Complex plane parameters for the viscoelastic beta process in poly(vinyl chloride)

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(Received 13 January 1987; accepted 8 June 1987)

Tensile–yield studies by Bauwens-Crowet *et al.* show that the high strain rate or low temperature behaviour of poly(vinyl chloride) may be determined by its beta process. In this work we made viscoelastic measurements covering the beta process over a temperature range of −140 to 20°C and a frequency range of 0.1–30 Hz. The complex compliance data is then represented with an expression analogous to the one proposed by Havriliak and Negami for the complex dielectric constants of polymers. The parameters in this expression as well as their temperature dependences are determined using the multiresponse statistical techniques developed by Havriliak and Watts. The complex compliance for the beta process of poly(vinyl chloride) can be represented with this expression to about the same accuracy as experimental error. The activation energy for the beta process was found to be 14.1 ± 1.2 kcal mol^{-1} which is in excellent agreement with the value of 14 determined from tensile yield studies. The α and β parameters for the relaxation function are discussed in terms of Mansfield's spring and dashpot model representing intra- and intermolecular interactions.

(Keywords: poly(vinyl chloride); viscoelasticity; complex plane)

INTRODUCTION

An impact mechanism study involves the construction of a failure envelope which is made by plotting the yield stress and fracture stress as a function of strain rate and temperature. Under those conditions where the yield stress is lower than fracture stress, a considerable amount of energy is dissipated and the material is considered to be tough. When the yield stress exceeds the fracture stress, yielding does not occur hence the energy expended is much lower and the material is considered to be brittle. The point at which the fracture and yield stresses are equal is called the brittle to ductile transition. Tensile yield studies by Bauwens-Crowet *et al.*[1] suggest that the yield stress behaviour of poly(vinyl chloride), PVC, at high strain rates or low temperatures is controlled by its beta relaxation process. Roetling observed similar behaviour in poly(methyl methacrylate)[2] and poly(ethyl methacrylate)[3]. More recently Ward[4] obtained similar results for linear polyethylene. These results suggest that as the strain rate is increased or the temperature is reduced the beta relaxation process can no longer respond to the applied strain so that yield stress increases until the fracture stress is reached and the test specimen breaks. For these reasons, an understanding of the beta relaxation mechanism is fundamental to the understanding of impact mechanisms in PVC as well as other polymers that exhibit shear banding in the glass phase.

Complex plane plots are an important method of representing dielectric relaxation behaviour of polymers. These plots are constructed by plotting the dielectric loss against the storage part of the complex dielectric constant. In these plots frequency is a running variable along the locus of experimental points. These loci take on simple geometric shapes and can be represented by equation (1), proposed by Havriliak and Negami[5].

$$\frac{\varepsilon^*(\omega)-\varepsilon_{00}}{\varepsilon_0-\varepsilon_{00}}=\{1+(i\omega\tau_0)^{\alpha}\}^{-\beta} \qquad (1)$$

In this expression $\varepsilon^*(\omega)$ is the complex dielectric constant at frequency ω which is generally expressed in rad s^{-1}, ε_0 and ε_{00} are the equilibrium and instantaneous dielectric constants, τ_0 is the relaxation time while α and β are parameters of the expression whose significance will be discussed below. The relaxation frequency, f_0 is related to the relaxation time through $\omega_0 = 1/\tau_0$. Graphical techniques[5] were developed to determine these parameters. Plots are constructed for each temperature of measurement and a new set of parameters is determined. In this way the temperature dependence of the five parameters of equation (1) can be determined.

Recently, however, efficient numerical techniques were developed by Havriliak and Watts[6,7] based on multiresponse statistical methods. This development simplified data analysis and temperature dependences of the parameters were determined in a single analysis. There are several advantages in using equation (1) to represent dielectric data. First, the data can be simply represented in terms of a few parameters and their temperature dependences. Second, estimation of important theoretical quantities such as the distribution of relaxation times is straightforward[5]. Finally, Mansfield[8] postulated a molecular model to represent the dielectric dispersions of polymers. In this model, he assumed the molecular orientation motions to be hindered by intra- as well as intermolecular interactions, which were represented by springs and dashpots. This model leads to complex plane loci which were quite

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similar to those of polymers, i.e. equation (1). His model is closer to a molecular interpretation of the α and β parameters than is the customary formal representation in terms of a distribution of relaxation times.

In this work we study the beta relaxation process observed in PVC below room temperature and in the frequency range of 0–30 Hz. The form of the expression used to represent the data is given by equation (2). The quantities in equation (2) are analogous to those in equation (1).

$$\frac{J^*(\omega)-J_{00}}{J_0-J_{00}}=\{1+(i\omega\tau_0)^{\alpha}\}^{-\beta} \qquad (2)$$

with $\omega_0=1/\tau_0$. The complex compliance is used in equation (2) because it, like the complex dielectric constant, is a relaxation function.

METHODS

Materials and test specimens

The compositions for the test specimens in this study are given in *Table 1*. The samples were milled 3.5 min after fluxing at 177°C. The melt was removed from the mill and compression moulded into $10\times10\times0.125$ in thick plaques; $2\times0.5\times0.125$ in test specimens were cut from the plaques for viscoelastic measurements.

Viscoelastic measurements

All the viscoelastic measurements were carried out in the Rheometrics Dynamic Spectrometer RDS-770 at frequencies of 0.1, 1.0, 7.962 and 31.85 Hz. The strain was 0.1% and the temperature range was −140 to 20°C. The measurements were made in the temperature sweep mode incremented 5°C. Emphasis in this study is placed on composition C. The measuring scheme was to make measurements at 0.1 Hz first in a temperature sweep mode starting at −140 and stopping at 20°C. When 20°C was reached, the test specimen was removed from its fixture, its dimensions were determined once again, then it was replaced in the fixture and rerun at 1.0 Hz in the temperature sweep mode starting at −140°C. This procedure was extended to 7.962, 1.0, 31.85 and finally to 1.0 Hz. Though this procedure appears tedious and cumbersome, this method of replication provides us with important statistical information about the experimental technique. Such statistical information is important because the beta process in PVC is small.

Table 1 Compositions of the compression moulded plaques

Sample	Stabilizer[b]	PHR of PVC[a] Lubricant[c]	Lubricant[d]	Process aid[e]
A	2	–	–	–
B	2	0.5	0.2	–
C	2	0.5	0.2	1.5

[a] The PVC used has a K58 value (1% cyclohexanone) and was manufactured by Firestone under the trade name FPC 9445

[b] The stabilizer used was a methyl tin compound, manufactured by Morton Thiokol under the trade name TM181

[c] The first lubricant used was a glycerol monostearate compound manufactured by Glycol, Inc. under the trade name of Aldo MS

[d] The second lubricant used was a calcium salt of partially saponified montan wax manufactured by Hoechst under the tradename of OP Wax

[e] The acrylic processing aid used was manufactured by Rohm and Haas Co. under the trade name of Paraloid K-120ND

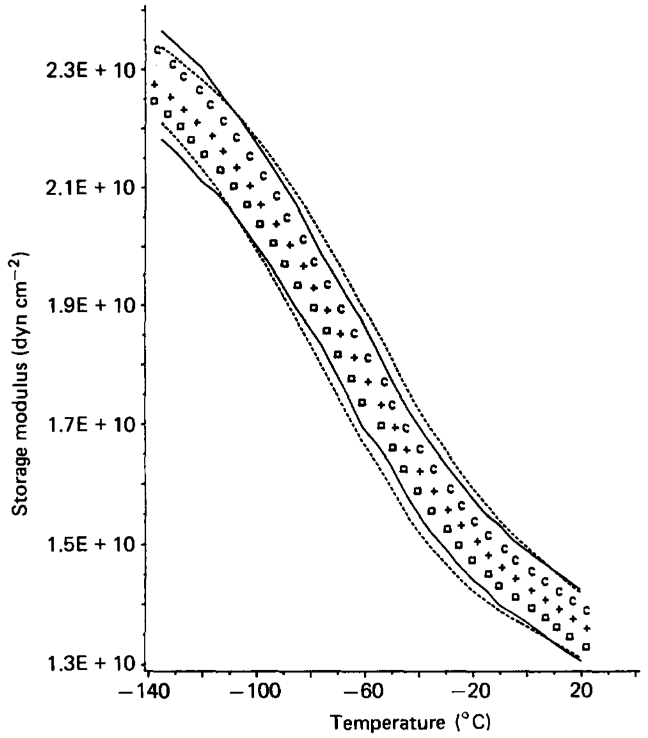

Figure 1 Real modulus plotted against temperature. E + 10 represents 10 raised to the power 10. The symbols represent a single and independent run as described in the text

Numerical analysis

Data sent to the main frame was assembled into a SAS (ref. 9) data set. SAS is a user-friendly, versatile statistical and graphics software package. All temperature interpolations and regression calculations were made using SAS as described elsewhere[6,10]. It is important to note that except where stated, the complex compliance has been reduced by 10^{10} in order to keep the numerical analysis within bounds.

RESULTS

Replication studies

The data for the temperature dependence of the real and imaginary parts of the complex modulus for three temperature sweeps at 1.0 Hz for specimen C are given in *Figures 1* and *2*, respectively. In both cases, the solid line represents the 95% confidence limits estimated from the three sweeps[10], while the broken line represents 95% confidence limits determined from a generalized error function reported elsewhere[10]. The agreement between the two limits suggests that the errors in these measurements are similar to those reported for other materials. In *Figures 3* and *4*, the solid and broken lines represent the same two confidence limits but the symbols represent experimental data for samples A and B obtained in the temperature sweep mode at 1.0 Hz. There is no significant difference in the storage modulus among the three formulations, although the loss modulus exhibits small differences not much larger than the 95% confidence limits. These observations led us to emphasize composition C in this study, with limited reference to compositions A and B. Composition C was chosen because it is similar to those used in many rigid modified PVC studies.

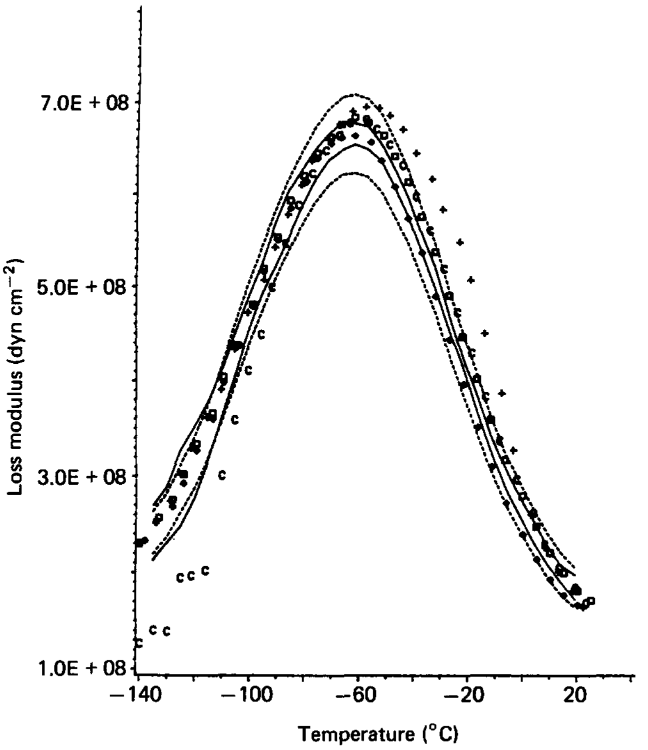

Figure 2 Loss modulus plotted against temperature. E+08 and the symbols are defined in *Figure 1*

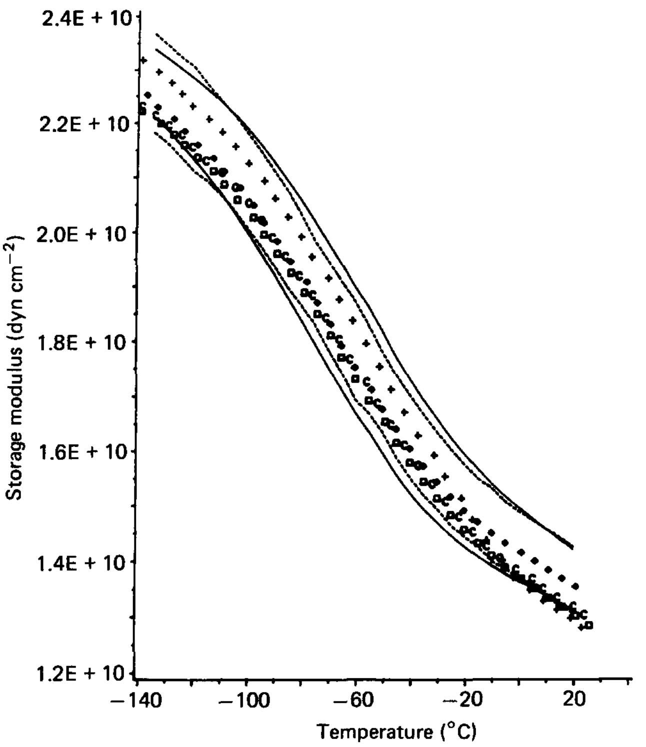

Figure 3 Real modulus plotted against temperature. E + 10 has been defined in *Figure 1*. The symbols represent independent runs and different compositions. □, +, C, represent composition A in *Table 2*; ◇, represents formulation B

Time–temperature shifting

The complex compliance was calculated from the complex modulus by assuming $J^*(\omega) = 1/G^*(\omega)$ where $G^*(\omega)$ is the complex modulus and $J^*(\omega)$ has been defined before. In addition, $J^*(\omega)$ was reduced by 10^{10}. The data was shifted along the frequency axis[11] to form the best overlay of the experimental points. The results of shifting the real and imaginary parts of the compliance are given in *Figures 5* and *6*. An Arrhenius plot of the shift factor *versus* reciprocal absolute temperature is given in *Figure 7*. The shift factor was adjusted to be −4.0 at room temperature for reasons discussed below. The band of points in the region of maximum loss is about 16%.

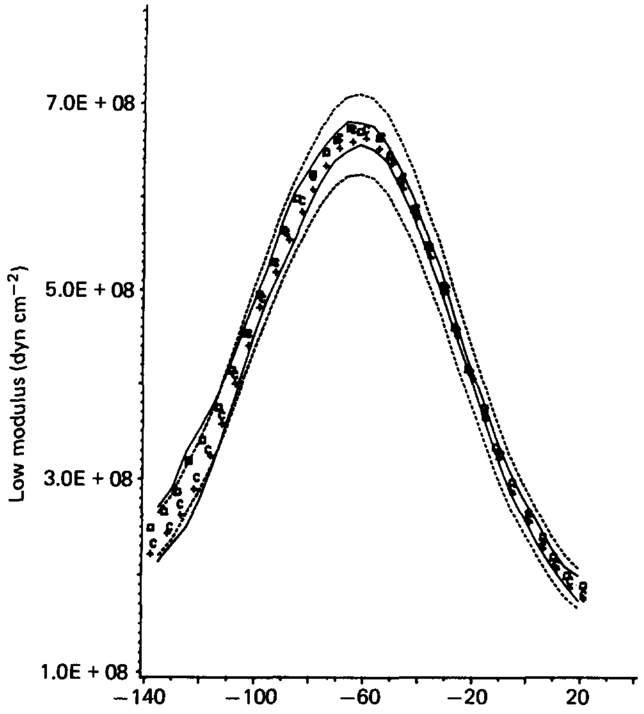

Figure 4 Loss modulus plotted against temperature. The units and compositions are defined in *Figure 3*

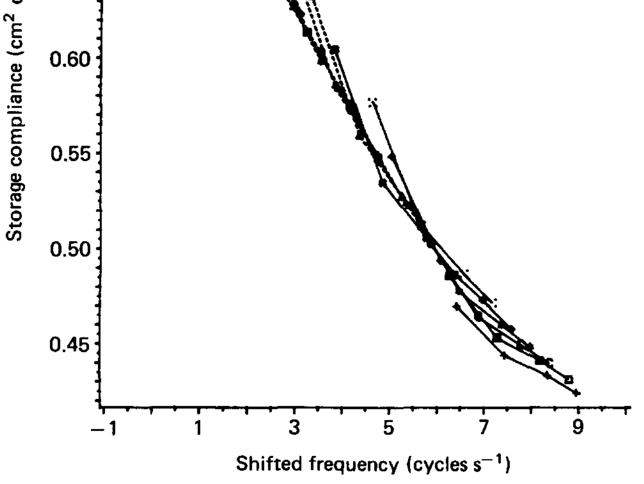

Figure 5 Real compliance plotted against shifted frequency at various temperatures (−140 to 20°C). The compliance has been reduced by 10^{10}

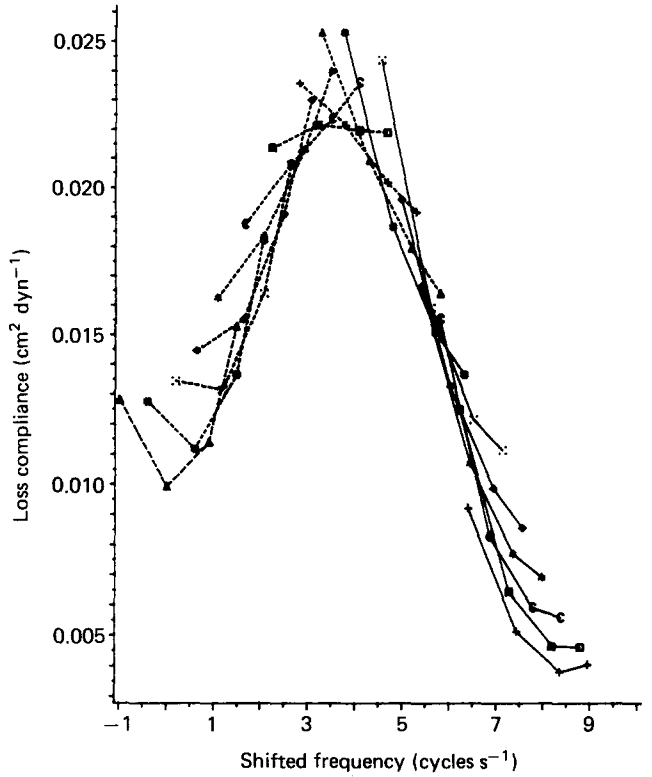

Figure 6 Loss compliance plotted against shifted frequency at various temperatures (−140 to 20°C). The compliance has been reduced by 10^{10}

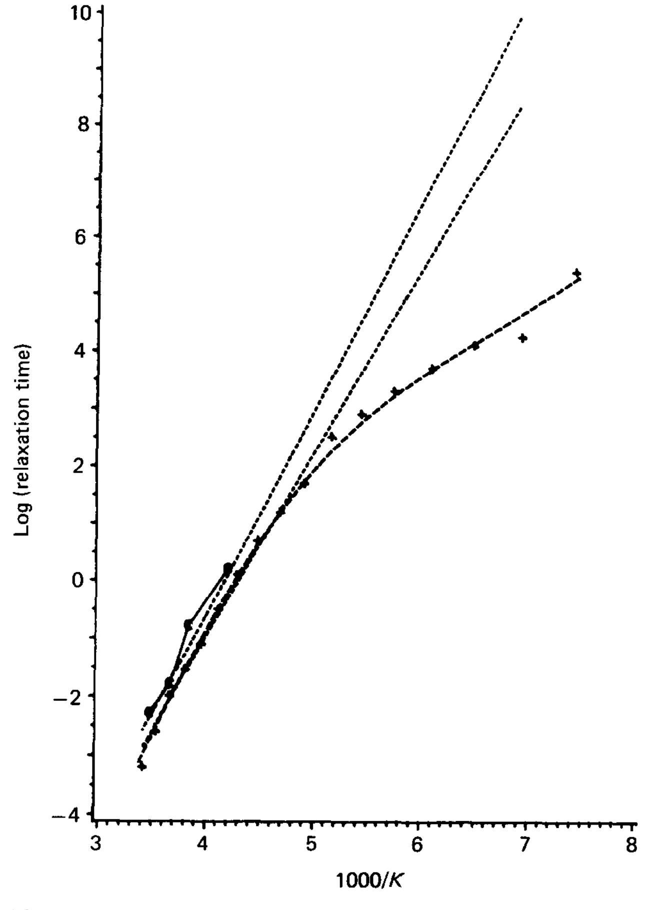

Figure 7 Log of relaxation times (s) plotted against 1000/*K*, where *K* is degrees in Kelvin for composition C. +, shift factors adjusted to be equal to relaxation time at room temperature; C, preliminary estimates of ○; ---, 95% confidence limits

Preliminary estimates of the complex plan parameters

As indicated earlier, the complex compliance data has been reduced by 10^{10} to prevent overflow during the calculations. In order to use the techniques described in reference 7, reasonable estimates of the five parameters in equation (2) and their temperature dependence are required. Without such estimates, convergence to a global minimum will not occur. If convergence does occur, it may very well be a local unrealistic minimum, thereby leading to a false evaluation of the parameters. This problem is acute with the beta process of PVC because much of the observed variability in the data is due to the temperature dependence of J_0 and J_{00}. This is readily apparent from the data in *Figure 8* where $J'(\omega)$ is plotted *versus* temperature for the four frequencies. Estimates of the high and low temperature slopes, i.e. the temperature dependence of J_0 and J_{00} was estimated using SAS's PROC GLM. These results are listed in *Table 2* under trial 0 which represents the initial trial parameters. The temperature dependence of the relaxation time is determined from complex plane plots of the data for each frequency. In such plots, i.e. at constant frequency, the temperature is a running variable along the locus of points. The definition of the relaxation time in reference 5 is still valid and was estimated in the same way. These results are given in *Figure 7*. The Arrhenius rate parameters were determined using SAS's PROC GLM. These results are listed in *Table 2* under trial 0. The α and β parameters were determined from a complex plane plot (i.e. constant frequency and variable temperature) as described elsewhere[5]. The initial trial parameters for α and β were assumed to be independent of temperature. These parameters are listed in *Table 2* under trial 0.

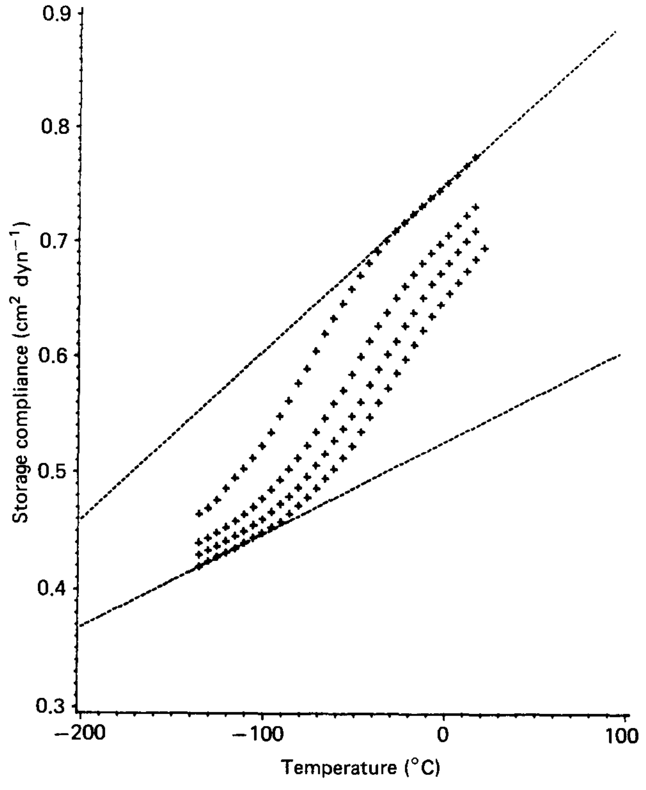

Figure 8 Real compliance reduced by 10^{10} plotted against temperature. The dashed lines represent the low temperature, i.e. J_{00} and high temperature J_0 limits of the compliance

Table 2 Summary of the regression results for the various trials

	Trial						
Parameter	0	1	2	3	4	5	6
J_0	0.747	0.717	0.723	0.724	0.675	0.672	0.672
s.d.	–	0.007	0.003	0.003	0.005	0.005	0.005
$J_0(T)$	0.0001	0.0005	0.0009	0.0010	0.0010	0.0010	0.0009
s.d.	–	0.0002	0.0001	0.0001	0.0001	0.0001	0.0001
J_{00}	0.534	0.302	0.292	0.234	0.296	0.291	0.324
s.d.	–	0.036	0.034	0.038	0.026	0.026	0.019
$J_{00}(T)$	0.0008	−0.0008	−0.0009	−0.0012	−0.0012	−0.0013	−0.0009
s.d.	–	0.0002	0.0002	0.0003	0.0003	0.0003	0.0002
Ln $(f_0)^a$	3.49	4.64	4.81	4.53	−1.78	1.93	1.69
s.d.	–	0.21	0.37	0.28	0.37	0.33	0.33
Ln (f_0) (T)	−7.24	−7.97	−7.96	−7.68	−7.69	−7.68	−7.41
s.d.	–	0.42	0.44	0.34	0.34	0.33	0.32
Alpha	0.3	0.36	0.32	0.33	0.33	0.34	0.37
s.d.	–	0.03	0.02	0.02	0.02	0.02	0.02
Beta	0.2	0.20	0.24	0.18	0.18	0.16	0.18
s.d.	–	0.03	0.04	0.03	0.03	0.02	0.02

$^a f_0 = 1/\tau_0$

Final estimation of the parameters

The parameters cited above were used for trial 1 and convergence occurred readily. A plot of the real and imaginary residuals *versus* temperature is given in *Figures 9* and *10*, respectively. The scaled determinant as well as the coefficients of variation for the real and imaginary compliance are given in *Table 3*. Trial 2 consisted of making slight adjustments to the real and imaginary parts of the compliance. These changes, as well as the results of the regression, are shown in *Table 3*. These adjustments were made on the basis of means of the residuals for these frequencies. Trial 3 consisted of similar adjustments but for the other frequencies. Trial 4 included a reference temperature centred in the middle of the experimental range of the data, i.e. −50°C. Often such changes improve the quality of fit because the magnitude of the parameters has been altered. In this study no improvement was found. Inspection of a complex plane plot of the 0.1 Hz data revealed a marked deviation from the circular arc behaviour expected at high temperatures. This observation suggests a significant contribution from the alpha to the beta process under these conditions. Four of the highest temperatures were deleted for the 0.1 Hz data to determine trial 5. Trial 6 consisted of small adjustments to data as indicated in *Table 3*. Several attempts were made to reduce the scaled determinant by expanding the number of terms in the model, but they all failed. These changes included introducing a temperature dependence term for the α and β parameters, or including a square term in the temperature dependence of J_0 or J_{00} or the relaxation time τ_0. Plots of the real and imaginary residuals with temperature for the best model (trial 6) are given in *Figures 11* and *12*, respectively. The variation of the 95% confidence limits for J_0 and J_{00} with temperature is given in *Figure 13*. The 95% confidence limits for their difference is also given. The upper limit for this difference was estimated by subtracting the lower limit of J_{00} from the upper limit of J_0, with a similar calculation for the lower limit of the difference. The 95% confidence limits with temperature for the α and β parameters are not given since they were found to be independent of temperature. The 95% confidence limits

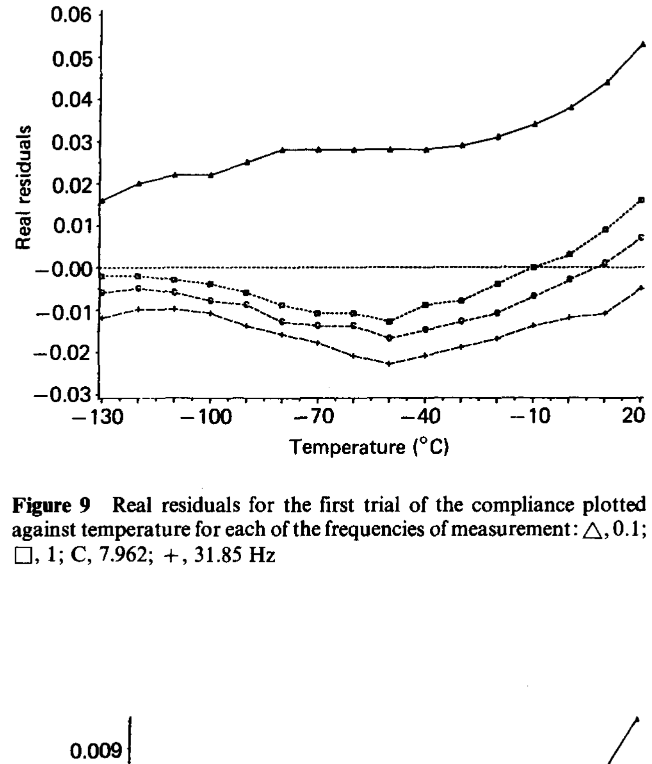

Figure 9 Real residuals for the first trial of the compliance plotted against temperature for each of the frequencies of measurement: △, 0.1; □, 1; C, 7.962; +, 31.85 Hz

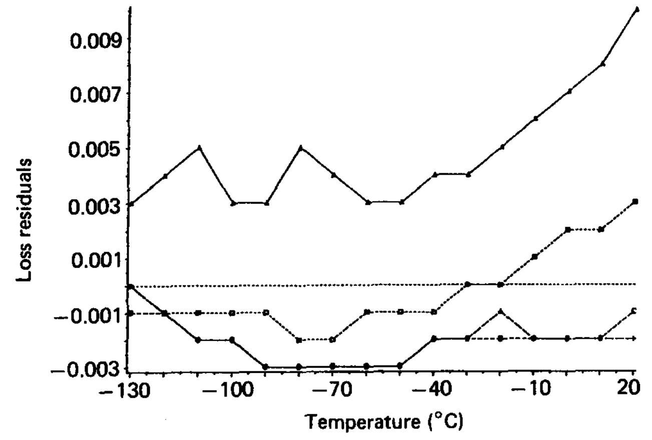

Figure 10 Loss residuals for the first trial of the compliance is plotted against temperature for each of the frequencies of measurement as given in *Figure 9*

Table 3 Summary statistics and adjustments made to the viscoelastic data of PVC

	Trial						
Parameter	1	2	3	4	5	6	%C[a]
0.1 Hz							
Real	–	−0.031	–	–	–	–	5
Imag.	–	−0.006	–	–	–	–	30
7.962 Hz							
Real	–	–	0.0069	–	–	0.0037	2
Imag.	–	–	0.0020	–	–	0.00013	10
31.85 Hz							
Real	–	0	–	–	–	0.0096	2
Imag.	–	0.0017	–	–	–	0.00013	9
T_c[b]	–	–	–	−50	−50	−50	–
SD[c]	1.25	0.32	0.20	0.20	0.15	0.06	–
c.v. (%)[d]							
Real	3.44	1.36	1.31	1.31	1.35	0.77	–
Imag.	21.84	9.36	7.42	7.42	6.72	7.04	–

[a] Per cent change, estimated from the total contribution to the observation divided by the mean of the observations
[b] Temperature selected to centre the viscoelastic data
[c] Scaled determinant × 10^6. The SD is the numerical value of the determinant at convergence divided by the number of observations in the data set
[d] Coefficient of variation calculated from the residuals and represents the model standard deviation

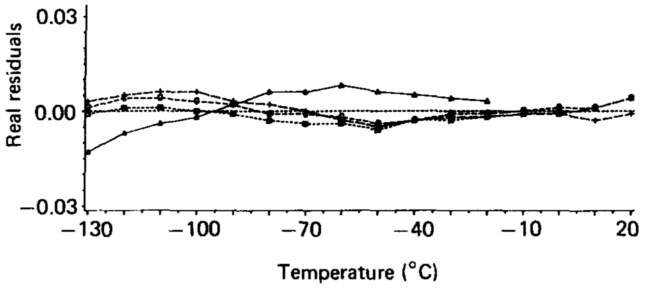

Figure 11 Real residuals for the final trial of the compliance plotted against temperature for each of the frequencies of measurement as given in *Figure 9*

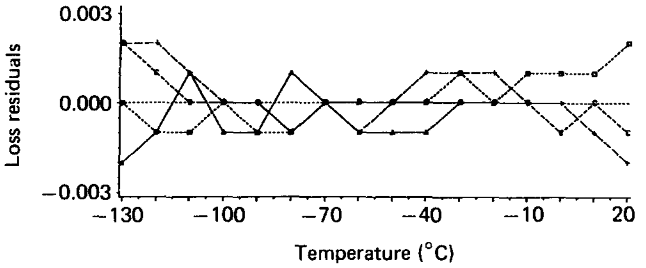

Figure 12 Loss residuals for the final trial of the compliance plotted against temperature for each of the frequencies of measurement as given in *Figure 9*

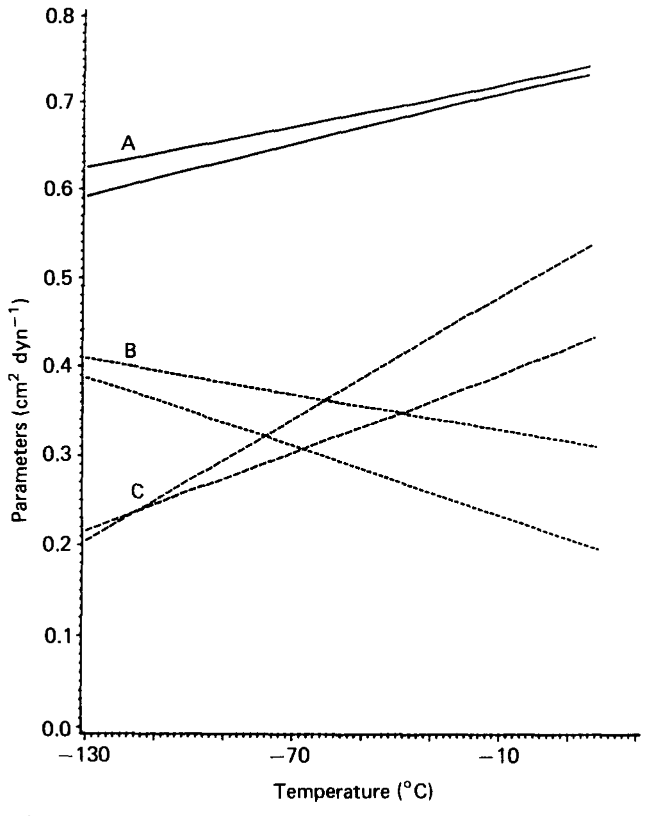

Figure 13 J_0 (A), J_{00} (B) and their difference (C) plotted against temperature. The units of the parameters are reduced by 10^{10}

for the relaxation time are given in *Figure 7*. A complex plane plot of the treated data is given in *Figure 14*.

Extension to the other compositions

Viscoelastic measurements were made on composition A from −140 to 20°C in 5°C increments and frequencies of 0.1, 1.0 and 7.962 Hz. The 1.0 Hz data was replicated three times and the mean values were used in the analysis. The techniques for reducing the residuals described in the previous section were used to reduce the residuals. No adjustments were made to the 1.0 Hz data. The results of the analysis are given in *Table 4*. Viscoelastic measurements were made on composition B from −140 to 20°C in 5°C increments and a frequency of 0.1 and 1.0 Hz. The 1.0 Hz data was not replicated. The results of the regression analysis are given in *Table 4*. Small adjustments were made to both frequencies since the 1.0 Hz data were not replicated.

DISCUSSION

Selection of suitable trial parameters required a considerable amount of data manipulation. This

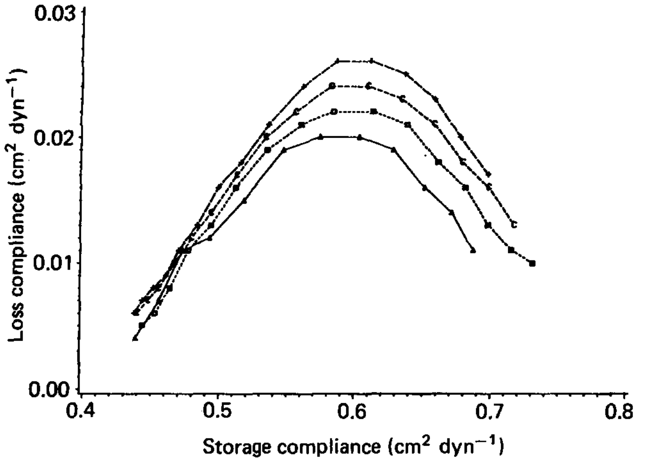

Figure 14 Complex plane plot of the real and imaginary parts of the complex compliance for each of the frequencies of measurement as given in *Figure 9*

Table 4 Summary of the regression results for the various compositions in *Table 1*

	Sample		
Parameter	A	B	C
J_0	0.696	0.695	0.672
s.d.	0.010	0.020	0.005
$J_0(T)$	0.0012	0.0013	0.0009
s.d.	0.0001	0.0003	0.0001
J_{00}	0.349	0.388	0.324
s.d.	0.038	0.091	0.019
$J_{00}(T)$	−0.0008	−0.0002	−0.009
s.d.	0.0003	0.0009	0.0002
$\mathrm{Ln}(f_0)$	−1.66	−1.37	−1.69
s.d.	0.66	1.13	0.33
$\mathrm{Ln}(f_0)(T)$	−7.09	−5.99	−7.41
s.d.	0.58	1.20	0.32
Alpha	+0.35	0.39	0.18
s.d.	0.04	0.08	0.02
Beta	+0.22	0.24	0.18
s.d.	0.06	0.12	0.02
SD[a]	6.0	1.63	0.149
C.V. (%)[b]			
Real	0.77	3.23	1.1%
Imag.	7.04	17.00	10.5%
Degrees of freedom	17	9	51

[a] Scaled determinant $\times 10^8$
[b] Coefficient of variation

difficulty occurs when dealing with small changes represented by multiparameter functions in the presence of experimental noise. Except for the selection of the temperature dependence of J_{00} all the other choices turned out to be quite reasonable. The residuals in the final fit could be reduced by the addition or subtraction of terms that were no larger than those found in replication studies carried out at 1 Hz. In no case were adjustments made to the 1 Hz data which was a mean of three independent runs. It should be pointed out that the addition of these small terms reduce the magnitude of the scaled determinant by a factor of 20 without altering significantly the five parameters of equation (2) or their temperature dependences. This result suggests that noise is being deleted from the data and that the final choice of parameters did not represent some bias. At the very least, equation (2) represents the 1.0 Hz data within experimental error and without any adjustments. In addition, equation (2) appears to represent the data at the other frequencies within the same error band as found in the 1 Hz case. The temperature dependences of J_0 or J_{00} are in opposite directions. This result has some significant implications. First, any attempt to normalize the data prior to time–temperature shifting by taking into account density changes with temperature would have been futile. In addition we see that as the temperature decreases, J_0–J_{00} also decreases, suggesting that the beta process is freezing out in a thermodynamic sense in addition to a rate sense, i.e. the relaxation time is increasing. The activation energy for the beta process in sample A was found to be 14.1 ± 1.2 kcal which is in excellent agreement with the value of 14 reported by Bauwens-Crowet *et al.*[1] It should be pointed out that the molecular weight of their PVC was unspecified; in addition, the dependence of activation energy on molecular weight is unknown. For that matter, the dependence of these five parameters on molecular weight or tacticity is unknown. The α and β parameters for the PVC beta process are similar to those of many dielectric dispersions of polymers. Mansfield's[8] model for dielectric dispersions is based on inter- and intramolecular interactions represented by springs and dashpots. Since α and β were found to be independent of temperature, then the parameters in his model are also independent of temperature. Taking values of $\alpha = 0.4$ and $\beta = 0.2$ leads to the (very approximate) estimation of $\log_{10} \beta C = -0.3$, and $\log_{10} R = -3$. Since βC is about 1, this suggests that the intramolecular interaction (spring constant) is not very strong. Furthermore, since R was defined by Mansfield to be the ratio of inter- to intramolecular relaxation times (friction coefficients), intermolecular interactions are still weaker. In other words, the intermolecular relaxation time is about 1/1000 that of the intramolecular value. These results suggest that the restrictions to segmental orientation come from chain stiffness and not from chain–chain interactions. Recent results of del Val *et al.*[12] suggest that thermally stimulated creep and depolarization experiments involve two processes, an alpha and a beta process, that have similar kinetic parameters. In other words, they concluded that these two mechanisms are the same in both effects. If we may assume that the viscoelastic and dielectric beta processes are one and the same, then dielectric measurements would provide us with still further information. Specifically, we would know the effective dipole moment associated with the viscoelastic beta process.

ACKNOWLEDGEMENT

The writers wish to express their appreciation to Mr L. Walters whose patience and experimental skill were a necessary part of this study.

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