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Relaxation intensity in some polyacrylates

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Abstract. Empirical formula suggested by Kita and Koizumi for evaluation of relaxation intensity in a limited range of frequency around the relaxation frequency for the Cole–Cole type distribution has been tested for poly butyl acrylate (PBA), Poly butyl methacrylate (PBMA) and poly isobutyl methacrylate (PiBMA).

The relaxation intensity $\Delta\varepsilon$ is expressed in terms of ε''_M, the dielectric loss maxima and W, the frequency separation for half, two thirds or three quarters of ε''_M, in the form $\Delta\varepsilon = \varepsilon''_M/[(C_1/W) + C_2 + C_3 W]$, where the numerical constants C_1, C_2, C_3 are given for the respective type of relaxation.

Keywords. Relaxation intensity; dielectric loss; dipole moments.

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1. Introduction

The dielectric relaxation intensity or the magnitude of dielectric dispersion provide considerable information regarding the effective dipole moments associated with the relaxation process and molecular motions of polar molecules (Smyth 1955; Hill *et al* 1969). For those molecules, which exhibit Debye type relaxation with a single relaxation time or a narrow distribution of relaxation times, intensities are easily evaluated from the dielectric constant measurements at low and the limiting high frequency (Hill *et al* 1969). The Cole–Cole (1941) plots of complex permittivity are among the widely used methods for the evaluation of the relaxation intensity. The relaxation intensity may be evaluated by taking integration of the dielectric loss data over the entire range of frequencies in the case of a broader distribution in relaxation times. However, difficulties arise in the evaluation of the relaxation intensity when dielectric loss data are available in a limited range of frequency around the loss maxima. Also in multiple relaxation process in which two or more loss peaks occur and portion of the loss peaks may overlap with each other in the frequency range of measurements, neither the Cole–Cole plots nor the integration of dielectric loss gives good accuracy in estimating the relaxation intensity. For such cases, Kita and Koizumi (1979) have developed an empirical formula based on the evaluation of the area of a triangle which is the loss maxima times the half width. The area remains constant within $\pm 3\%$ with the half width, roughly estimating the relaxation intensity. In calorimetric loss measurements (Vincett 1969), where dielectric constants are not available, the method seems to be adequate for the estimation of $\Delta\varepsilon$.

A method of estimating the dielectric increment, was suggested earlier by Fröhlich (1958) by considering the loss curve as a trapezoid with sides approximated by tangents at the half width points. This method however does not give very accurate results for $\Delta\varepsilon$.

The accuracy of the triangle approximation was examined for Cole–Cole (1941), Davidson-Cole (1950) and William-Watts (Williams and Watts 1970; Williams *et al* 1971) type of distribution by Kita and Koizumi (1979). Validity of the method by Kita and Koizumi was analyzed for Cole-Davidson distribution by our group (Chauhan *et al* 1982; Gupta and Shukla 1989). The maximum error in the evaluation of the relaxation intensity was found to be around $\pm 1\%$. In order to investigate further, the studies were exended for the Cole–Cole distribution in some polyacrylate. The data of poly butylacrylate (PBA), poly butylmethacrylate (PBMA) and poly isobutyl methacrylate (PiBMA) earlier reported by Murthy *et al* (1979) were analyzed using the above method. An excellent agreement between the observed and the calculated values of $\Delta\varepsilon$ has been reached.

2. Approximation by a triangle to a quadratic equation

The relaxation intensity $\Delta\varepsilon$ expressed by the Kramer-Krönig relation (Fröhlich 1958) is given by

$$\Delta\varepsilon = \frac{2}{\pi}\int_0^{\infty} \frac{\varepsilon''(\omega\tau)}{\omega\tau}\,\mathrm{d}(\omega t) = S\frac{2}{\pi}\ln 10 = 1{\cdot}4659\,S \tag{1}$$

where ε'' is the dielectric loss, ω the angular frequency, τ the relaxation time and S the area under the $\varepsilon'' - Z$ curve, calculated by the integration

$$S = \int_{-\infty}^{+\infty} \varepsilon''(Z)\,\mathrm{d}z; \quad Z = \log \omega\tau.$$

The area $S/\Delta\varepsilon$ under $\varepsilon''/\Delta\varepsilon$ vs. Z curve can be approximated roughly by the area of a triangle $S_1/\Delta\varepsilon$ which is half width ($W_{1/2}$) times the maximum value of the normalized dielectric loss $\varepsilon''_M/\Delta\varepsilon$.

The normalized dielectric loss $\varepsilon''(\omega)/\Delta\varepsilon$ is expressed by the following relation for the Cole–Cole relaxation

$$\frac{\varepsilon''(\omega)}{\Delta\varepsilon} = \frac{\sin(\pi\beta/2)}{2[\cos h\beta y + \cos(\pi\beta/2)]}; \quad y = \ln\omega\tau \tag{2}$$

where β is the distribution parameter of the relaxation times ($1 \geqslant \beta > 0$) with $\beta = 1$ yielding the Debye type of relaxation and τ is the characteristic relaxation time.

To evaluate $S_1/\Delta\varepsilon$, the values of $\varepsilon''(\omega)/\Delta\varepsilon$ are calculated at each frequency for a particular value of β and a graph of $\varepsilon''(\omega)/\Delta\varepsilon$ vs log $\omega\tau$ is drawn. The value of normalized dielectric loss maximum $\varepsilon''_M/\Delta\varepsilon$ evaluated from the plot may also be calculated by the following relation which comes out to be similar to the value deduced from the plot,

$$\frac{\varepsilon''_M}{\Delta\varepsilon} = \frac{1}{2}\tan(\pi\beta/4). \tag{3}$$

The half width $W_{1/2}$ was determined by solving the equation

$$\tfrac{1}{2}\varepsilon''_M = \varepsilon''(\omega) \tag{4}$$

using the Newton-Raphson (Margenau and Murphy 1956) method.

This equation has two solutions ω_1 and ω_2 ($\omega_1 > \omega_2$). The half width is given as

$$W_{1/2} = \log \omega_1 - \log \omega_2. \tag{5}$$

The $S_1/\Delta\varepsilon$ and $W_{1/2}$ may be approximated by a quadratic equation of $W_{1/2}$ as

$$\frac{S_1}{\Delta\varepsilon} = C_1 + C_2\, W_{1/2} + C_3\, W_{1/2}^2 \tag{6}$$

which may be rewritten

$$\Delta\varepsilon = \varepsilon''_M \cdot \left[\frac{C_1}{W_{1/2}} + C_2 + C_3\, W_{1/2}\right]^{-1} \tag{7}$$

where C_1, C_2 and C_3 are numerical constants. Providing $S_1/\Delta\varepsilon$ and $W_{1/2}$ at various β values, the constants were evaluated using the method of least square (Margenau and Murphy 1956). The constants were also determined for two-third and three-quarter widths which are separations between log ω's where ε'' is the two-third and three-quarter of the dielectric loss maximum ε''_M.

3. Results and discussion

PBA, PBMA and PiBMA investigated earlier by Murthy *et al* (1979) exhibited Cole–Cole type relaxation behaviour. The empirical model for the relaxation intensity proposed by Kita and Koizumi was suitably applied to these three systems. The numerical constants used for evaluating the parameter are reported in table 1. The values of the relaxation intensity at different temperatures are given in table 2. A comparison between the evaluated and experimental results has also been made. Figure 1 shows plot of $\varepsilon''/\Delta\varepsilon$ vs log $\omega\tau$ for PBMA with $\beta = 0{\cdot}86$.

Table 2 reveals that PBA yielded $\Delta\varepsilon_{cal}$ of 0·575, 0·618 and 0·690 at 213 K, 223 K and 233 K respectively for half width. These values were compared with the corresponding experimental values of 0·574, 0·620 and 0·689. The error observed in the estimation of $\Delta\varepsilon$ was 0·17%, 0·32% and 0·14% respectively. The maximum error in estimation of $\Delta\varepsilon$ was 0·32 amongst all the three widths i.e. $W_{1/2}$, $W_{2/3}$ and $W_{3/4}$.

Another system, PBMA exhibited an excellent agreement between the calculated and experimental values of $\Delta\varepsilon$, which can be seen from $\Delta\varepsilon_{cal}$ values of 0·327, 0·388 and 0·427 for half width at the temperatures of 213 K, 223 K and 233 K respectively. The corresponding $\Delta\varepsilon_{obs}$ values were 0·327, 0·387 and 0·427 at the above mentioned temperatures. The error involved in the estimation of $\Delta\varepsilon$ was found to be 0·0%, 0·26% and 0·0%. At increasing width i.e. $W_{2/3}$ and $W_{3/4}$ the errors in determination of $\Delta\varepsilon$ were found to be zero.

Similarly, PiBMA also exhibited good agreement between $\Delta\varepsilon_{cal}$ and $\Delta\varepsilon_{obs}$ values. This system gave an excellent agreement even at the three-quarter width ($W_{3/4}$). For

Table 1. Numerical constants in the equation $\Delta\varepsilon = \varepsilon''_M[(C_1/W) + C_2 + C_3 W]^{-1}$ for estimation of $\Delta\varepsilon$, the relaxation intensity for $\Delta\varepsilon''_M$, the loss maximum and W, the separation between log ω's for $\varepsilon''_M/\Delta\varepsilon$ of 1/2, 2/3 and 3/4.

W	C_1	C_2	C_3
		PBA	
1/2	−4·6765957	7·2709	−2·5147528
2/3	−0·0603448	0·174488	0·2430029
3/4	−0·7035436	1·6025695	−0·4954087
		PBMA	
1/2	0·7065005	−0·0002936	−0·0594073
2/3	−0·910614	2·85282	−1·5031434
3/4	2·2267258	−3·33294	1·3400764
		PiBMA	
1/2	0·5030217	0·032399	0·0328189
2/3	3·8279157	−6·1351713	2·7671725
3/4	−0·4672977	1·793862	−0·9482974

Table 2. Values of W, $\Delta\varepsilon_{cal}$ and $\Delta\varepsilon_{obs}$ for Cole–Cole relaxation for PBA, PBMA and PiBMA at various temperatures along with the % error involved in the estimation using eq. (7).

Temperature			1/2			2/3			3/4		
K	β	$\Delta\varepsilon_{obs}$	W	$\Delta\varepsilon_{cal}$	error %	W	$\Delta\varepsilon_{cal}$	error %	W	$\Delta\varepsilon_{cal}$	error %
						PBA					
213	0·85	0·574	1·47	0·575	0·17	1·12	0·575	0·17	0·96	0·573	0·17
223	0·84	0·620	1·48	0·618	0·32	1·108	0·618	0·32	0·935	0·621	0·16
233	0·83	0·689	1·50	0·690	0·14	1·08	0·690	0·14	0·92	0·688	0·14
						PBMA					
213	0·89	0·327	1·40	0·327	0·0	1·03	0·327	0·0	0·853	0·327	0·0
223	0·88	0·387	1·42	0·388	0·26	1·04	0·387	0·0	0·857	0·387	0·0
233	0·86	0·427	1·45	0·427	0·0	1·06	0·427	0·0	0·865	0·427	0·0
						PiBMA					
213	0·87	0·387	1·37	0·387	0·0	1·015	0·387	0·0	0·827	0·387	0·0
223	0·86	0·420	1·39	0·420	0·0	1·022	0·421	0·24	0·844	0·420	0·0
233	0·85	0·469	1·41	0·469	0·0	1·024	0·468	0·21	0·860	0·469	0·0

this system, the maximum error in estimating $\Delta\varepsilon$ was 0·24% for all the three widths.

Values of $\Delta\varepsilon$ are almost independent of W, being constant within ± 1% and being in good agreement with the values of $\Delta\varepsilon_{obs}$. The maximum error observed in all the three polymers was 0·32%. Amongst all the three investigated systems, PBMA exhibited an excellent agreement for all the three widths. It thus seems that the empirical formula suggested by Kita and Koizumi holds good for the evaluation of

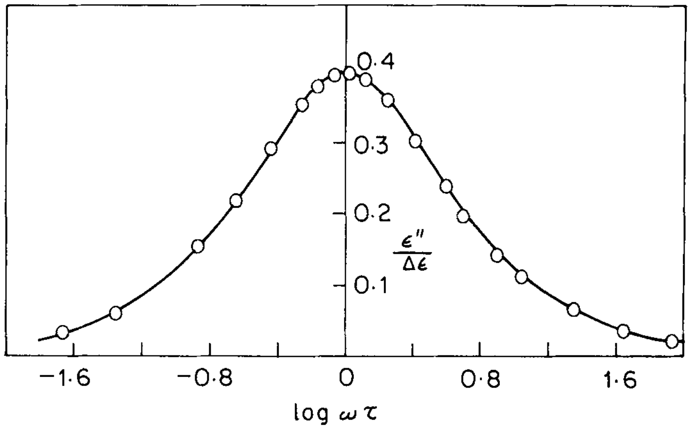

Figure 1. Plot of $\varepsilon''/\Delta\varepsilon$ vs log $\omega\tau$ for PBMA with $\beta = 0{\cdot}86$ at 233 K.

relaxation intensity where the data are available in the limited range of frequency and for various kinds of distributions including the Cole–Cole type behaviour.

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