Comparing graphical and statistical methods for analysing dielectric dispersions of polymers represented in the complex plane

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The expression proposed by Havriliak and Negami to represent the dielectric relaxation data of polymers is combined with multi-response statistical methods to provide objective parameter estimates and measures of precision. The graphical and multi-response methods are compared using the data for twelve polymers. The temperature dependence of the relaxation parameters for poly(vinyl acetate) is also treated with the multi-response techniques and compared with those previously reported. The statistical techniques lead to a much quicker, objective estimation of parameters, and permit sensitive analysis of residuals to reveal important sources of discrepancy.

(Keywords: dielectric dispersion; complex plane; poly(vinyl acetate); statistical analysis)

INTRODUCTION

There are several reasons for reexamining the dielectric relaxation data of polymers reported previously[1]. First considerable progress has been made in statistical techniques for treating data. From the statistical information we can derive estimates for the reliability of the model used to represent the data. Secondly, Mansfield[2] has improved the theoretical understanding of dielectric relaxation behaviour of polymers to the point where it is important to have such limits on the reliability of data representation to permit valid interpretation of the parameters.

Havriliak and Negami[1] observed that the shapes of dielectric relaxation processes of polymers could be represented by the expression

$$\frac{\varepsilon^*(\omega)-\varepsilon_\infty}{\varepsilon_0-\varepsilon_\infty}=\{1+(i'\omega\tau_0)^\alpha\}^{-\beta} \tag{1}$$

In this expression $\varepsilon^*(\omega)$ is the complex dielectric constant measured at radian frequency $\omega=2\pi f$, where f is the oscillator frequency in Hz. The quantities ε_∞ and ε_0 represent the instantaneous and equilibrium dielectric constants, respectively. The parameters α and β are formally related to the distribution of relaxation times[1] while τ_0 is the relaxation time. This expression has the significance that no new parameters were needed to represent the data: when $\alpha=1$ the Cole–Davidson[3] expression is obtained, and when $\beta=1$ the Cole–Cole[4] expression is obtained.

Given a data set consisting of the real and imaginary values at various frequencies, the parameters were estimated graphically coupled with a subjective evaluation of the fit in the complex plane. Recently, the authors[5] have applied multi-response statistical techniques[6–8] to obtain objective estimates of the parameters in expression (1) and to determine statistical quantities that indicate the goodness of fit.

OUTLINE OF THE STATISTICAL METHODS

A method for analysing data in which there are multiple responses was proposed by Box and Draper[8]. We suppose there are M responses measured in N cases, and the expected responses (theoretical values) depend on P parameters. For the dielectric data, $M=2$, corresponding to the real and imaginary values, $P=5$, corresponding to the parameters ε_0, ε_∞, α, β and τ_0, and N specifies the number of frequencies used to generate the responses. If the real and imaginary data are gathered into an N by 2 matrix Y with elements (y_{nm}), $n=1, 2, \ldots N$, $m=1, 2$, and the expected responses into an N by 2 matrix H with elements (h_{nm}), $n=1, 2, \ldots N$, $m=1, 2$, then, as shown in ref. 8, the best estimates of the parameters are those which minimize the determinant $\det(Z'Z)$, where $Z=Y-H$ is the N by 2 matrix of residuals, $z_{nm}=y_{nm}-h_{nm}$. An efficient computational procedure for determining the best estimates, together with summary statistics to provide approximate parameter confidence limits, is given in Bates and Watts[6,7]. It is important to note that this statistical model accounts for covariances between the real and imaginary values of $\varepsilon^*(\omega)$.

The above procedure can be used directly to analyse data for a polymer at a single temperature. To combine data for a polymer at several temperatures, it is necessary to write the dielectric parameters as a function of temperature, T. We assume that each of the parameters ε_0, ε_∞, α, β and $\log(\tau_0)$ may depend on temperature in any of the following ways: const, temp, square temp, or 1000/temp; where temp = temperature − $T(0)$, with $T(0)$ a reference temperature selected to be in the middle of the experimental temperature range so as to reduce unnecessary parameter correlations. Note that the logarithm of relaxation time is used because it is assumed that $\log(\tau_0)$ should follow an Arrhenius relationship.

SINGLE TEMPERATURE ESTIMATES

Results

The results for single temperature estimates are given in *Table 1*. The results for poly(carbonate) and syndiotactic poly(methyl methacrylate) (s-PMMA) have been described elsewhere[5]. For each polymer, the first line in *Table 1* gives the parameter estimates reported previously using graphical techniques, the second line the estimates using the statistical approach, and the third line the parameter standard error. The % coefficient of variation is 100 times (standard deviation of residuals)/(average response). For example, for poly(carbonate), the standard deviation of the residuals for the real component was 3.42, giving a % coefficient of variation of 100 times (0.0023/3.42) = 0.07 %.

In *Table 2* we give the average and standard deviation of the % relative difference between the two methods. For example, for poly(carbonate), the % relative difference for α is 100(0.80 − 0.77)/0.77 = 3.9 %. The average % difference for α for all the polymers was 6.7 % with a standard deviation of 13 %.

Discussion

A study of the residuals for the single temperature measurements was not carried out for all polymers

Table 1 Comparison of the dispersion parameters determined from graphical and statistical techniques[a]

						% Coefficient of variation	
Polymer name, temperature and ref.	ε_0	ε_∞	$\log(f_0)$	α	β	Real	Imaginary
Poly(carbonate)	3.64	3.13	6.81	0.80	0.29	–	–
	3.64	3.12	6.85	0.77	0.29	0.07	2.3
	0.002	0.004	0.04	0.01	0.01		
Polychloroprene −26°C	5.96	2.44	7.13	0.75	0.53	–	–
	5.85	2.63	7.37	0.57	0.51	0.64	6.7
	0.03	0.05	0.22	0.03	0.06		
Poly(cyclohexyl methacrylate) 121°C	4.24	2.46	5.34	0.84	0.25	–	–
	4.33	2.45	5.33	0.71	0.33	0.16	7.5
	0.02	0.02	0.07	0.03	0.02		
Poly(iso-butyl methacrylate) 102.8°C	3.97	2.38	8.28	0.72	0.41	–	–
	4.02	2.36	8.28	0.71	0.50	0.92	1.6
	0.01	0.01	0.05	0.02	0.02		
Poly(n-butyl methacrylate) 59.0°C	4.28	2.41	7.31	0.53	0.68	–	–
	4.29	2.44	7.06	0.62	0.60	0.54	6.7
	0.01	0.01	0.11	0.02	0.04		
Poly(n-hexyl methacrylate) 48°C	3.95	2.42	4.24	0.83	0.47	–	–
	3.96	2.48	4.40	0.74	0.66	0.18	2.7
	0.01	0.02	0.05	0.02	0.05		
Poly(nonyl methacrylate) 42.8°C	3.51	2.44	7.82	0.79	0.53	–	–
	3.51	2.44	8.18	0.73	0.65	0.24	1.5
	0.01	0.01	0.13	0.02	0.05		
Poly(n-octyl methacrylate) 21.5°C	3.86	2.58	9.08	0.84	0.45	–	–
	3.88	2.61	9.60	0.73	0.66	0.02	1.4
	0.01	0.02	0.14	0.15	0.05		
Poly(vinyl acetal) 90°C	6.70	2.65	5.98	0.81	0.35	–	–
	6.7	2.5	6.43	0.89	0.30	2.14	2.8
	0.1	0.1	0.07	0.1	0.05		
Poly(vinyl acetate)[b] 66°C	8.62	2.74	6.84	0.91	0.45	–	–
	8.61	3.02	7.11	0.90	0.51	1.9	2.5
	0.02	0.01	0.01	0.01	0.01		
Syndiotactic poly(methyl methacrylate)	4.48	2.55	9.28	0.04	1.0	–	–
	4.32	2.52	7.96	0.53	0.55	1.2	1.1
	0.01	0.02	0.08	0.01	0.03		
Poly(vinyl formal) 130°C	6.45	3.00	7.69	0.58	0.46	–	–
	5.85	2.62	7.37	0.56	0.51	0.64	7.0
	0.03	0.06	0.22	0.03	0.06		

[a] In all cases the first line represents the data obtained from graphical techniques, the second line the results from the current investigation, the third line the standard error of the parameters for the statistical parameters

[b] The parameters for poly(vinyl acetate) were obtained as the multi-temperature study reported here

because much of the experimental data was obtained from line graphs without actual experimental values reported. In the case of poly(carbonate)[5] the imaginary residuals were all negative, so that a small phase shift term produced random residuals. The non-random behaviour of the residuals in this case may have been due to a phase shift in the bridge detector or a small out-of-balance in the ratio arms of the bridge. There was reasonable agreement between the two methods, but the results in *Table 3* suggest a bias. The average % difference for ε_0 and ε_∞ was very small, but for any particular polymer ε_0 tended to be larger while ε_∞ tended to be smaller for the graphical estimate thereby making $\varepsilon_0 - \varepsilon_\infty$ larger by as much as 10%. In general α and $\log(\tau_0)$ tended to be overestimated while β was underestimated.

We see from *Table 1* that a typical coefficient of variation for the real part is about 0.5% and for the imaginary component, about 4%. The difference in the coefficient of variation is in keeping with the accuracy of most bridges which can measure the real component of the dielectric constant about 10 times more accurately than the imaginary component.

MULTIPLE TEMPERATURE ESTIMATES

Results

Initial attempts to treat all of the poly(vinyl acetate) data for the temperature range 48°C–85°C, assuming the parameters to depend linearly on temperature, failed to converge. The temperature range was therefore temporarily reduced to 66°C–72°C and convergence was obtained. Different temperature dependences for the parameters were tried to determine their effect on the scaled determinant, and because plots of the residuals with frequency showed a strong linear dependence, a linear impedance correction term was introduced. A summary of the steps taken and their effect on the scaled determinant and on the variances of the real and imaginary components is given in *Table 3*. Eventually the entire temperature range of the data was used and satisfactory residuals were obtained.

Table 2 Summary statistics for % relative differences[a] of dispersion parameters

Parameter	Mean	Standard deviation
ε_0	0.095	0.59
ε_∞	−0.077	16.0
$\log(\tau_0)$	1.8	3.6
α	6.7	13.0
β	−10.0	16.0

[a] 100 × (graphical estimate − statistical estimate)/(statistical estimate)

In *Figures 1* to *3* we have plotted the estimated relaxation parameters as a function of temperature. In these Figures, the broken lines represent the approximate 95% confidence band of the parameters obtained from the present statistical study while the plus's and solid lines represent the results using graphical techniques and reported earlier[1]. The fitted values are in the centre of the confidence band. In *Figure 4* we have plotted the real residuals for poly(vinyl acetate) at 69°C. The broken line represents residuals from a model without an impedance correction term and the solid line represents residuals from a model with an impedance correction term. Note that it was not possible to obtain graphical estimates for the parameters over the entire temperature range.

Discussion

Actual temperature and frequency data for poly(vinyl acetate) were available to that a study of the residuals could be carried out. The relationship between real residuals and linear frequency shown in *Figure 4* may

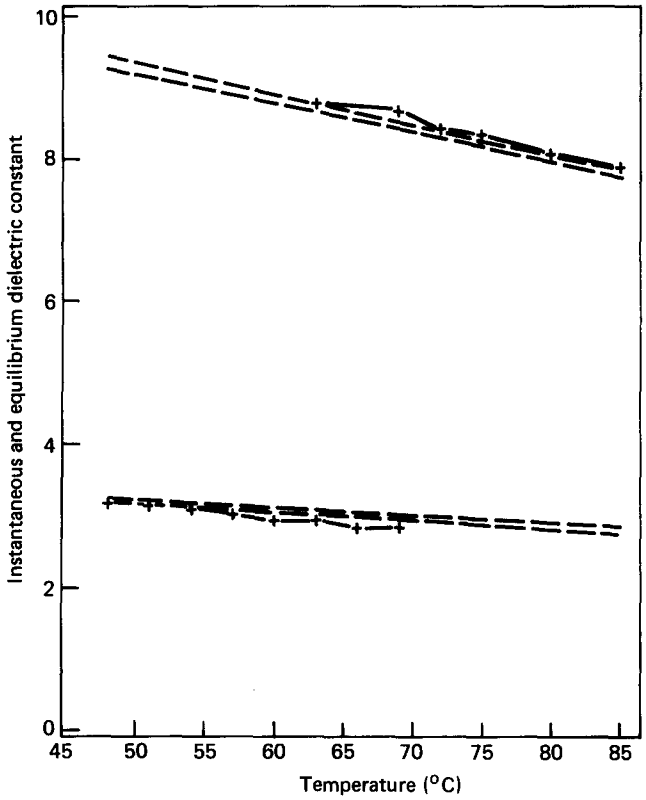

Figure 1 Comparison of the instantaneous and equilibrium dielectric constant with temperature for the two methods of parameter estimates. The pluses represent the graphical method[1] while the broken lines represent the 95% confidence limits derived from the statistical method

Table 3 Steps taken to analyse frequency and temperature dependence of $\varepsilon^*(\omega)$ for poly(vinyl acetate)

Trial No.	Description of the changes in the model	Scaled determinant	Real variance	Imaginary variance
A	Temperature range 66°C–72°C. All parameters assumed linear in temperature	21	2.0	2.0
B	As in A, but temperature range 60°C to 80°C	2000	3.0	3.0
C	As in B, but ε_0 assumed quadratic	1730	2.5	4.0
D	As in C, but deleted 2 outliers	1290	2.0	4.0
E	Temperature range 60°C to 80°C, all parameters linear, except $\ln f$ quadratic	50	2.0	2.0
F	Temperature range 60°C to 80°C. ε_0, ε_∞ linear; $\ln \tau_0$ quadratic; α, β constant	58	2.0	2.0
G	As in F, but introduced impedance correction	60	1.0	2.0
H	Temperature range 48°C to 85°C. As in G but deleted a third outlier	80	0.1	0.5
I	Temperature range 48°C to 85°C. As in H but refined the impedance correction factor	70	0.1	0.4

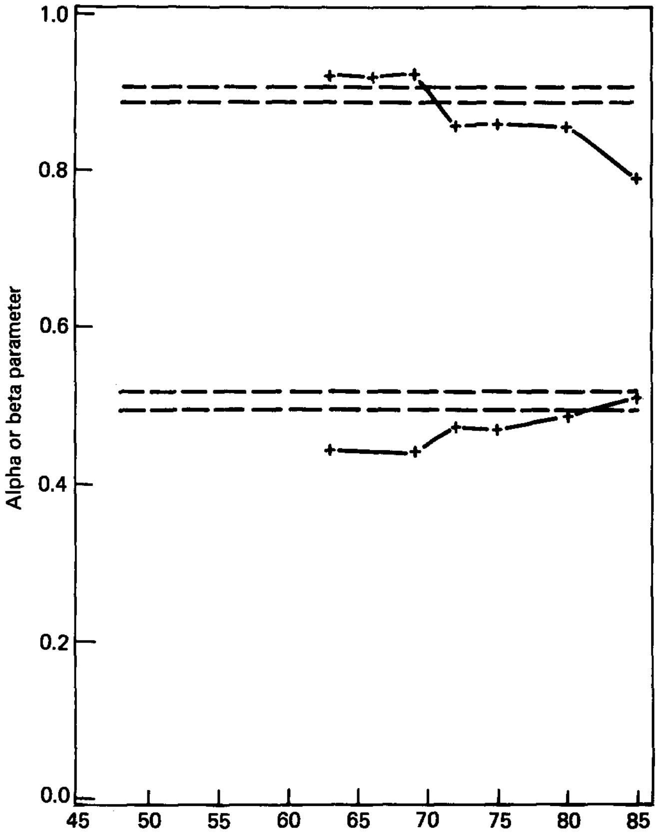

Figure 2 Comparison of the beta and alpha parameters with temperature. The pluses represent the values determined from the graphical method[1] while the broken lines represent the 95 % confidence limits derived from the statistical method

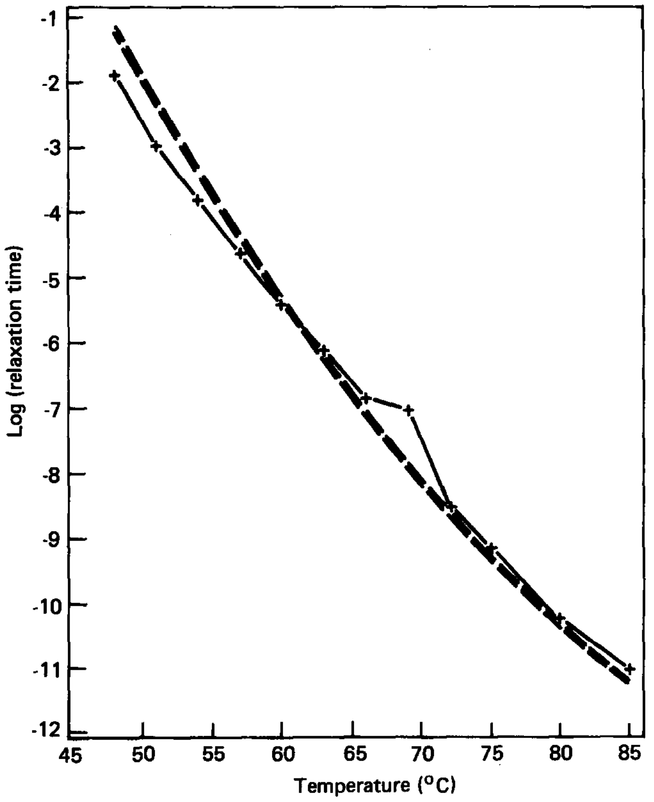

Figure 3 Comparison of log relaxation time with temperature for the two methods of data reduction. The pluses represent the graphical method[1] while the broken lines represent the 95% confidence limits derived from the statistical method

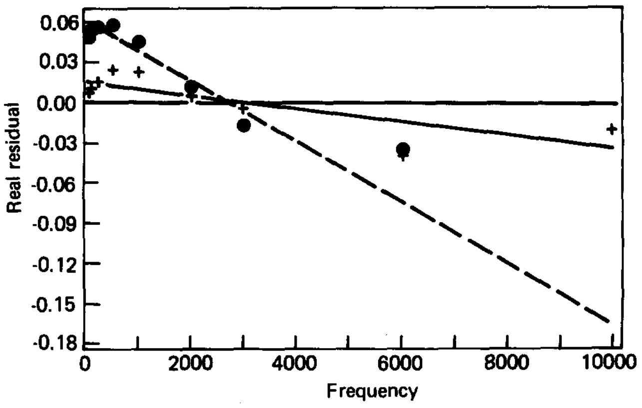

Figure 4 Plot of the real residuals *versus* frequency for poly(vinyl acetate). The filled circles represent the residual with no impedance correction and the pluses represent the residuals with impedance correction

originate from line impedances connecting the dielectric cell to the bridge. It is of interest to note that no such relationship occurred for the imaginary part.

The results in *Figures 1* and *2* show that the graphical results are quite similar to the statistical results, particularly if we assume the error band for the graphical results to be 2 or 3 times that of statistical results. The temperature dependence of the relaxation frequency is slightly lower for the statistical results than it is for the graphical results. Though the mean difference is small, e.g. 6.9 % with a standard deviation of 19 %, it does appear to be larger than the corresponding result in *Table 2*.

CONCLUSIONS

An important advantage of the method described here is the objective evaluation of the parameters, such as in the case for syndiotactic PMMA. The change in the β parameter estimates from 1.0 to 0.55 has the effect of making the shape of this (side chain) process consonant with all other polymer main chain processes. Another important advantage is the analysis of residuals, which can reveal important sources of experimental error as illustrated for poly(carbonate) and poly(vinyl acetate). The answer to the question of the ultimate reliability of equation (1) in representing the dielectric relaxation of polymer will have to await more precise experimentation.

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