Effect of a methylmethacrylate–ethylacrylate copolymer on the dynamics of the viscoelastic beta process in poly(vinyl chloride)

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Viscoelastic properties of blends of poly(vinyl chloride) (PVC) with a methylmethacrylate–ethylacrylate copolymer (CP) at various levels (0 to 25 wt%) were determined over a frequency range of 0.1 to 500 rad s^{-1} and a temperature range of -140 to $20°C$. This experimental range is sufficient to characterize the dynamics of the viscoelastic beta process in PVC in terms of a five parameter relaxation function proposed by Havriliak and Shortridge[1]. The parameters of the relaxation function and their dependence on temperature were determined by the multi-response statistical techniques developed by Havriliak and Watts[13,14]. The parameters are then represented in terms of CP concentration in PVC. The dependence of the parameters on concentration is discussed in terms of the general relaxation mechanism of Mansfield[17], the more specific ring flip process of Perchank[16] in polycarbonate, or the segment-flip model in PVC.

INTRODUCTION

This work is another in a series of papers[1,2] pursuing the observation that the beta process, observed in the glassy phase of polymers, determines their tensile yield properties at high strain rates or low temperatures. This correlation is based on the work of Roetling[3–5], Bauwens-Crowet et al.[6], as well as Havriliak and Shortridge[7] who observed that the activation energies obtained from viscoelastic measurements were similar to those obtained from an extension of the tensile yield model originally proposed by Ree and Eyring[8]. Ree and Eyring treated tensile yield as segments jumping over energy barriers, similar to their model for viscous flow because there was evidence to suggest that strain increased at constant yield stress. Roetling[3–5], as well as Bauwens-Crowet et al.[6] extended the Ree-Eyring[8] model by assuming two independent processes, i.e. an alpha (slow) and beta (fast) to represent the tensile yield data as a function of strain rate and temperature.

Earlier work was directed at examining neat polymers such as poly(vinyl chloride) (PVC)[1,7] with differing molecular weight, polycarbonate (PC), or impact modifiers blended with PVC[9,10]. The modifiers studied were typical methylmethacrylate–butadiene–styrene (MBS) core–shell modifiers. In these blends, modifiers were found to enhance the viscoelastic beta process already present in PVC. Specifically, the magnitude of the relaxation process is bigger, i.e. $J_0 - J_\infty$ is larger, the relaxation time is shorter, and, finally the distribution of relaxation time parameters α and β change in a way that concentrates the relaxation process in the impact time scale at room temperature. In the present study we examine the effects of a methylmethacrylate–ethylacrylate copolymer (CP) on the segmental dynamics of the viscoelastic beta process in PVC. This copolymer was chosen because there is some evidence to suggest that it is miscible, at least in the range that is used, with PVC[11].

For example, the blends are clear even though the refractive indices are sufficiently different to cause hazing. The viscoelastic alpha peak of PVC measured at 1 Hz increases systematically with increasing CP level. Finally, d.s.c. curves confirm the viscoelastic observations.

METHODS

Materials and test specimens

The CP used in this study was prepared by emulsion polymerization of methylmethacrylate (MMA) and ethylacrylate (EA) monomers in a weight ratio of MMA/EA = 90/10. The CP has a weight average molecular weight of $1.8 \pm 0.2 \times 10^6$ and a number average molecular weight of $0.5 \pm 0.1 \times 10^6$. The CP was isolated by spray drying and used without any further purification. Powder blends were prepared from the materials by dry mixing. The PVC used in this study is Geon 110×377 (manufactured by BF Goodrich Co., Cleveland, Ohio 44131, USA) with an approximate weight average of 56 000 (i.e. $K = 49$). All powder mixes contain an organotin stabilizer (Thermolite 66, manufactured by M&T Chemicals Inc. Rahway, NJ 07065, USA) at a level of 2%. The copolymer percentage is expressed in terms of wt% of PVC plus stabilizer. The ingredients were mixed in a high intensity mixer, milled at 165°C for 2 min after fluxing and finally compression moulded, first at 150°C for 2 min and then cooled to 50°C over 5 min.

Viscoelastic measurements

All the viscoelastic measurements were carried out in the Rheometrics Dynamic Spectrometer RDS-770 at a frequency of 0.1, 6.28, and 500 rad s^{-1}, i.e., the lower and upper frequency limits as well as their mid-point. The strain was 0.1% and the temperature range was -140 to $20°C$. The measurements were made in the temperature sweep mode, at increments of 5°C. The measuring scheme

was to make measurements at $6.28\,\text{rad}\,\text{s}^{-1}$ 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 and its dimensions were determined once again. Then it was replaced in the fixture and rerun at $0.1\,\text{rad}\,\text{s}^{-1}$ in the temperature sweep mode starting at $-140°C$. This technique was extended to $500\,\text{rad}\,\text{s}^{-1}$ and finally to $6.28\,\text{rad}\,\text{s}^{-1}$. Although this procedure appears to be tedious and cumbersome, this method of replication provided us with important statistical information about the experimental technique. Such statistical information is important because the beta process in PVC is not very large relative to the experimental error associated with the viscoelastic measurements.

Numerical methods

Viscoelastic data were sent to the main frame (IBM Model 3090) and assembled into a SAS data set (SAS Institute, SAS Circle, Box 8000, Cary, North Carolina, 27511, USA). All regression analyses were done in SAS. It is important to note that, except where indicated, the complex compliance was reduced by 10^5 and has SI units of $cm^2\,N^{-1}$.

Havriliak and Shortridge[9] proposed equation (1) to represent the complex compliance, $J^*(\omega)$, as a function of radian frequency $\omega = 2\pi f$ where f is in Hz, at constant temperature.

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

In this expression, $J^*(\omega)=J'(\omega)+iJ''(\omega)$ is the complex compliance, $J'(\omega)$ is the real or storage part of the complex compliance while $J''(\omega)$ is the imaginary or loss part of the complex compliance, and $i=(-1)^{1/2}$. The usual method of determining these parameters is to construct a complex plane plot at a single temperature, determine the parameters of equation (1) graphically, and then repeat the analysis for other temperatures. In this way, a temperature dependence of the five parameters can be determined.

Havriliak and Watts[12,13] have developed a much more powerful statistical technique for analysing complex data when these depend on temperature and frequency in a fashion than can be represented by equation (1). In this method, which is based on multi-response statistical methods, the variation of the complex compliance with frequency and temperature is pooled to form a single data set. The complex compliance is assumed to be given by equation (1) and the temperature dependence of the five parameters is assumed to be given by equations (2)–(6).

$$J_0 = I_1 + C_1(T-T_0) \qquad (2)$$

$$J_\infty = I_2 + C_2(T-T_0) \qquad (3)$$

$$\log_e(f_0)=I_3+C_3(RK-RK_0) \qquad (4)$$

$$\alpha = I_4 + C_4(T-T_0) \qquad (5)$$

$$\beta = I_5 + C_5(T-T_0) \qquad (6)$$

In these expressions, T is in $°C$, T_0 is a reference temperature, chosen to centre the experimental data at $T-T_0=0$, $RK=1000/(273+T)$, $RK_0=1000/(273+T_0)$ and finally, $\tau_0=1/f_0$, or $\log_e(\tau_0)=-\log_e(f_0)$. These equations, except for equation (4), assume a linear

dependence of the parameter on temperature, while equation (4) is essentially an Arrhenius plot of the relaxation time. The statistical techniques used to evaluate the parameters, derivatives of equation (1) and other important numerical techniques are described in references 12 and 13. In this way it is not necessary to have a complete frequency range to define the parameters at a single temperature.

RESULTS

Preliminary results

The frequency dependence of the real and imaginary parts of the complex compliance in the beta process region of PVC for all 7 compositions at $6.28\,\text{rad}\,\text{s}^{-1}$, is given in *Figures 1* and *2*, respectively. In this experimental region there is an overlapping of the high temperature region of the beta process in PVC with the low temperature region of the beta process in the CP. To proceed further it is necessary to delete the effects of the copolymer from the viscoelastic properties of the blend. If we assume that the complex compliances are additive and in direct proportion to their concentration, we have at any temperature T and frequency ω

$$J^*(\omega)=(1-c)J^*_{PVC}(\omega)+cJ^*_{CP}(\omega) \qquad (7)$$

In this expression $J^*_{PVC}(\omega)$ is the PVC contribution, while $J^*_{CP}(\omega)$ is the CP contribution to the total complex compliance, c is the concentration of CP, and $1-c$ the concentration of PVC. Rearranging equation (7) leads to equation (8).

$$(1-c)J^*_{PVC}(\omega)=J^*(\omega)-cJ^*_{CP}(\omega) \qquad (8)$$
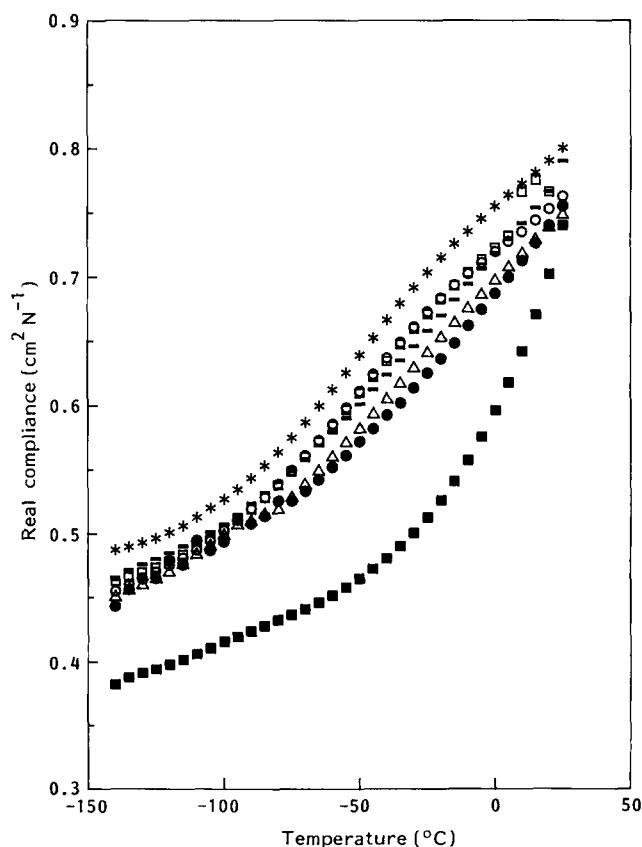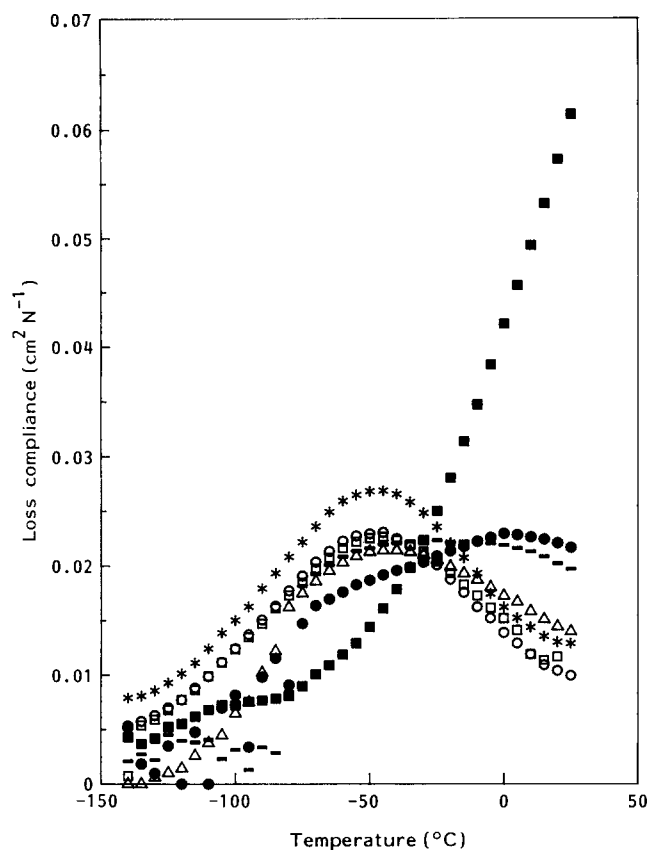

Figure 1 The real part of the complex compliance, at $6.28\,\text{rad}\,\text{s}^{-1}$ and reduced by 10^5, is plotted against temperature for the seven materials. $*$, 0 wt%; ○, 2 wt%; □, 5 wt%; △, 10 wt%; —, 15 wt%; ●, 25 wt%; ■, 100 wt%
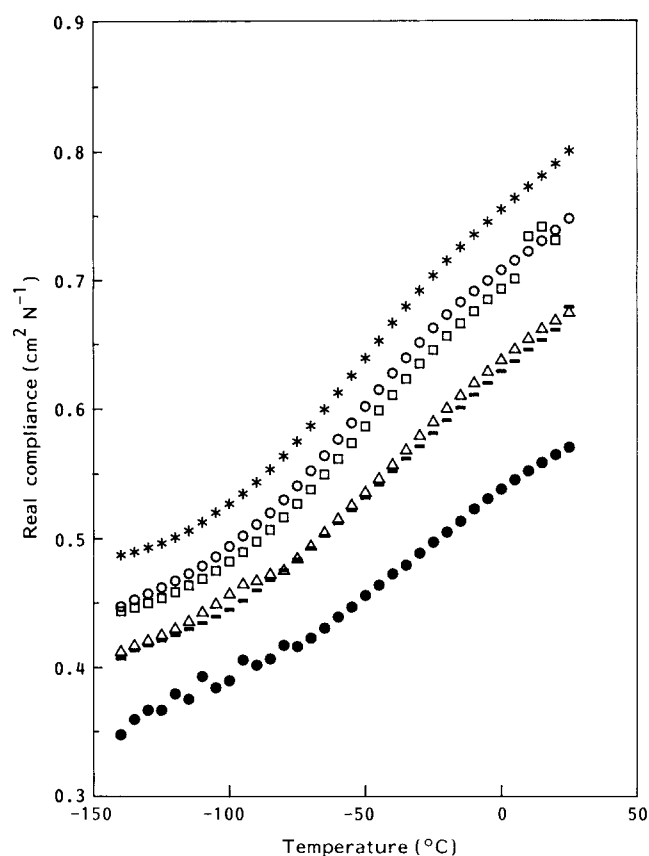
Figure 2 The imaginary part of the complex compliance, at 6.28 rad s^{-1} and reduced by 10^5, is plotted against temperature for the seven materials. $*$, 0 wt%; ○, 2 wt%; □, 5 wt%; △, 10 wt%; —, 15 wt%; ●, 25 wt%; ■, 100 wt%
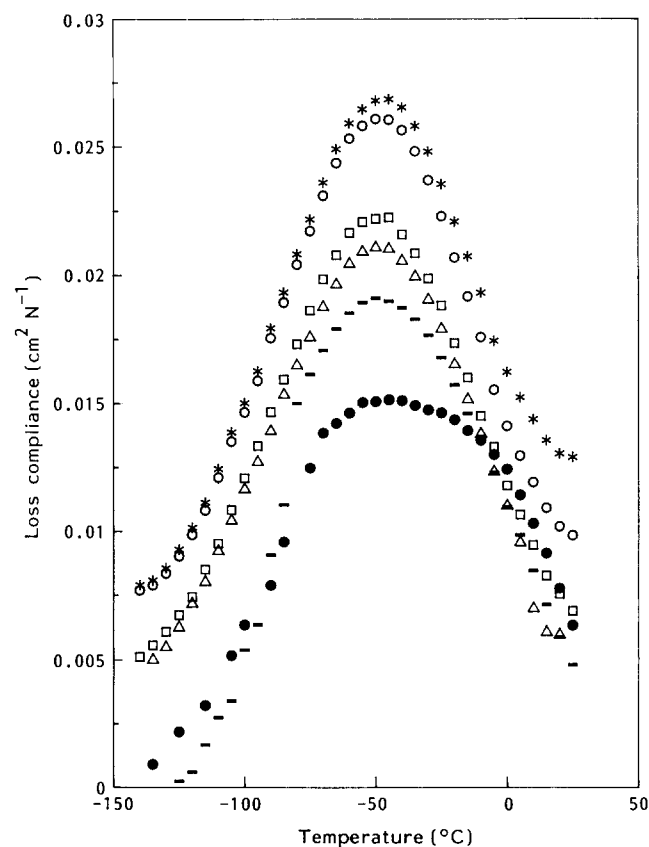

Figure 3 The real part of the complex compliance, at 6.28 rad s^{-1}, reduced by 10^5 and corrected for the contribution of CP, is plotted against temperature for six of the materials. $*$, 0 wt%; ○, 2 wt%; □, 5 wt%; △, 10 wt%; —, 15 wt%; ●, 25 wt%

Plots of the real and imaginary compliances for $(1-c)J^*_{PVC}(\omega)$ with temperature at 6.28 rad s^{-1} for the six compositions are given in *Figures 3* and *4*. Complex plane plots are given in *Figures 5* and *6*, respectively, of $(1-c)J^*_{PVC}(\omega)$ and $J^*_{PVC}(\omega)$ for the five blends and neat PVC. *Figure 6* demonstrates that the locus of $J^*_{PVC}(\omega)$ in the complex plane depends on copolymer level and cannot be accounted for by concentration of CP alone.

Results of the regression

The viscoelastic data, i.e. $(1-c)J^*_{PVC}(\omega)$, were regressed using the techniques already cited. Small additions (subtractions) were made to the data to improve the quality of the fit. These corrections are first given in *Table 1* as absolute changes, then summarized in percent change relative to the mean of the real or imaginary compliances. Except for the 500 rad s^{-1} data, the changes are small in percentage terms and suggest strongly that these are random in nature. The corrections for the 500 rad s^{-1} data are much larger, though about the same as the reproducibility of the measurements. A summary of the statistical results of the regression is given in *Table 2*, while the parameters of equation (1) and their dependence on temperature assumed in equations (2)–(6) are given in *Table 3*. The real and imaginary residuals at 6.28 rad s^{-1} (first run) are plotted against temperature in *Figures 7* and *8* respectively, for each of the compositions. The upper and lower dashed lines in *Figures 7* and *8*, represent the 95% confidence limits from an extensive replication study[13], estimated from the mean of the real and imaginary parts of the compliance.

Figure 4 The imaginary part of the complex compliance, at 6.28 rad s^{-1}, reduced by 10^5 and corrected for the contribution of CP, is plotted against temperature for the polymer blends. $*$, 0 wt%; ○, 2 wt%; □, 5 wt%; △, 10 wt%; —, 15 wt%; ●, 25 wt%
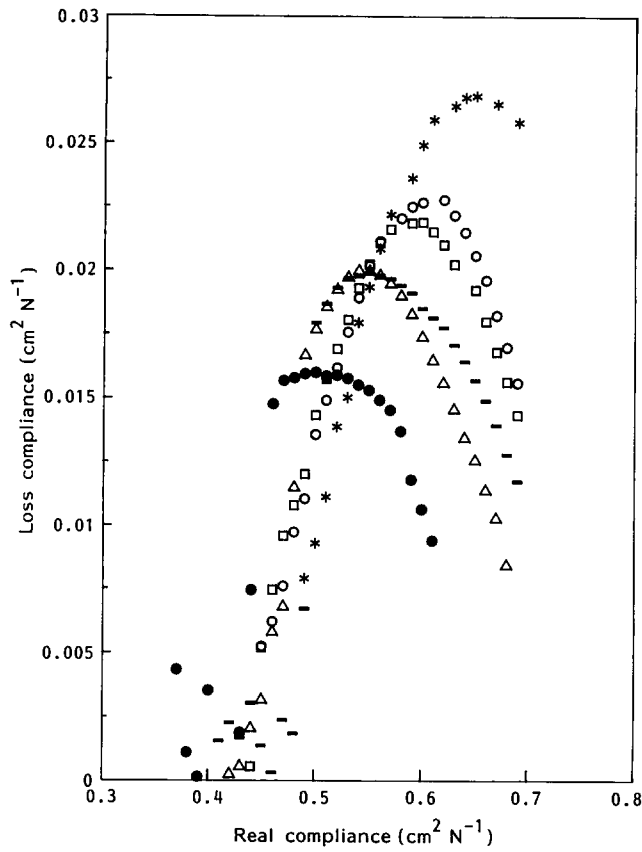
Figure 5 Complex plane plot of the corrected data in *Figures 3* and *4* for the six materials. ✳, 0 wt%; ○, 2 wt%; □, 5 wt%; △, 10 wt%; —, 15 wt%; ●, 25 wt%

Figure 7 Plot of the real residuals with temperature for the six materials. ✳, 0 wt%; ○, 2 wt%; □, 5 wt%; △, 10 wt%; —, 15 wt%; ●, 25 wt%

Figure 6 Complex plane plot of the corrected and scaled data in *Figures 3* and *4* for the six materials. ✳, 0 wt%; ○, 2 wt%; □, 5 wt%; △, 10 wt%; —, 15 wt%; ●, 25 wt%
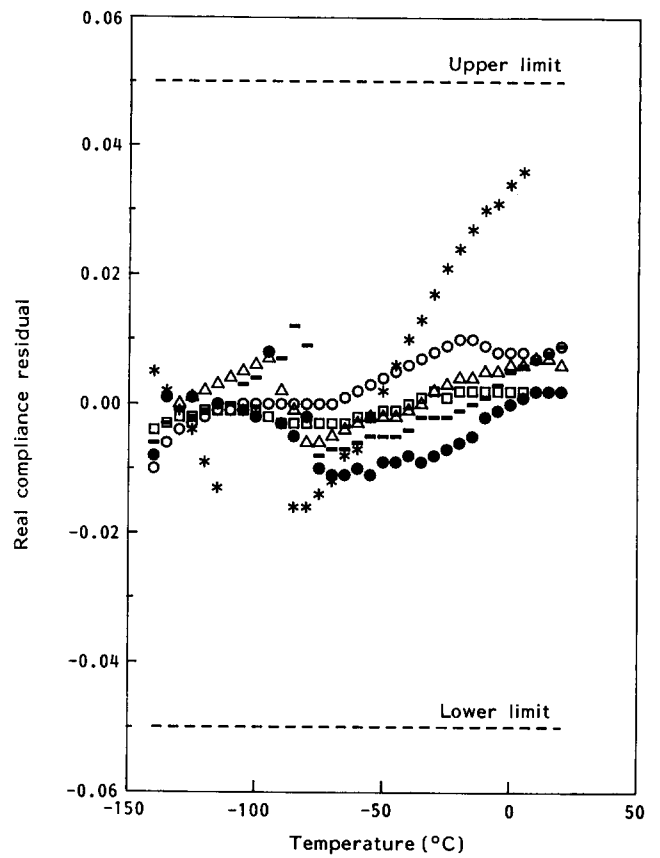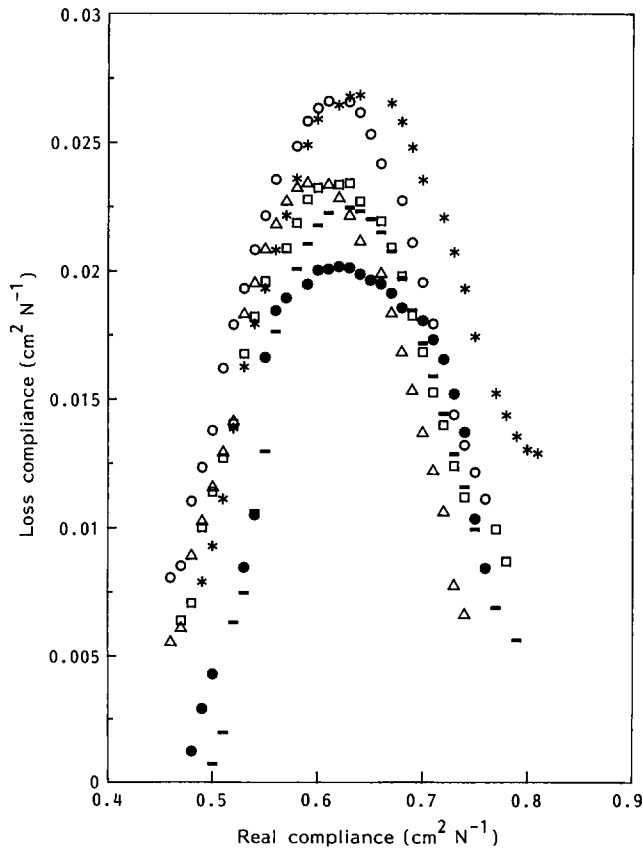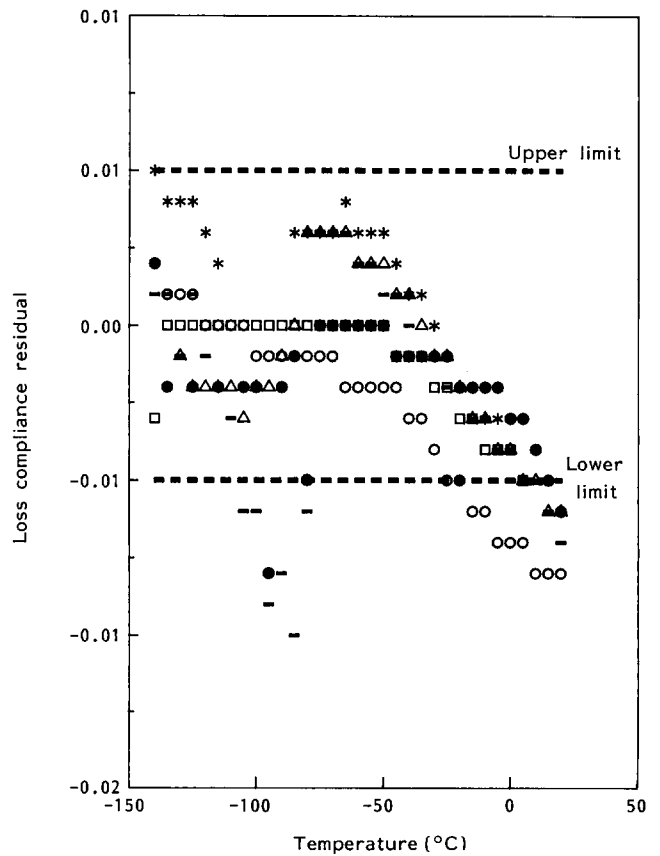

Figure 8 Plot of the imaginary residuals with temperature for the six materials. ✳, 0 wt%; ○, 2 wt%; □, 5 wt%; △, 10 wt%; —, 15 wt%; ●, 25 wt%

Table 1 Summary of the corrections made to the complex compliance in order to improve the quality of the fit

Frequency rad s⁻¹	0wt% CP	2wt% CP	5wt% CP	10wt% CP	15wt% CP	25wt% CP	Sum[a]	%
6.28								
R	−0.012	0.004	0	−0.01	−0.01	0.012	−0.003	−0.6%
I	0	−0.002	0	−0.004	−0.004	0	−0.002	−12%
0.1								
R	0.008	0	0	0	0	0	0.001	0.2%
I	0.01	0	0	0	0	0	0.001	6%
500								
R	−0.055	−0.035	−0.055	−0.065	−0.085	−0.036	−0.055	−10%
I	0.014	−0.003	−0.003	−0.003	−0.003	0	0.001	6%
R−6.28								
R	−0.006	0.01	0	−0.012	−0.002	0	−0.001	−0.2%
I	0.003	−0.006	0	−0.0035	−0.0035	0	−0.001	−6%

[a] Sum is defined as the sum of columns 2 through 6 while % is the ratio of the sum to the mean compliance in the data set × 100

Table 2 Summary of the statistical quantities for representing the temperature and frequency dependence of the complex compliance of the polycarbonate of PVC/copolymer blends in terms of equation (1)

Parameter	0wt% CP	2wt% CP	5wt% CP	10wt% CP	15wt% CP	25wt% CP
s.d.	1.1	7.6	0.9	0.5	0.3	0.3
CV						
R, %	2.2	0.8	0.8	0.7	1.0	1.7
I, %	17	20	15	18	21	18
DF	92	106	120	118	124	116

Table 3 Equation (1) parameters and their confidence limits for representing the viscoelastic beta process of the PVC/copolymer blends

Equations (2)–(6) parameter	0wt% CP	2wt% CP	5wt% CP	10wt% CP	15wt% CP	25wt% CP
I_1	0.77	0.73	0.72	0.68	0.75	0.55
s.d.	0.01	0.01	0.01	0.01	0.02	0.02
C_1	0.005	0.0007	0.0008	0.0008	0.0006	0.0007
s.d.	0.0001	0.0001	0.0001	0.0001	0.0001	0.0003
I_2	0.44	0.37	0.30	0.35	0.33	0.33
s.d.	0.03	0.02	0.02	0.01	0.02	0.01
C_2	−0.0008	−0.0007	−0.0012	−0.0006	−0.0009	−
s.d.	0.0002	0.0001	0.0002	0.0001	0.0002	−
I_3	−2.7	−1.56	−2.77	−2.97	−4.87	−1.76
s.d.	0.38	0.44	0.43	0.4	0.9	1.2
C_3	−6.4	−6.6	−7.5	−6.0	−6.5	−6.0
s.d.	0.4	0.2	0.4	0.02	0.5	0.9
I_4	0.56	0.26	0.27	0.29	0.21	0.22
s.d.	0.04	0.01	0.02	0.01	0.02	0.04
C_4	−	−	−	−	−	−
s.d.	−	−	−	−	−	−
I_5	0.16	0.37	0.23	0.29	0.34	0.52
s.d.	0.03	0.04	0.03	0.03	0.07	0.13
C_5	−	−	−	−	−	−
s.d.	−	−	−	−	−	−
Reference temperature, °C	−50	−50	−50	−50	−50	−50

The next step in the analysis is to represent the coefficients in equations (2)–(6) in terms of the concentration, c, of CP. For the present purpose we assume a linear representation, that takes the form for I_1

$$I_1 = I_{10} + m_1 c \qquad (9)$$

with similar forms for the other coefficients in equations (2)–(6). The results of this regression are listed in *Table 4*. Included in that table are the parameters of equation (9), as well as statistical information describing the fit. Pooled s.d. represents the average parameter standard deviation.

Table 4 Dependence of equations (1) and (2)–(6) parameters on copolymer level as stated by equation (9)

Parameter	I_{10}	s.d.	Pooled s.d.	M_1	s.d.	R square
I_1	0.75	0.05	0.01	−0.6	0.2	0.6
I_2	0.38	0.05	0.02	−0.3	0.2	0.4
I_1-I_2	0.38	0.04	−	−0.34	0.21	0.4
I_3	−2.3	0.9	0.8	−9.0	4.5	0.3
C_3	−6.6	0.6	0.5	−1.5	2.9	0.07
I_4	0.34	0.06	0.03	−0.6	0.3	0.5
I_5	0.22	0.07	0.07	0.8	0.4	0.6

DISCUSSION

Perhaps the most important result of this work is that shown in *Figure 6*, which shows the beta relaxation process to be disappearing faster than can be accounted for by concentration of CP alone. There is a systematic decrease in the height of the complex plane plot even though this process is small, particularly when compared to experimental error. It is unlikely that any errors in the complex compliance of CP, used to account for the contribution of CP, could account for these changes because the concentration of copolymer and the magnitude of the tail is small except at higher temperatures. The higher temperatures, i.e. those above 0°C were deleted anyway because of the overlapping PVC alpha process noted in other work[1].

Table 4 summarizes the influence of CP on the beta process in PVC at the reference temperature of $-50°C$. The parameter $I_1 - I_2$, represents the magnitude of the beta process which was found to approach zero as the concentration of CP approaches unity, well within experimental error. In addition, $J_\infty \to 0$ as the concentration of the copolymer approaches unity. The slope of the rate process is essentially independent of CP concentration, as indicated by its R square $= 0.07$, as well as the magnitude and uncertainty of its dependence on concentration.

The other three parameters depend on CP level. The relaxation frequency is strongly dependent on CP concentration and as $CP \to 1$, τ_0 becomes three orders of magnitude slower. As the concentration of $CP \to 1$, $\alpha \to 0$ and $\beta \to 1$ or perhaps larger. This suggests that the process is broadening significantly and at the same time becoming more symmetrical.

Earlier discussions[1] have interpreted the beta process in PVC to be a twisting motion of a chain segment about its long axis, i.e. segment flipping. The dynamics of the beta process in PVC and PC, as defined by equations (1)–(6), were found to be similar. One of the differences between the two sets of parameters is that the relaxation frequency of PC, at the reference temperature of $-50°C$, is about three orders of magnitude faster. The beta process in PC has been interpreted as ring-flips, i.e. rotation of the phenyl groups about their C_1-C_4 bonds. The calculations of Perchank *et al.*[15] show that a stiff lattice inhibits the ring-flipping process in PC. In this work we have shown experimentally that introduction of a stiff polymer chain into the PVC matrix not only reduces the magnitude of the beta process in terms of dilution but also affects the dynamics of the process in

such a way that can be interpreted as inhibition. Though the activation energy is independent of CP level, the parameters α and β change in such a way that their correlation with their environment has been increased. In addition, there is a significant slowing down of the beta relaxation process at the reference temperature. This observation suggests significant changes in the entropy of activation (related to the pre-exponential term in the rate plot) rather than changes in the activation energy.

CONCLUSIONS

One of the advantages of the numerical techniques described in this work is that a detailed analysis can be made on the influence of additives to the beta relaxation processes of polymers such as PVC. The beta process in PVC is small, and experimental errors are significant so that there is a fair amount of uncertainty in these parameters. On the other hand, Mansfield[16] and Perchank *et al.*[15] have provided theoretical insights into the nature of the beta process that provide us with an unprecedented view of polymer dynamics in the glass phase. The results of this work have shown that not only is there a dilution effect in proportion to concentration but there is an interaction effect that prevents the beta process from flipping as readily in a PVC/CP matrix as it can in a neat PVC matrix.

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