

Calculation of Dielectric Loss of Gamma Relaxation Process in Polyethylene at Low Temperature

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Synopsis

A method has been investigated to obtain the absorption intensity of the dielectric γ relaxation process in polyethylene by calculation. A correlation factor for evaluation of the effective dipole moment of polar groups in solid polyethylene is introduced on the assumption that with expanding distribution of relaxation time and/or increasing temperature, the extent of the canceled dipole moment due to the orientation motions of the polar groups under an alternating electric field will increase. Comparison of the calculated dielectric loss tangent with the observed one supports the assumption.

INTRODUCTION

Elucidation of factors affecting the dielectric loss of polyethylene is very important in developing low-dielectric-loss material suitable for the inner insulation of a submarine coaxial cable used in the microwave region because it points to a way by which the dielectric loss in the material can be reduced. According to the Onsager-Kirkwood equation,¹ the factors are mainly the relaxed and unrelaxed dielectric constants, the dipole moment and the number of polar groups in the polymers and the temperature. The factors concerned with frequency and the distribution of relaxation time are also added on consideration of Cole-Cole's relationship.² On this basis, an equation for the dielectric loss tangent ($\tan \delta$) in polyethylene has been proposed,³ indicating that the dielectric loss tangent of polyethylene at room temperature in a microwave frequency is probably proportional to the mean-square value of the dipole moment of the polar groups. The influence of crystallinity on the dielectric loss in polyethylene⁴ and the behavior of the dielectric γ relaxation process in polyethylenes with various degrees of branching and/or with various heat treatments at low temperatures⁵ has been reported. In a subsequent study, it was found that the values of the loss tangent calculated via the equation in which the degree of crystallinity was considered did not agree with those observed at low temperatures.

In this article, it is shown that an agreement of the calculated loss tangent with the observed one is obtained on consideration of the effective dipole moment of polar groups in the amorphous phase and defects in the crystalline phase in polyethylene.

EXPERIMENTAL

Polyethylenes with various degrees of branching and/or various heat treatments were used in this study. Sheets and films of the polyethylenes were prepared by pressing in a vacuum (below 2×10^{-5} torr) at 170°C and then quenching under a water press or cooling at various uniform cooling rates.

The dielectric loss was measured with a capacitance bridge (Type 1621, made by General Radio) in the frequency range of 10 to 10^4 Hz and temperature of ca. -90 to -130°C .

The number of polar groups in polyethylene ca. 0.1–0.8 mm thickness was determined from infrared spectra which were obtained with a Fourier transform spectrometer model JIR-03F.

Densities of the specimens were determined by use of a water–isopropyl alcohol density gradient column at 23°C .

The degrees of crystallinity of the specimens were estimated from the densities as 1.014 g/cm^3 for the crystalline phase and 0.850 g/cm^3 for the amorphous phase of polyethylene.

RESULTS AND DISCUSSION

Table I shows the number of polar groups per 1000 main-chain carbon atoms in polyethylenes with various degrees of branching. In high-pressure-process polyethylene (HPPE), most polar groups are methyl groups and the next most frequent ones are the vinylidene groups. In medium-pressure-process polyethylene (MPPE), the vinyl groups are comparably larger in number than other polar groups. Few carbonyl groups are contained in each polyethylene.

The following equation for the dielectric loss tangent of the γ relaxation process in low-loss polyethylene has been proposed:¹

$$\tan\delta = \frac{2\pi}{kT} \frac{1}{2\epsilon_0 + \epsilon_\infty} \left(\frac{\epsilon_0 + 2}{3} \right)^2 \frac{\rho N_A}{14 \times 10^3} \frac{\sin(\beta\pi/2)}{\cosh\beta x + \cos(\beta\pi/2)} n\mu^2 \quad (1)$$

where k is Boltzmann's constant, T is the absolute temperature, x is given by $x = \ln(\omega\tau)$, ω is angular frequency, τ is the relaxation time, ϵ_0 is the dielectric constant at $\omega = 0$, ϵ_∞ is the constant at $\omega = \infty$, ρ is the density, N_A is Avogadro's number, β is Cole–Cole's parameter, n is the number of polar groups, and μ^2 is the mean-square value of the permanent dipole moment of the polar groups.

Table II shows a comparison of the observed loss tangent with the loss tangent

TABLE I
Number of Polar Groups per 1000 Main-Chain Carbon Atoms in Polyethylene

Sample	Carbonyl		Double bond		Methyl
	Ketonic	Aldehydic	Vinyl	Vinylidene	
HPPE					
EF2	0.010	0.000	0.025	0.250	41
EG2	0.002	0.005	0.013	0.105	24
EG3	0.003	0.004	0.012	0.089	17
MPPE					
E22	0.001	0.000	0.651	0.009	12
E6	0.001	0.000	0.782	0.020	4
E29	0.001	0.000	0.772	0.013	0.07
E39	0.001	0.000	0.737	0.013	0.00

TABLE II
Comparison of Observed and Calculated^a Dielectric Loss Tangents of Polyethylene at -105°C and 100 Hz

	EF2	EG2	EG3	E22	E6	E29	E39
$\tan \delta_{\text{cal}} (\times 10^{-6})$	133	59.3	47.2	45.4	31.9	21.0	23.9
$\tan \delta_{\text{obs}} (\times 10^{-6})$	61.1	49.0	51.0	48.6	42.1	35.0	43.7
$\tan \delta_{\text{cal}}/\tan \delta_{\text{obs}}$	1.66	1.21	0.92	0.91	0.76	0.60	0.55

^a Dipole moments $\mu (\times 10^{-18})$ used here were 2.72 for carbonyl,⁶ 0.35 for vinyl and vinylidene,⁷ and 0.08 for methyl groups.⁸

obtained by multiplying the value calculated from eq. (1) by $(1 - \chi_w)$ on the consideration that the loss tangent in polyethylene in the range of microwave frequencies at room temperature decreases with increase in degree of crystallinity (χ_w), where β was estimated from curve-fitting $\tan \delta$ vs. frequency and temperature data, as described in the previous report.⁵ Taking the number of methyl groups as a parameter of the degree of branching in polyethylene, the value of the calculated loss tangent decreases with decrease in the degree of branching and then the value is reduced to about one-half the observed one compared with that with the most degree of branching. The discrepancy probably results from unsuitable evaluation of the contribution of the polar groups to defects in the crystalline phase polyethylene.

Generally, it is said that branching and heteroconjugation in high-molecular-weight chains are excluded from the crystals, or that they form defects in the crystals. The possibility of an exclusion of the polar groups from the crystal is more likely in the case of molecular chains with a very small content of polar groups, as in polyethylene, because in such a case a fair part of the crystalline phase can form without polar groups in the crystals.

Table III shows the loss tangents calculated from eq. (1) on the assumption that all polar groups in polyethylene are contained in either the amorphous phase or in defects in the crystalline phase. All the calculated loss tangents are larger than the observed ones. Some speculations on the discrepancy follow.

First, it is possible that the calculated loss tangent was overestimated, if the polar groups in low-loss polyethylene are contained in the part of the crystalline phase where the polar groups cannot make the orientation motion. If this assumption is correct, the part where the orientation motion is hindered must increase with increasing branching. The fact that the lattice constant of the polyethylene crystals increases with increasing branching has been reported by Walter and Redding.⁹ This implies that increasing branching makes the crystals bulky. According to this idea, with increasing branching the crystalline part hindering the orientation motion of polar groups must decrease; the difference between the calculated and observed values of the loss tangents must decrease.

TABLE III
Comparison of Observed and Calculated Dielectric Loss Tangents of Polyethylene Based on Assumption that all Polar Groups are Contained in Either the Amorphous Phase or in Defects of Crystals, at -105°C and 100 Hz

	EF2	EG2	EG3	EG2	E6	E29	E39
$\tan \delta_{\text{cal}} (\times 10^{-6})$	190	115	94.0	92.2	80.1	59.0	64.4
$\tan \delta_{\text{cal}}/\tan \delta_{\text{obs}}$	3.11	2.35	1.84	1.90	1.90	1.69	1.50

However, the observed data are contrary, as shown in Table III. Therefore, this speculation as cause of the discrepancy is difficult to accept.

Second, the discrepancy could be attributed to the overestimation of the dipole moments for the polar groups in solid polyethylene because those moments in low-molecular-weight compounds in the gas or liquid state where the polar groups may be liable to move compared with those in the polyethylene are used in Table III. If this assumption is correct, the discrepancy between values of the calculated and observed loss tangent should decrease with decreasing activation energy, which is considered as a parameter of ease for the orientation motion of the polar groups. Figure 1 shows the relationship between the activation energy and the ratio of the calculated loss tangent to the observed. The discrepancy between calculated and observed values increases with decreasing activation energy, contrary to the assumption.

The third speculation is as follows. The effective dipole moments may be smaller than those used in Table III because part of the dipole moments will cancel each other out. That is, the relaxation times in polyethylene regarded as a multiple relaxation process have a distribution; the differences between the orientation motions of the polar groups will take place under an alternating electric field; some of the dipole moments of the polar groups with shorter or longer relaxation times than the most frequent relaxation time will cancel each other out. Therefore, the expanding distribution of the relaxation time results in an increase in the canceled dipole moment and thus in decreasing effective dipole moment. An increase in temperature is also considered to result in increasing extent of the canceled dipole moment, which is ascribed to an increase in the randomness of the phase constants of the harmonic motions for the orientation of the polar groups.

Let us introduce a correlation factor r which expresses the rate of the uncanceled dipole moment and is zero when the orientation motions of polar groups are entirely random and thus all the dipole moments are canceled, and is unity when none of the moments is canceled. The effective mean-square value of the dipole moment of polar groups, μ^2 , is then defined as follows:

$$\sum \bar{\mu}_i^2 = r \sum \mu_i^2 \quad (2)$$

where μ_i^2 is the mean-square value of the dipole moment of each polar group in low-molecular-weight compounds. The factor r is calculated from the observed value of the loss tangent, eqs. (1) and (2).

Figure 2 shows the temperature dependence of r in polyethylenes with various

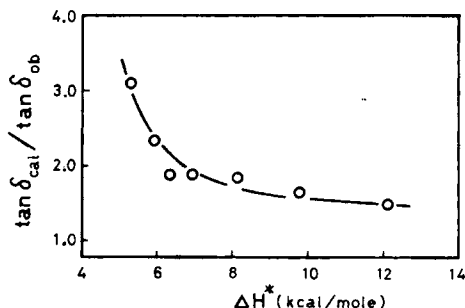


Fig. 1. Relation between activation energy ΔH^* and $\tan \delta_{cal} / \tan \delta_{obs}$ at ca. -105°C and 100 Hz.

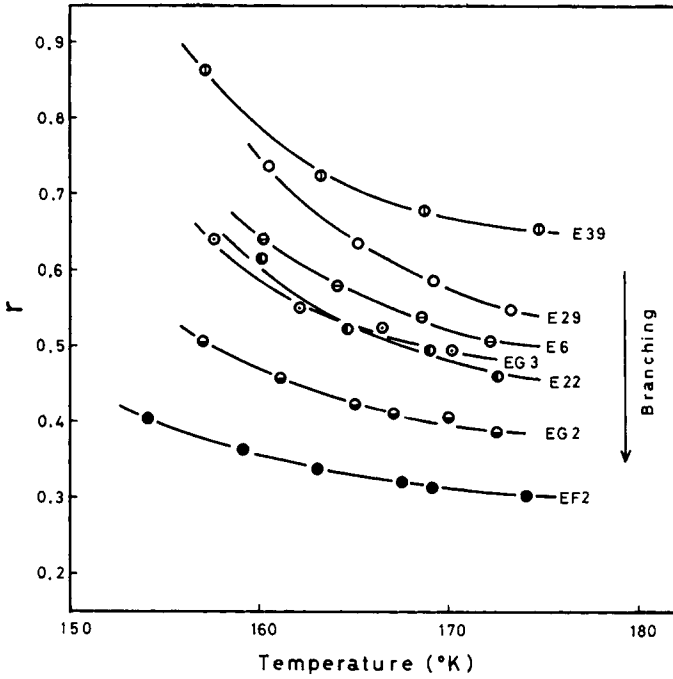


Fig. 2. Temperature dependence of factor r in polyethylenes with various degrees of branching.

degrees of branching. With increasing temperature, r decreases and gradually approaches a certain value around -80 to -90°C corresponding to the glass transition temperature of polyethylene, as described in the previous report.⁵

Figure 3 shows the relationship between r and Cole-Cole's parameter β corresponding to the distribution of relaxation time at a certain temperature. The r value decreases with decreasing β and/or with increasing temperature. These facts seem to support the assumption that the extent of the cancellation in dipole moments increases with the expanding distribution of the relaxation time and/or

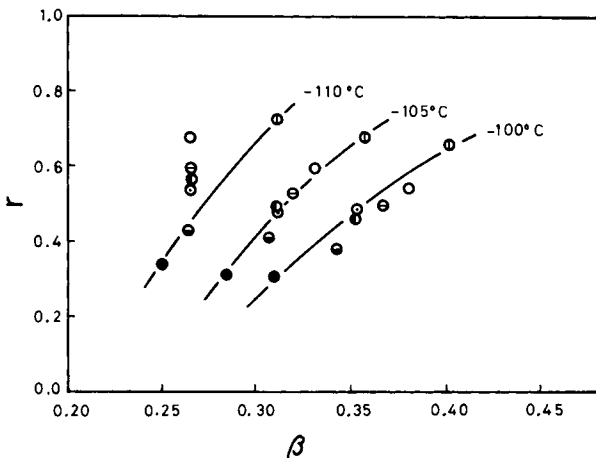


Fig. 3. Relation between β and r at different temperatures.

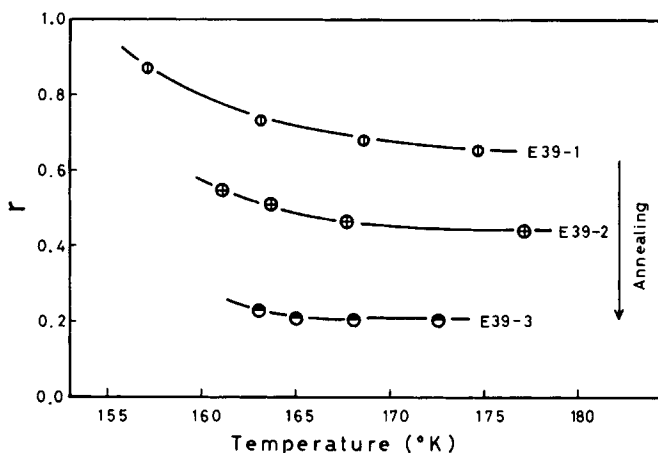


Fig. 4. Temperature dependence of r in polyethylenes with different heat treatments.

with increasing randomness of the phase constant in the harmonic motions of the polar groups. The temperature dependence of r diminishes at temperatures above -80 to -90°C , at which the relaxation time ascribed to the local mode relaxation is similar to that due to defects in the crystalline phase. This suggests that the extent of the canceled dipole moments due to the increasing randomness of the phase constant caused by the thermal motions of polar groups is almost saturated at that temperature.

Figure 4 shows the temperature dependence of r in polyethylenes with different degrees of crystallinity resulting from different heat treatments. With increasing temperature, r decreases and then reaches a plateau around -80 to -90°C . The temperature dependence of r in polyethylenes with different heat treatments is similar to that in polyethylenes with various degrees of branching. The effect due to heat treatment is similar to that due to increasing branching, as previously described.⁵ Therefore, the interpretation of r in polyethylenes subjected to different heat treatments is apparently similar to that in polyethylenes with various degrees of branching. This finding suggests that the decreasing dielectric loss in the γ relaxation process in polyethylene with increasing crystallinity at room temperature is due to increasing cancellation of dipole moments because of the expanding distribution of the relaxation time, not to the increasing number of the polar groups which cannot make the orientation motion because of incorporation of the polar groups into the crystals.

CONCLUSIONS

The dielectric γ relaxation process in solid polyethylene below -80 to -90°C is found to be moderately complicated. An introduction of a correlation factor which expresses the effective dipole moment of polar groups enables one to obtain the absorption intensity of a dielectric γ relaxation process in polyethylenes with various degrees of branching and/or with various heat treatments by calculation.

It will become possible to introduce the factor theoretically when the relaxation time, the distribution, and the difference of phase constant in harmonic motion of each polar group in the amorphous phase and defects in the crystalline phase in polyethylene are elucidated.

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