representing a degree of coupling strength brought from the molecular environment. Usually in amorphous polymer or polymer solution, β_k increases with temperature or decrease with the increase of polymer concentration.[10,17]

Aqueous solution of poly(vinyl methyl ether)(PVME) has a lower critical solution temperature(LCST). This means that intra- and inter- chain interaction increases as the temperature increases. In Fig.3, the parameter β_k is plotted against temperature. It decreases with the increase of temperature. This offers on evidence of the validity of the coupling model.

The Kahlrausch function is essentially applicable to dielectric relaxation of polymer. Nevertheless a sufficient explanation of the deviation in the high frequency region is required.

§ 4. Ergodic relaxation

Palmer et al.[16] have suggested existence of pure exponential decay for glassy materials, that is, the ergodic relaxation at very long times. The relaxation time τ_m estimated loosely

from the present result of PVAc at 26.85 ℃ is 4.4×10^5s and very far away from the Kohlrausch region of $t \leq 3 \times 10^4$s. According to the theory, the current of the Kohlrausch form crosses over to pure exponential type at $t \sim \tau_m$. It should be noted that behavior of the Kohlrausch form at long times is not much different from the pure exponential behavior. Therefore it will be very difficult to distinguish these two decay.

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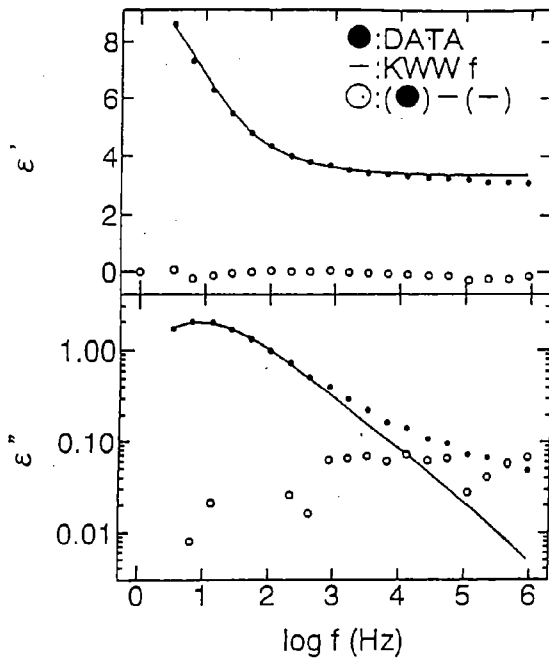
Fig. 1. Comparison of dielectric dispersion
and absorption curves obtained experimentally
at 53 °C with those calculated by the
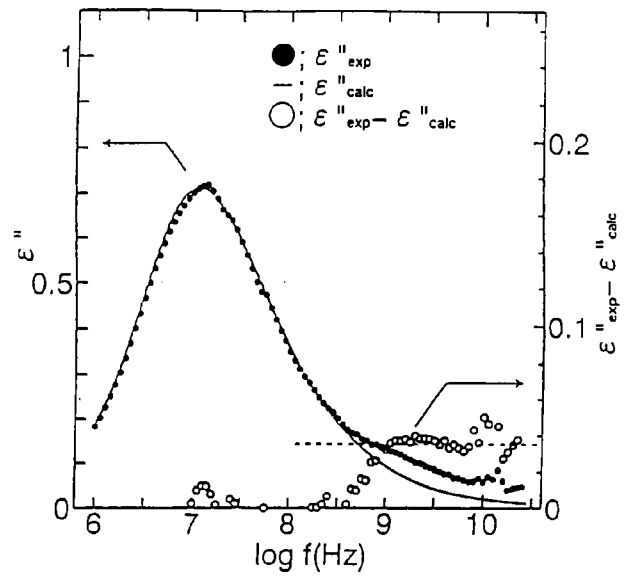Kohlrausch function.

Fig. 2. Comparison of PVAc (50wt%)
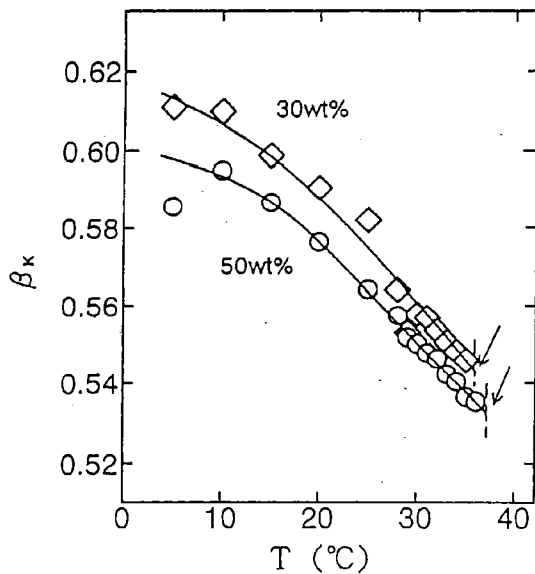in benzen at 25 °C with that calculated
by the Kohlrausch function.

Fig. 3. Temperature dependence
of coupling parameter β_k for
poly(vinyl methyl ether)
(PVME) in aqueous solution.

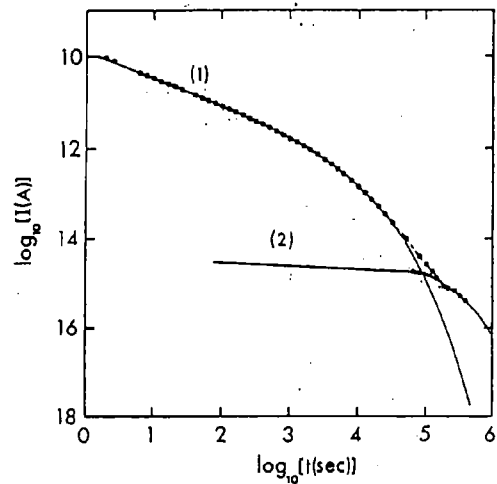Fig. 4. Discharge current of PVA
at 26.85 °C.
(1) Current calculated by the
Kohlrausch function with
$\beta_k=0.470$, $\tau^*=2.53\times10^3$s,
and $\varepsilon_0-\varepsilon_\infty=7.44$.
(2) Current calculated by the Debye
equyation with $\tau_m=4.4\times10^5$s, and
$\varepsilon_0-\varepsilon_\infty=0.51$. The discharge
current is proportional to $-d\phi(t)/dt$.