

Effect of methylmethacrylate–butadiene–styrene modifiers on the viscoelastic beta process in poly(vinyl chloride)

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Tensile yield studies on poly(vinyl chloride) (PVC) indicate that the high-strain-rate or low-temperature behaviour may be determined by its beta process. In a previous study we examined the viscoelastic beta process of unmodified PVC over the temperature range -140 to 20°C and frequency range 0.1 to 30 Hz. In this study we extend these measurements to methylmethacrylate–butadiene–styrene (MBS) modified PVC over the same frequency and temperature ranges. In both studies the complex compliance can be represented in terms of an expression that takes the form originally proposed by Havriliak and Negami for the complex dielectric dispersions observed in polymers. These parameters and their dependence on temperature were determined using the multi-response statistical techniques developed by Havriliak and Watts. In either case the complex compliance for the beta process of PVC can be represented with this expression to within experimental error. MBS modification of PVC appears to increase the magnitude of the beta process (i.e. $J_0 - J_{\infty}$ is larger), decrease the relaxation time at room temperature, and decrease the width of the distribution of relaxation times, so that it is more intense in the estimated impact time region at room temperature.

(Keywords: PVC; beta process; MBS; modifiers; viscoelastic relaxation)

INTRODUCTION

Fracture in ductile materials comes about when yield stress exceeds fracture stress. Tensile yield studies on poly(vinyl chloride) (PVC) by Bauwens-Crowet *et al.*¹ suggest that the beta process determines the yield stress at high strain rates or at low temperatures. We reported² on the viscoelastic beta process parameters of unmodified PVC represented by:

$$\frac{J^*(\omega) - J_{\infty}}{J_0 - J_{\infty}} = [1 + (i\omega\tau_0)^{\alpha}]^{-\beta} \quad (1)$$

In equation (1), $J^*(\omega)$ is the complex compliance measured at frequency ω (rad), J_0 and J_{∞} are the equilibrium and instantaneous compliances, τ_0 is the relaxation time, and α and β are parameters to be discussed below. Equation (1) is the viscoelastic analogue of the complex dielectric expression proposed by Havriliak and Negami³. Each of the five parameters of equation (1) may be temperature-dependent. The parameters and their dependence on temperature were determined by multi-response statistical techniques developed by Havriliak and Watts^{4,5} for dielectric dispersions. The technique was found to work equally well for viscoelastic dispersions. Equation (1) was found to represent the viscoelastic beta process of unmodified PVC within experimental error. Formally, the parameters α and β are related to the distribution of relaxation times³. A molecular interpretation can be made in terms of a time-dependent correlation function, as developed by Cole⁶. More recently, Mansfield⁷ proposed a model for the time-dependent correlation function in terms of springs and dashpots, which were

supposed to represent inter- and intramolecular interactions.

METHODS

Materials and test specimens

The compositions for the test specimens in this study are given in Table 1 and are the same specimens as those used in an extensive infra-red study⁸. The samples were milled 3.5 min after fluxing at 350°C . The melt was

Table 1 Description of composition for the plaques used in this study

Sample no.	Stabilizer ^b	(phr of PVC ^a)			Modifier type at 13 phr
		First lubricant ^c	Second lubricant ^d	Processing aid ^e	
A	2	0.5	0.2	1.5	—
B	2	0.5	0.2	1.5	MBS I ^f
C	2	0.5	0.2	1.5	MBS II ^f

^aThe PVC used in this study has a K58 value (1% cyclohexanone) and was manufactured by Firestone under the code name FPC 9445

^bThe stabilizer used in this study is a methyl-tin compound, manufactured by Morton Thiokol under the trade name TM181

^cThe first lubricant is a glycerol monostearate compound manufactured by Glycol Inc. under the trade name Aldo MS

^dThe second lubricant used in this work is a calcium salt of a partially saponified montan wax manufactured by Hoechst under the trade name OP Wax

^eThe acrylic processing aid used in this work was manufactured by the Rohm and Haas Co. under the trade name K-120ND

^fThese are MBS modifiers prepared by emulsion polymerization of butadiene, styrene and methylmethacrylate. Their overall proprietary compositions are approximately the same and they differ only in the minor component levels. The emulsion particle diameters are 100 to 200 nm

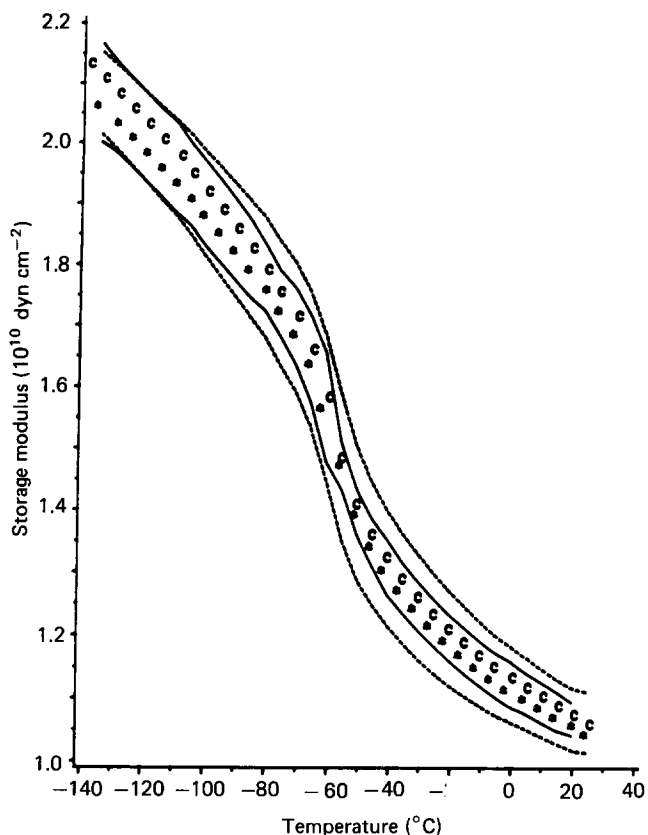


Figure 1 The real modulus plotted against temperature. The symbols * and C represent individual runs as described in the text for composition B

removed from the mill and compression moulded into 10 inch \times 10 inch \times 0.125 inch thick plaques; 2 inch \times 0.5 inch \times 0.125 inch test specimens were cut from the plaques for viscoelastic measurements. Test specimen A was described previously².

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, 31.85 and 79.62 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. 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, 31.85, 79.62 and finally to 1.0 Hz. Though this procedure appears to be 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.

Numerical analysis

Data sent to the mainframe computer were assembled into a SAS* data set. SAS is a user-friendly, versatile statistical and graphics software package. All

temperature interpolations, regression calculations and preliminary estimates of the parameters were made using SAS as described elsewhere^{2,4,9}. 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 temperature dependence of the real and imaginary parts of the complex modulus for two temperature sweeps at 1.0 Hz data for specimen B are given in Figures 1 and 2, respectively. In both cases, the full curves represent the 95% confidence limits estimated from the two sweeps, while the broken curves represent 95% confidence limits determined from a generalized error function reported elsewhere⁹. The agreement between the two limits suggests that the errors in these measurements are similar to those reported for other materials. Results for composition C are similar to those in Figures 1 and 2.

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 were shifted along the frequency axis¹⁰ 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 3 and 4. An Arrhenius plot of the shift factor (represented by '+'s) versus reciprocal absolute

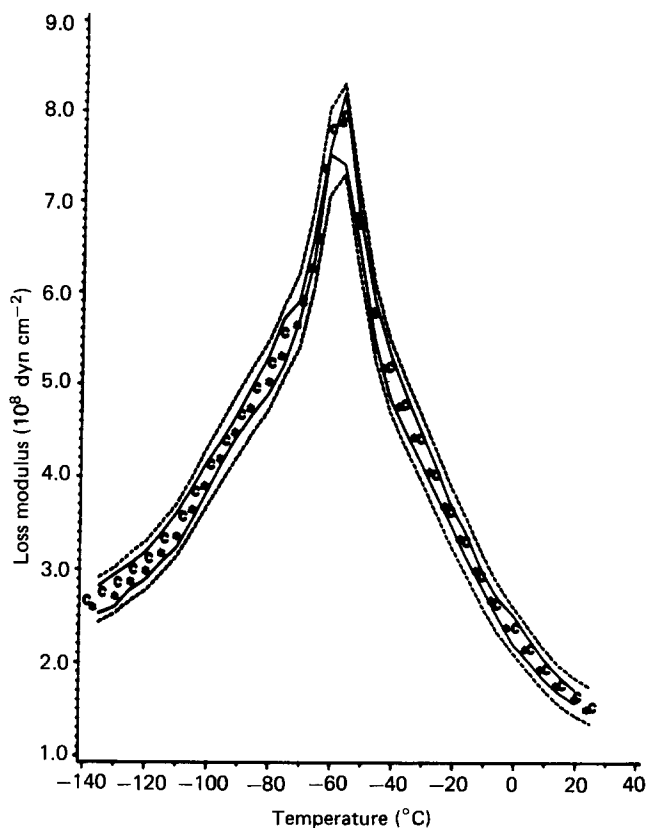


Figure 2 The loss modulus plotted against temperature for composition B. The symbols are defined in Figure 1

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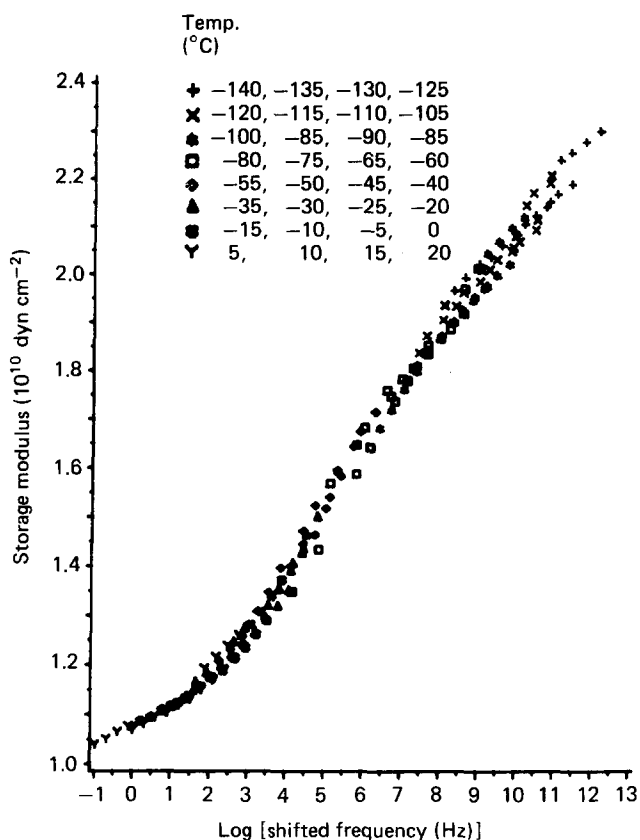


Figure 3 The real modulus plotted against shifted frequency for composition B

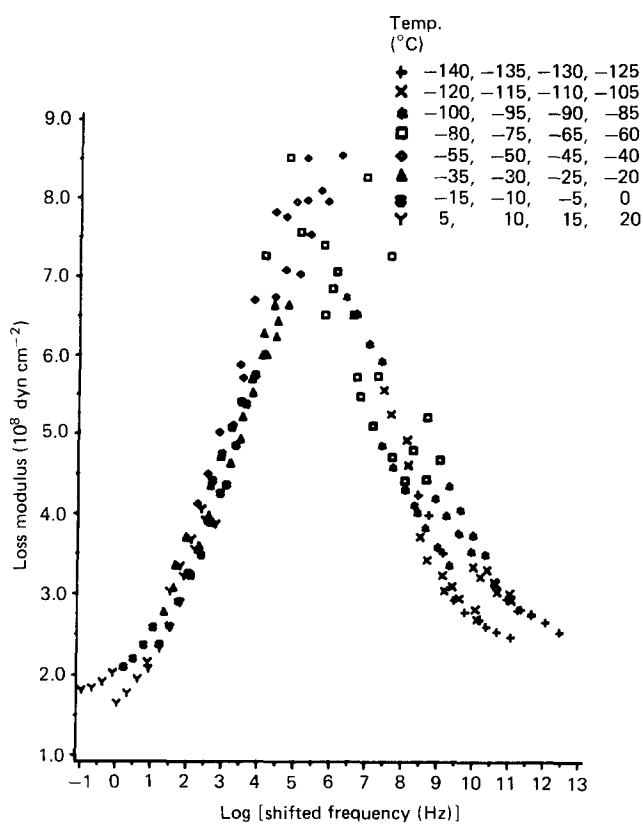


Figure 4 The loss modulus plotted against shifted frequency for composition B

temperature is given in Figure 5. The shift factor was adjusted to be -5.0 at room temperature, for reasons that will become apparent in the next two sections. The band of points in the region of maximum loss is about 19%, which is somewhat larger than experimental error, whereas the band of points in the real shifted data is smaller than the experimental error.

Estimation of the parameters

Trial parameters were estimated using techniques reported elsewhere². Convergence occurred readily even when the data file consisted of the entire set of data (i.e. about 160 points). In all cases mean values for the 1.0 Hz data were used. Small adjustments were made to the compliance values at the other frequencies to minimize the residuals. These adjustments are given in Table 2. In no case were adjustments made to the 1.0 Hz data. Plots of the real and imaginary residuals *versus* temperature are given in Figures 6 and 7, respectively, for specimen B; the vertical axis was chosen to be the mean value of the compliance of all the data used in the regression. The scaled determinant as well as the coefficients of variation for the real and imaginary compliance are given in Table 2. The results of the regression are given 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

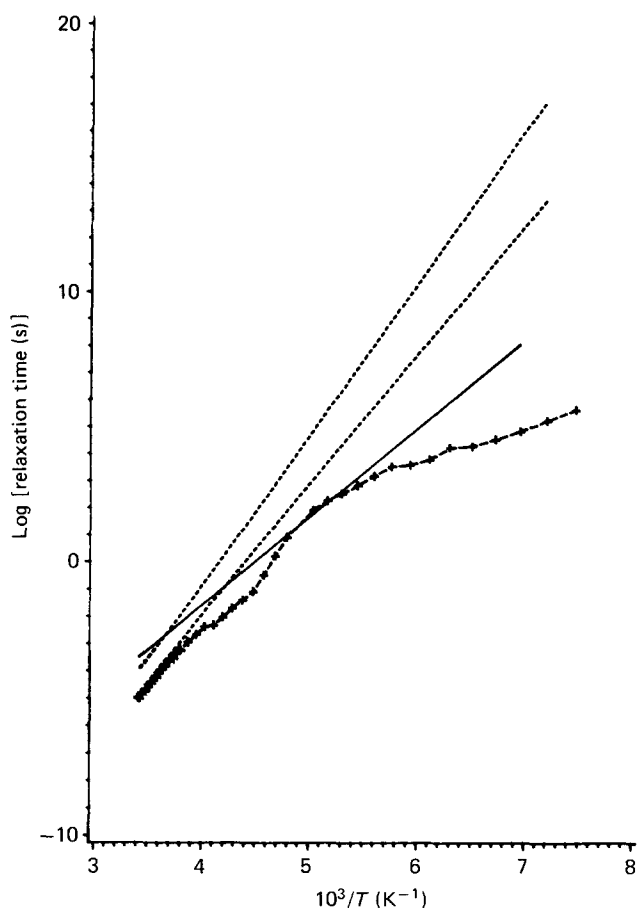


Figure 5 Log(response time) plotted against $1/T$ for composition B. The '+'s represent shift factors, adjusted to be equal to relaxation time at room temperature. The broken lines represent the upper and lower confidence limits of the relaxation time determined in this study while the full line represents unmodified PVC

Table 2 Summary of the statistical quantities for representing the compositions in Table 1 in terms of equation (1)

Parameter	Sample A	Sample B	Sample C
0.1 Hz			
Real	-5%	-3.0%	-3.0%
Imaginary	-30%	-18.0%	-10.0%
7.962 Hz			
Real	+2%	-0.3%	+0.4%
Imaginary	+10%	-10.0%	+0.6%
31.85 Hz			
Real	-2%	+0.7%	+0.4%
Imaginary	-9%	+2.0%	+8.5%
79.62 Hz			
Real	-	+3.0%	-0.7%
Imaginary	-	+0.5%	-4.5%
Scaled determinant	1.49×10^{-9}	2.1×10^{-7}	1.35×10^7
Coefficient of variation			
Real	1.1%	1.9%	1.8%
Imaginary	10.5%	14.7%	12.9%
Degrees of freedom	51	146	156

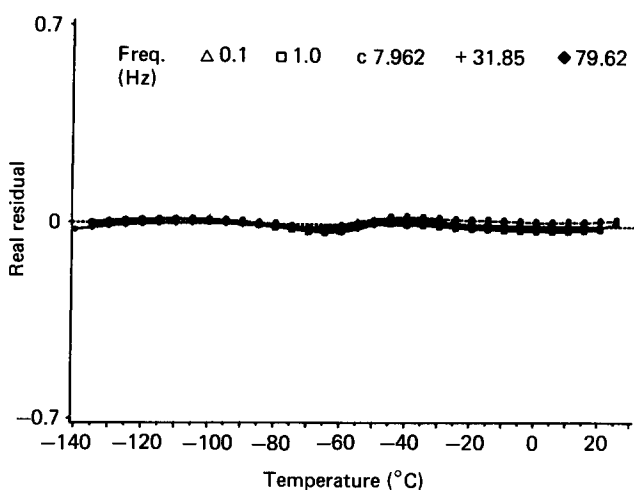


Figure 6 The real residuals for the final trial of composition B plotted against temperature for each of the frequencies of measurement. The vertical axis was chosen to represent the mean compliance of the range that was studied

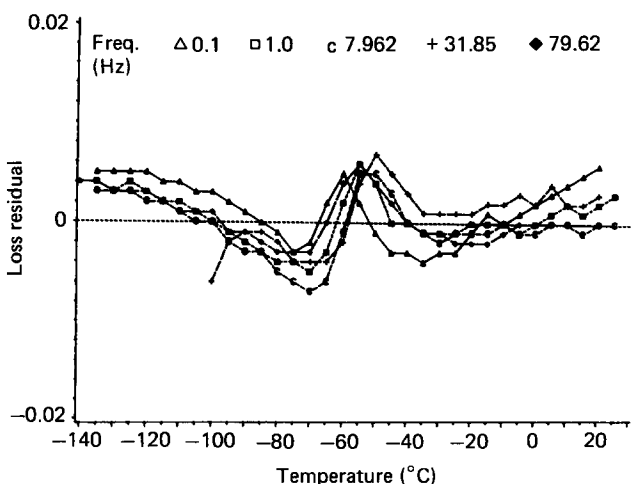


Figure 7 The loss compliance for the final trial of composition B plotted against temperature for each of the frequencies of measurement. The vertical axis was chosen to represent the mean loss compliance of the range that was studied

β parameters, or including a square term in the temperature dependence of J_0 or J_∞ or the relaxation time τ_0 . The variation of J_0 or J_∞ along with their 95% confidence limits with temperature is given in Figure 8 for composition B; composition C is not included because it is similar to composition B. Included in that figure are the predicted values for composition A. A plot of $J_0 - J_\infty$ with temperature is given in Figure 9 along with the predicted value for composition A; composition C is not included because it is similar to composition B. The 95% confidence limits for the relaxation time are given in Figure 5. A complex plane plot of the treated data is given in Figure 10 and for the fitted data in Figure 11.

Table 3 Summary of the parameters of equation (1) for the compositions in Table 1

Parameter	Sample A	Sample B	Sample C
J_0	0.672	0.926	0.898
Std. dev.	0.005	0.013	0.012
$J_0(T)$	0.0009	0.0009	0.0009
Std. dev.	0.0001	0.0002	0.0002
J_∞	0.324	0.399	0.354
Std. dev.	0.019	0.020	0.021
$J_\infty(T)$	-0.0009	-0.0008	-0.0011
Std. dev.	0.0002	0.0002	0.0002
$\ln f_0$	-1.69	-2.39	-3.83
Std. dev.	0.33	0.79	0.64
$\ln f_0(T)$	-7.41	-11.76	-11.22
Std. dev.	0.32	0.54	0.51
α	0.18	0.21	0.24
Std. dev.	0.02	0.01	0.01
β	0.18	0.44	0.31
Std. dev.	0.02	0.06	0.03
Reference temperature (°C)	-50	-50	-50

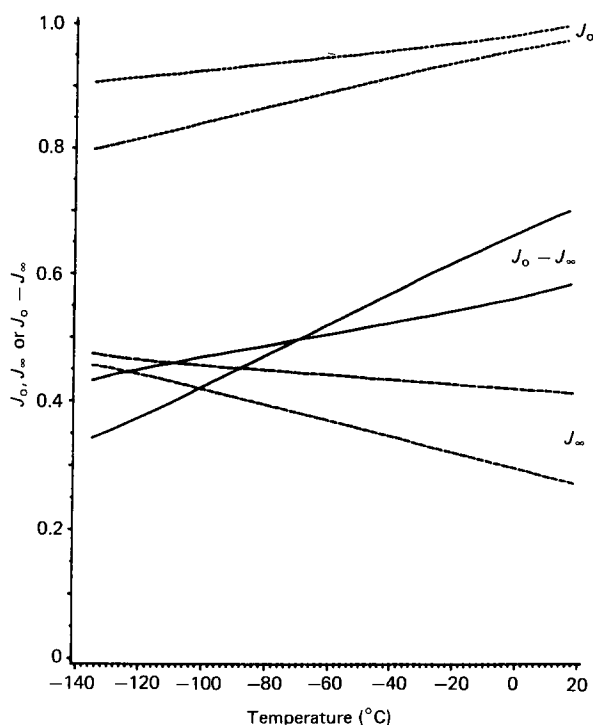


Figure 8 J_0 , J_∞ and their difference plotted against temperature for composition B

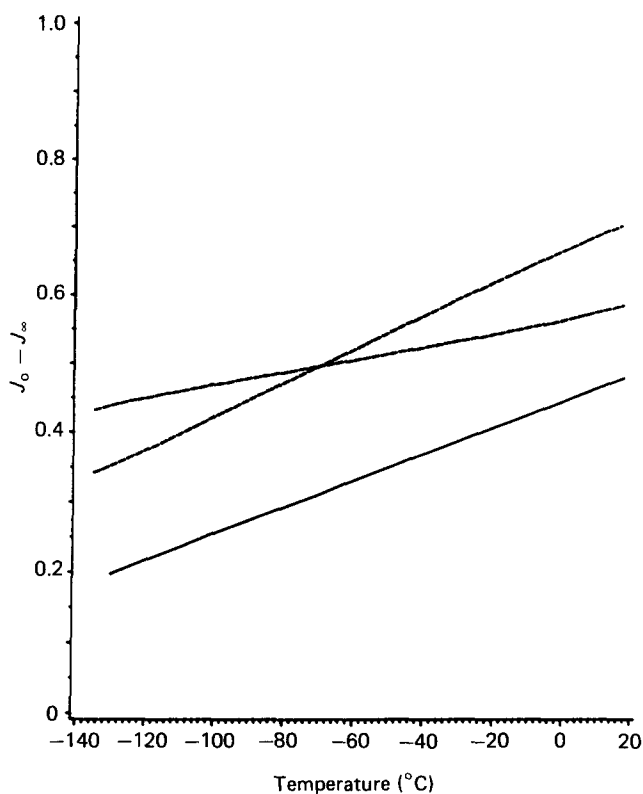


Figure 9 The difference $J_0 - J_\infty$ for modified (broken lines) and unmodified PVC (full line) plotted against temperature. The two broken lines represent upper and lower limits as defined in the text for composition B

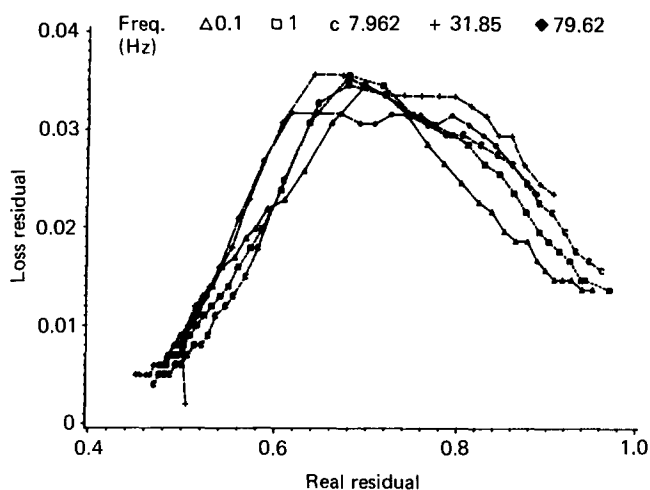


Figure 10 A complex plane plot of the experimental data after treatment to reduce the residuals for composition B

DISCUSSION

In previous work⁹, the advantages of interfacing a viscoelastic device with a mainframe computer was described; we referred to this interface as 'POLYREOM'. In this discussion we wish to re-emphasize the importance of such an interface. First, the original error bands were determined by replication studies on three different and unrelated polymers to those in the present study. In the present case, PVC and MBS-modified PVC, the error bands reported by SAS were found to represent adequately the experimental variance for these materials. For this reason, we continue to believe that we have

developed a reasonable estimate of variance for our particular set of conditions, i.e. strain, frequency, specimen geometry, instrument, operator, etc. Secondly, the original set of data obtained in a graphical form and reproduced in *Figure 11* is inadequate for any kind of meaningful analysis. The differences are small, nearly the size of the pen line, and are readily overlooked or ignored. However, we found these differences to be amenable to analysis provided care is taken to keep track of experimental error. This observation suggests that the graphics available with the instrument is inferior to the instrument, which is capable of much greater precision than implied by the charts. The viscoelastic parameters of PVC and the MBS modifiers must be quite similar because evidence for their presence is meagre. The evidence consists of a slight peak in the loss tangent or loss modulus curves at -65°C as shown in *Figure 11*, or the behaviour of the real and imaginary residuals as shown in *Figures 6* and *7*. This behaviour suggests that modification enhances the existing PVC beta process through impedance matching of modifier and PVC. In other words, modification enhances deformations that are already present and does not introduce any new ones. The parameters J_∞ for modified and unmodified PVC are quite similar. This result suggests that there is no change in the instantaneous response to the system. The instantaneous response of the system is probably due to the deformations of the valence bond angles so that it is a purely elastic response. The parameter J_0 has increased considerably so that their difference, i.e. $J_0 - J_\infty$, has nearly doubled over most of the temperature range. This difference represents the magnitude of the beta process, which is a dissipative process. The beta process is the one thought to describe the tensile yield behaviour at high strain rates and low temperatures. Increasing the magnitude of the beta process should enhance the energy dissipation of the blend. The relaxation time at room temperature is nearly two decades shorter for modified PVC, suggesting a much faster mechanism process. In addition the activation energy for the beta process has been increased. It is not clear what this change does to the yield behaviour, since the frequency factor has also been changed. In addition to the changes cited above, the β parameters have increased from 0.2 to 0.31–0.43 without

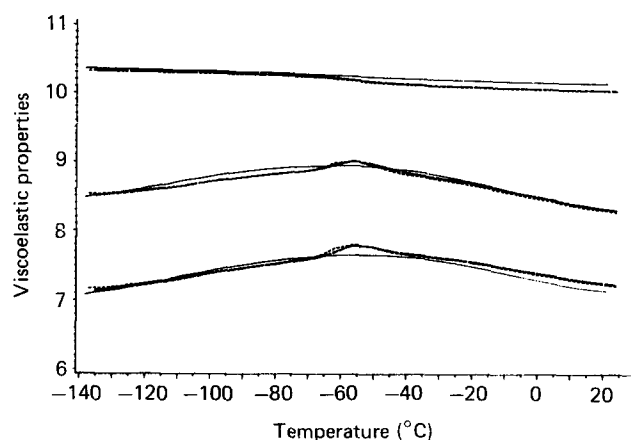


Figure 11 A plot of the original viscoelastic parameters against temperature at 1 Hz. The magnitude of the scale is similar to the original graphical data. All three compositions are represented here (—, PVC; ----, comp. A; - · - ·, comp. B)

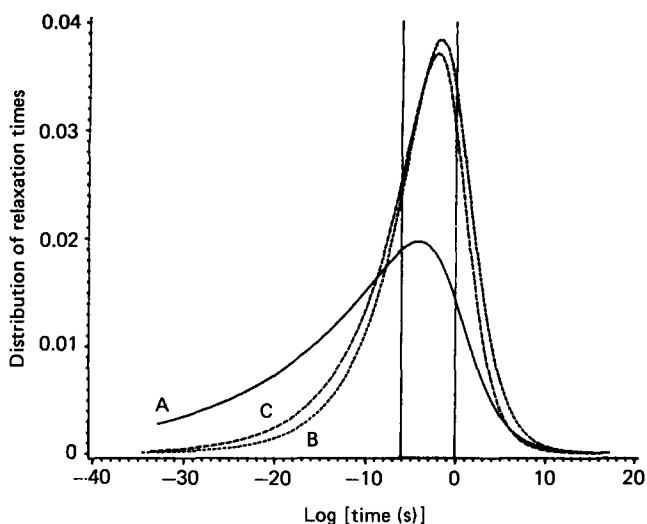


Figure 12 The distribution of relaxation times plotted against time at room temperature. The two vertical lines represent the approximate time region where impact processes are expected to take place

any apparent change in the α parameter. The α and β parameters are formally related to the distribution of relaxation times³ and given by:

$$F(y) = (1/\pi) y^{(1-\alpha)} \sin \beta \theta [y^{2(1-\alpha)} + 2y^{(1-\alpha)} \cos \pi(1-\alpha) + 1]^{-\beta/2} \quad (2)$$

$$\theta = \arctan \left(\frac{\sin \pi(1-\alpha)}{y^{(1-\alpha)} + \cos \pi(1-\alpha)} \right)$$

where $y = (\tau/\tau_0)$ and τ is time in seconds. Substitution of the α , β and τ_0 parameters for room-temperature

conditions leads to the results shown in Figure 12. The two vertical lines represent the range of 1 to 10^{-6} s, which is the range where most impact processes take place. The results shown in Figure 12 suggest that another effect of modification is to decrease the width of the distribution function in such a way as to increase the density in the timescale where impact processes are thought to take place. In other words not only has the magnitude of the beta process been increased, and its response time shortened, but the distribution of relaxation times in the impact region has been enhanced.

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REFERENCES

- 1 Bauwens-Crowet, C., Bauwens, J. C. and Homes, G. *J. Polym. Sci. (A-2)* 1969, 7, 735
- 2 Havriliak, S. and Shortridge, T. J. *Polymer* in press
- 3 Havriliak, S. Jr and Negami, S. *Polymer* 1967, 8, 161
- 4 Watts, D. and Havriliak, S. Jr, 'Design Data and Analysis' by some friends of Cuthbert Daniel (Ed. C. Mallows), Wiley, New York, 1986
- 5 Havriliak, S. Jr and Watts, D. *Polymer* 1986, 27 (10), 1509
- 6 Cole, R. H. *J. Chem. Phys.* 1965, 42 (2), 637
- 7 Mansfield, M. L. *J. Polym. Sci., Polym. Phys. Edn.* 1983, 21 (5), 787
- 8 Havriliak, S. Jr and Shortridge, T. J. Spring 1987 SPE Meeting of the SPE, Los Angeles
- 9 Havriliak, S. Jr, 'Computer Applications in the Polymer Laboratory', (Ed. T. Provder), ACS Symp. Ser., American Chemical Society, Washington DC, 1986
- 10 Ferry, J. D. 'Viscoelastic Properties of Polymers', 3rd Edn, Wiley, New York