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The dielectric properties of a commercial polyvinylchloride

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The dielectric response of a commercial polyvinylchloride is examined in terms of the cluster model of dielectric relaxation, and compared with a sample from which the plasticizer had been extracted. An interpretation of the approach to the glass transition in terms of scaling concepts is outlined and related to the hierarchical dynamics of the cluster model. In this picture the α dynamics goes over naturally to the β dynamics on small size scales. The plasticizer is shown to contribute a quasi-d.c. electrical transport above the glass transition, which at higher temperatures causes the formation of an electrode barrier layer.

1. Introduction

The dielectric properties of polyvinylchloride (PVC) have been investigated over a number of years, particularly in relation to the use of the material as a commercial insulator and general plastic. Fuoss [1] initially observed the presence of two distinct relaxation processes, which are now commonly recognized as the α and β relaxations occurring above and below the glass transition temperature, respectively. More recently Kisbényi [2] amongst others [3–5] has examined the effect of the plasticizer which is introduced into the polymer to improve the mechanical, ageing and electrical properties. Kisbényi observed that the introduction of a plasticizer generally decreased the glass transition temperature. He suggested that the role of the plasticizer was to decrease the interaction between the Cl–Cl dipoles in adjacent molecules, and to increase the mobility of the polymeric chains [6] so that the material converted to a rigid glassy state at lower temperatures. The technique used by Kisbényi [2] in his investigations was that of measuring the dispersion in the real part of the permittivity as a function of temperature at the single frequency of 30 Hz.

Adachi and Ishida [7] studied the PVC–tetrahydrofuran system and observed three distinguishable dispersion processes, the α, β' and γ. Following convention the α signature was given to the relaxation process dominant above the glass transition temperature and this, together with the process observed in the lowest temperature region investigated, the γ process, were considered to have their bases in segmental motions of the polymer chain and the motion of the plasticizer, respectively. The intermediate process of relaxation, β', was assigned to the local relaxation mode of the PVC–tetrahydrofuran complex. A second type of intermediate process, β, was observed for weak concentrations of the tetrahydrofuran plasticizer and also in PVC itself, and was considered to be due to secondary relaxation in the polymer. It was also observed that the magnitude of the β' and γ processes increased with increasing plasticizer concentration, which confirmed that these processes must be based on the tetrahydrofuran or the interaction of the tetrahydrofuran with the polymer.

The highly polar nature of the C–Cl bond in PVC suggests that the permittivity of the material, and the dispersion associated with the individual relaxation processes, should both be large. Experimentally this is not the case, although the magnitudes are larger than for non-polar polymers. Reddish [8] has suggested the existence of an anti-ferroelectric like structure

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in the polymer, which would result in the observed small magnitude of the response to an electric field. The material is, however, still useful to study, having measurable losses in an accessible frequency range. The present investigation examines a commercial plasticized PVC and characterizes the material over an extended frequency and temperature range. The plasticizer was then removed and the sample re-investigated to determine which of the original processes were dependent on the presence of the plasticizer. All the relaxation processes uncovered in these investigations have been characterized, and the plasticized and non-plasticized material is discussed in terms of the cluster model of dielectric relaxation [9].

As well as the processes observed by Adachi and Ishida [7] a fourth relaxation process has been determined in the plasticized sample. This is a high-temperature, low-frequency, quasi-conduction relaxation. On removing the plasticizer the process was replaced by a d.c. conduction of smaller magnitude.

2. Experimental details

The dielectric measurements were carried out using the Chelsea Frequency Response analyser [10] which allows examination over the frequency range from 10^{-4} to 10^4 Hz with a resolution of the order of 1 part in 10^4 in loss angle. The experimental data are reported in terms of complex capacitance, as the measurements of the dielectric properties are more accurate than the measurements of sample thickness and electrode areas. An extended temperature range, from 150 to 373 K, has been used and the results are reported in temperature-normalized form [11, 12]. The PVC sample was obtained from commercial insulating tape, as this was considered to be representative of general-duty commercial materials.

After the plasticized sample had been fully investigated the sample of tape was refluxed in diethyl ether for 18 h in order to remove all the plasticizer. It was checked that this distillation period was sufficient by weighing a test sample before and after refluxing for 6 and 12 h. No weight decrease was observed between these periods. The diethyl ether/plasticizer solution was fractionally distilled to recover the plasticizer, which was then examined by infra-red spectroscopy and identified as di-(2-ethylhexyl)phthalate [13] which is itself polar. It was found from this investigation that the commercial PVC contained about 15 wt % plasticizer.

For a number of the processes investigated the dielectric increment was small, so that although the loss component of the capacitance could be measured there was little dispersion in the real component. In these cases only the loss data will be presented. Similarly as the loss peaks are very broad and do not show dispersion on equal log/log scales, the capacitance log scale has been increased over that of the frequency log scale. It has been found elsewhere that unequal log scales can lead to difficulties when there is significant scatter in the experimental data, but the results reported here contained little scatter and no difficulties were encountered.

3. Analytical procedure

It has been shown experimentally [14] and analytically [9] that the response of a single dielectric relaxation process can be described in terms of the dielectric susceptibility as

$$\chi(\omega) = \chi(0)F(\omega/\omega_x) \qquad (1)$$

where $\chi(0)$ is the magnitude of the response, ie. the dielectric increment, ω is the frequency of measurement and ω_x is the characteristic frequency or relaxation rate of the process. In general both $\chi(0)$ and ω_x are sensitive to the external variables of the system, and usually the latter is particularly sensitive to temperature. Examination of Equation 1 shows that the results obtained over a range of frequencies at different temperatures can be reconstructed on log/log plots of susceptibility against frequency to give a single frequency- and magnitude-normalized master response. The changes in characteristic frequency and magnitude then appear as translations in the susceptibility and frequency axes, as they are multiplicative factors. This approach applies directly to the imaginary part of the complex capacitance and to the real part when allowance is made for the additional effect of the "infinite" frequency capacitance. The normalization technique of data presentation not only allows an effectively wider frequency window to be obtained, but reduces the individual experimental errors and makes theoretical plot fitting more accurate [11].

The nature of the relaxation process is contained in the spectral shape function $F(\omega/\omega_x)$

defined in Equation 1. Using the cooperative cluster model of relaxation, two of the present authors have described both the loss peak behaviour [9] and the quasi-d.c. or anomalous low-frequency dispersion relaxation [15] first observed by Jonscher [16]. For the loss-peak case

$$F(z) = F_0(1 + \mathrm{i}z)^{n-1} \times {}_2F_1\left(1 - n, 1 - m; 2 - n; \frac{1}{1 + \mathrm{i}z}\right) \quad (2)$$

where z is the reduced frequency (ω/ω_p) with ω_p the characteristic frequency for the loss peak and m, n ($0 < n$; $m < 1$) are correlation indices describing, respectively, the inter-cluster exchange fluctuations and the intra-cluster excitations. Under low-frequency dispersion conditions

$$F(z) = F_0(1 + \mathrm{i}z)^{n-1} \times {}_2F_1\left(1 - n, 1 + p; 2 - n; \frac{1}{1 + \mathrm{i}z}\right) \quad (3)$$

where p ($0 < p < 1$) is the correlation index of the inter-cluster charged particle transport and the reduced frequency z is now normalized in terms of ω_c, the characteristic frequency of the dispersion. In Equations 2 and 3 ${}_2F_1(, ; ;)$ is the Gaussian hypergeometric function and F_0 is a normalization parameter such that $F(0)$ is unity [9, 15].

Examination of Equations 2 and 3 shows that any relaxation process can be characterized by the four parameters $\chi(0)$, ω_x, n and either m or p. The significance of the magnitude of these parameters will be discussed later. Their importance here is that in the reporting of the experimental data these are the only parameters that are of significance. It has been observed [17] that the correlation indices m and n are constant under varying temperature conditions in a physically stable phase of a material. This is of use in two ways. Firstly it aids the determination of regular phases in a multi-phase system, and secondly in well-defined phases only the single values of m and n require to be determined and reported.

4. Results

4.1. Plasticized PVC

Similar loss processes to the three reported by Adachi and Ishida [7] in PVC–tetrahydrofuran were observed in the PVC–di-(2-ethyl-hexyl)-phthalate system investigated here. These have been termed the α, β and γ following convention. A fourth relaxation process, however, has been identified and has been termed the A relaxation. Fig. 1 presents an Arrhenius plot of the characteristic frequencies of all four relaxations.

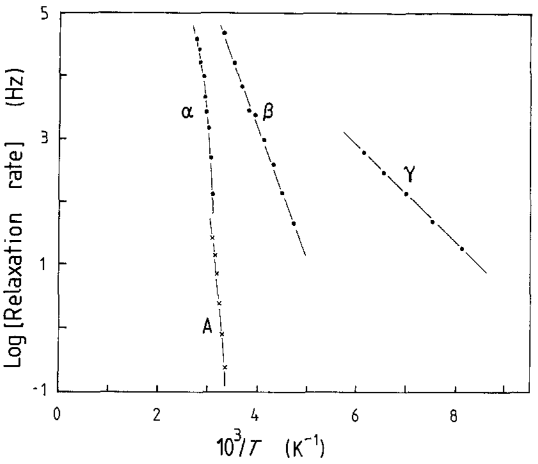

Figure 1 An Arrhenius plot of the relaxation rates for plasticized PVC. Standard nomenclature is used except for the process marked A which is a quasi-d.c. conductivity process.

4.1.1. The γ relaxation

Fig. 2 presents the frequency- and magnitude-normalized master spectral response function observed in the frequency range 3×10^{-3} to 10^4 Hz and over the temperature range 123 to 163 K. This loss process could not be characterized at frequencies much less than that of the maximum loss, as at the highest temperatures

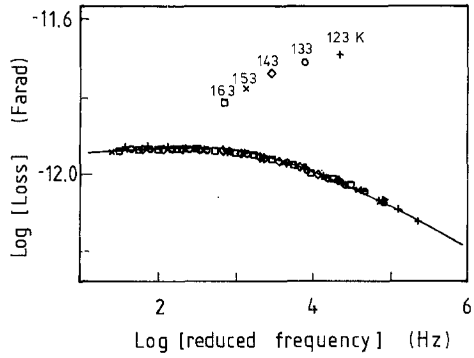

Figure 2 Spectral response of the γ process shown in Fig. 1. The plot has been normalized from data measured at the indicated temperatures. These temperature points give the inverse shifts required to construct the plot. The figure is scaled at 153 K, and the parameters used to obtain the theoretical continuous plot are given in Table I.

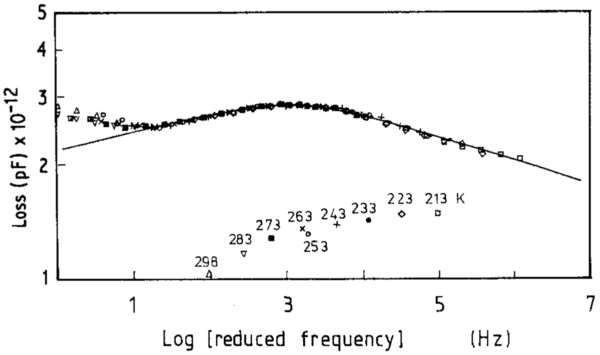

Figure 3 Spectral response of the β process in normalized form. The plot is scaled at 243 K.

the larger magnitude of the β relaxation masked the response. However, the data that could be obtained normalizes cleanly, even with the large log-scale ratio, and the temperature indicated points in the upper part of the diagram define the relative shift of the characteristic frequency and magnitude of the response [11]. The limited information available in the higher, normalized, frequency range indicates a gradient in this plot of about -0.1; hence $n_\gamma \simeq 0.9$, as the asymptotic high-frequency limit of Equations 2 and 3 is $\chi(\omega) \propto (\mathrm{i}\omega)^{n-1}$. It can be seen that the loss characteristic is very broad, with a poorly characterized peak value.

4.1.2. The β relaxation

The spectral response of the β relaxation, in normalized form, is shown in Fig. 3. In this case it has been possible to recover the complete shape with the limiting gradients at high and low normalized frequencies of -0.061 and 0.044, from which we have $n_\beta = 0.939$ and $m_\beta = 0.044$, since the asymptotic low-frequency limit of Equation 2 is $\chi''(\omega) \propto (\omega)^m$. Fig. 4 shows in detail the Arrhenius plots for both the relaxation rates and the magnitudes of response for both the γ and β relaxations. In both cases the relaxation rates are activated, with activation energies of 0.15 eV and 0.43 eV, respectively. The temperature dependencies of the dielectric dispersions are weak, but both increase at higher temperatures.

4.1.3. The α relaxation

The normalized spectral response observed for the α relaxation is shown in Fig. 5. In the lower frequency region the characteristic is dominated by a conductivity-like response which, as the two sets of data do not normalize together, has a different temperature dependence to that of the loss peak. In the Fig. 5 the normalization has been carried out to recover the loss peak, and from this plot m_α can be determined as 0.11_5 and n_α as 0.85. Fig. 6a shows the detail of the Arrhenius plot of the relaxation rate and magnitude of response. The latter can be seen to be essentially constant over the temperature range in which the relaxation could be observed, whilst the former shows the characteristic curvature with rapidly decreasing relaxation rate on decreasing the temperature. This is commonly associated with the glass-like increase in viscosity as the glass transition temperature is approached from above. Elsewhere it has been shown that this type of response can be characterized by a power-law dependence of the relaxation rate on a reduced temperature [18], i.e.

$$\omega_\mathrm{p} \propto (T - T_\mathrm{g}')^r \qquad (4)$$

where T_g' is defined to be the temperature at which the relaxation rate becomes zero. The magnitude of r is an indicator of the degree to which the transition at T_g' involves a discontinuity in molecular transport. For example, in a perfect single crystal with a well-defined solidification temperature r would be infinite, whereas

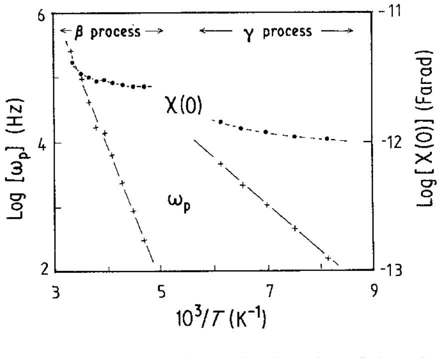

Figure 4 An expanded-scale Arrhenius plot of the relaxation rates and magnitude of the dispersion for the β and γ processes.

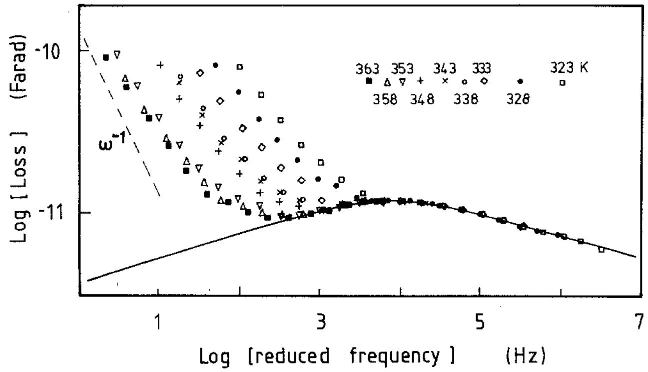

Figure 5 Spectral response of the α process in normalized form. The plot is scaled at 348 k and has been constructed to emphasize the loss peak behaviour. At low relative frequencies a d.c. conductivity can be seen which does not have the same temperature behaviour as the loss process.

in polymers r has been found in the range 10 to 20 [18]. Fig. 6b gives a power-law plot of the relaxation rate data shown in Fig. 6a, using a transition temperature T_g' of 300 K. From this plot it can be seen that the pertinent value of r here is 5.3.

4.1.4. *The A process*

The normalized complex capacitance response for the final process of relaxation observed in the plasticized PVC is shown in Fig. 7. Both the real and imaginary components have been presented here, as the dispersion in the loss component was accompanied by a dispersion of similar magnitude in the capacitance. The characteristic of this plot is contained in Equation 3, for which the asymptotic low-frequency behaviour is of the form $\chi(\omega) \propto (i\omega)^{+p}$. The continuous curves through the experimental data have been obtained from Equation 3 using $p_A = 0.65$ and $n_A = 0.85$. The characteristic frequency can be obtained from the theoretical plot ($z = 1$) and is indicated in Fig. 7. Determination of the characteristic frequency ω_c is necessary in order to scale the shift of the response with temperature. Fig. 8a gives the Arrhenius plot of the relaxation rate and Fig. 8b the equivalent temperature-reduced power-law plot. The latter confirms that the rate of relaxation slows down in a similar manner to that of the α-process, and indicates a zero-rate temperature, T_{gA}', of 278 K with a power index of 6.1. The unusual feature of this response is that it continues to be observed below the zero-rate temperature of the α response, 300 K, and careful examination of the individual data contained in the spectral response curve in Fig. 7 shows no indication of any modification at $T_{g\alpha}'$.

Above 323 K the A relaxation gives way to the response shown in Fig. 9a. The essential feature here is the dominance of a d.c. conductance in series with a dispersive layer capacitance, which form part of the complete equivalent circuit illustrated in Fig. 9b. In order to recover the response shown in Fig. 9a it is necessary to have the capacitance of the layer greater than 10^{-6} F at 10^{-5} Hz, a dispersion of the form $(i\omega)^{-0.5}$ and a series conductance of magnitude 4.9 10^{-9} S. It should be noted that the conductivity exhibited here is the same conductivity that has already been observed in the low-frequency part of the α response of Fig. 5, and the upper plot in Fig. 9c shows it to be activated with a cross-over from a low temperature barrier of 0.41 eV to a higher value of 1.5 eV at 363 K.

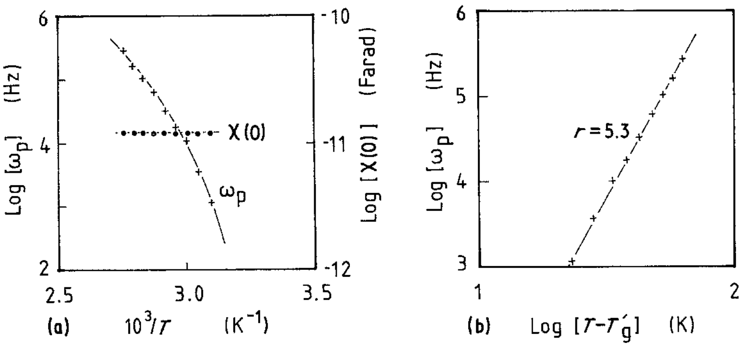

Figure 6 (a) Arrhenius plot for the magnitude of response and relaxation rate of the α process. The strong curvature in the rate curve is indicative of the onset of a glass-type transition. (b) Log/log plot of the relaxation rate for the α process as a function of reduced temperature. T_g' has been taken as 300 K to obtain this plot, and the gradient is 5.3.

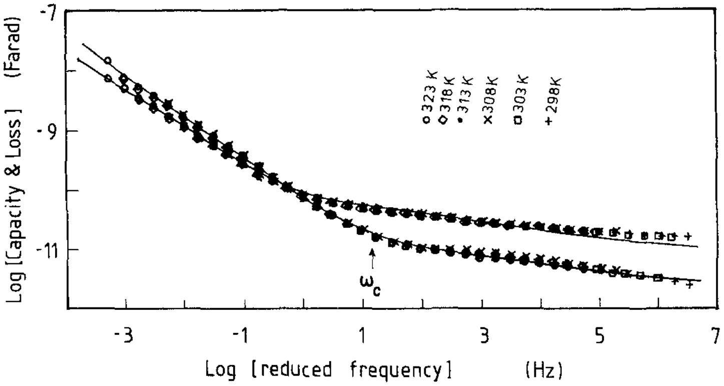

Figure 7 Spectral response of the A process of relaxation. The plot is scaled at 318 K and shows typical quasi-d.c. conduction. The curves through the data points have been obtained from Equation 3 with the values of parameters listed in Table I.

The weak loss peak observed in the region of 10^4 Hz in Fig. 9a is the previously discussed α-dispersion acting in parallel with the bulk conductance, as indicated in Fig. 9b. When this element was incorporated using Equation 2 and the values of the circuit elements taken as shown in Fig. 9b, the theoretical curves fitting the data in Fig. 9a were obtained.

4.2. Plasticizer-extracted PVC

After extraction of the plasticizer only two loss processes were observed in the sample, the α' and the β', corresponding broadly to the α and β processes in the plasticized material. In contrast with the plasticized material, no evidence for a relaxation process of the A form was found; instead a weak d.c. conductivity was observed at all temperatures.

4.2.1. The β' process

Fig. 10 shows the normalized loss for the lower temperature relaxation, the β' process. Again an expanded scale has been used as the spectral response is broad. The Arrhenius plot for both the rate of relaxation and the amplitude of the response is shown in Fig. 11a. Here the magnitude of the response appears to be activated with an activation energy of 0.054 eV, a value which although small is nonetheless approximately $3kT$, in the middle of the temperature range of observation. For this reason Boltzmann statistics can just be expected to apply and a genuine activation energy can be deduced. The temperature dependence of the relaxation rate, however, shows non-Arrhenius behaviour with the observed rate at low temperatures in excess of those expected from an extrapolation of the high-temperature data.

These data are replotted in Fig. 11b in the form of log (rate) as a linear function of temperature, and the plot shows a respectable straight line with a gradient of 0.068 K^{-1}. It has been shown [18] that this plot is characteristic of an activated tunnelling between parabolic potential wells. The gradient of the plot gives a tunnelling distance of either 7.7 nm for electron tunnelling or 0.18 nm for proton tunnelling. The height of the potential barrier through which the particle tunnels can be determined by making

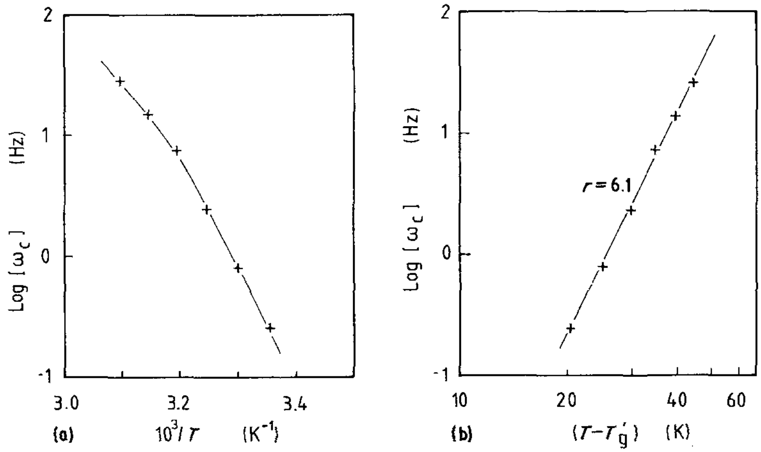

Figure 8 (a) Arrhenius plot of the relaxation rate for the A process. (b) Log/log reduced-temperature plot for the relaxation rate of the A process. The gradient of the plot is 6.1 and T'_{gA} was taken as 287 K.

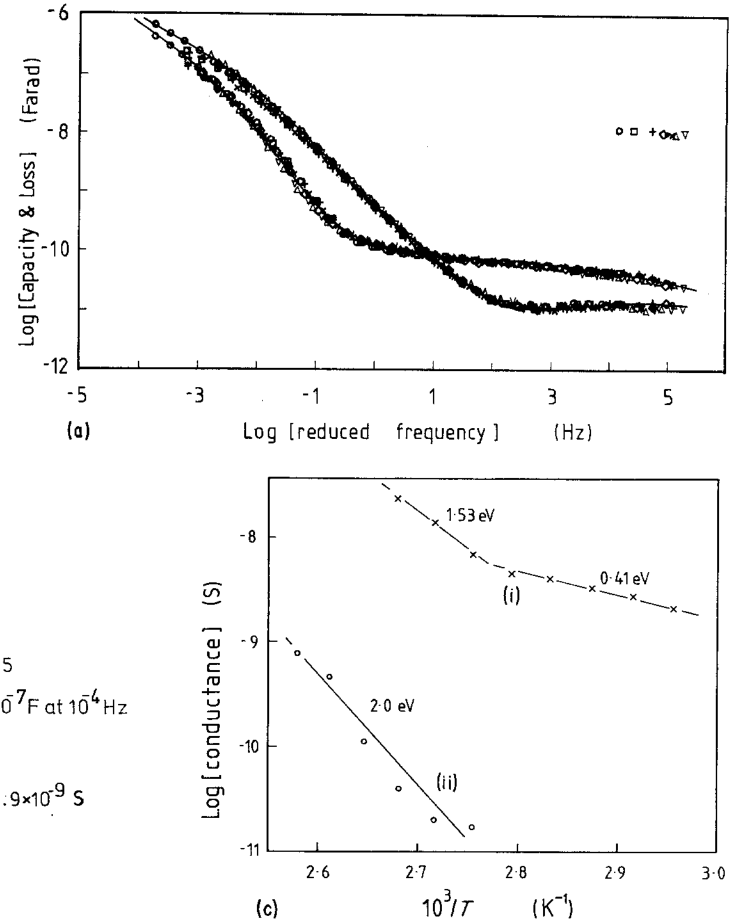

Figure 9 (a) Spectral response of the high-temperature dispersion process in plasticized PVC: (▽) 338 K, (△) 343 K, (◊) 348 K, (·) 353 K, (♦) 358 K, (+) 363 K, (□) 368 K, (○) 373 K. The plot is scaled at 353 K. (b) Schematic diagram of the dispersion elements used to obtain the continuous curves shown in (a). The values quoted are for 353 K. (c) Arrhenius plots of the conductance in (i) plasticized and (ii) unplasticized PVC.

use of the extrapolated zero-temperature rate, 1.7×10^{-5} Hz, to give a value of 0.53 eV, independent of the nature of the tunnelling particle but assuming a pre-exponential lattice vibration frequency of 10^{13} Hz.

4.2.2. *The α′ process*

In the temperature range over which the α′ process was observed, 353 to 382 K, the low-frequency response was dominated by the presence of a d.c. conductance (Fig. 12). The α′ peak itself was broad and the relaxation rate was strongly dependent on temperature, as can be seen in the Arrhenius plot of Fig. 13a. This plot shows a characteristic slowing down which is similar to the α process in the plasticized material. Fig. 13b shows this rate to be of the reduced-temperature power-law form with a transition temperature of 338 K, 38 K higher than that observed in the plasticized α material. The power-law exponent in the reduced temperature plot is 14.7, almost three times larger than that observed in the plasticized material.

In the spectral response plots of Fig. 10 and 12

TABLE I Spectral parameters for PVC.

Response region	*m*	*p*	*n*	(*m* + *n*)	Fig. No.
Plasticized					
γ	< 0.015	–	0.895	0.91	2
β	0.042_5	–	0.94	0.99	3
α	0.15	–	0.87	1.02	5
A	–	0.65	0.85	–	7
Unplasticized					
β′	0.14_2	–	0.937	1.08	10
α′	0.19	–	0.86	1.05	12

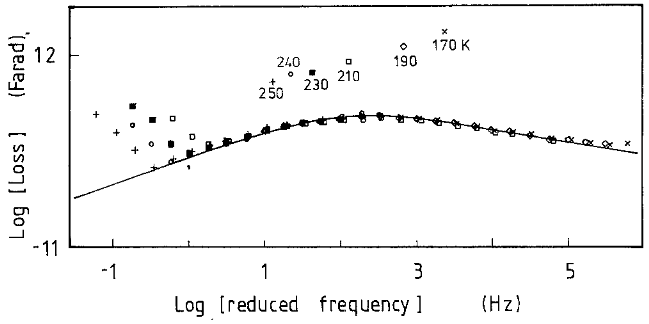

Figure 10 Spectral response of the β' process in unplasticized PVC. The plot is scaled at 240 K and the parameters used to fit the theoretical curves are given in Table I.

the continuous curves fitting the data have been determined from the spectral functions of Equations 2 or 3, using the relevant parameters which are listed in Table I.

5. Discussion

The results described in the previous section confirm in outline the conclusions of previous authors [2–5] concerning the influence of plasticizers on the dielectric properties of the parent polymer. Thus we find that the polar plasticizer reduces T_g', the asymptotic temperature at which the system becomes rigid, and also generates an extra dielectric response, γ, in the glassy state. However we also find that in the present case the plasticizer has a considerable influence upon charge transport in the system through the introduction of the response labelled A, and the generation of barrier effects above 323 K.

The magnitude of the dielectric dispersion associated with the peaked loss processes α, α', β, β', and γ was observed to be small, in agreement with previous work [1–7]. No change, however, in the temperature dependence of ω_p and $\chi(0)$ was observed in either the plasticized or unplasticized material in the temperature range where Reddish [8] suggested an anti-ferroelectric transition to occur. Therefore some other explanation must be sought for the weak response in this potentially highly polar material.

A microscopic interpretation of the role of the plasticizer in the modification of the dielectric response of PVC necessarily requires an equivalent understanding of the glass transition in polymers in general. Although the general features of the molecular motions involved are known [19, 20], the details of the relationship between model and experiment is more elusive. In the following subsections we examine each type of dielectric response individually, and attempt to interpret the complete information that characterizes the response in terms of the cluster model [9] of dielectric response as it applies to polymeric systems.

The cluster model envisages relaxing systems in general to be composed of an array of weakly connected clusters. Relaxation within the clusters occurs through the displacement of fractions of the total cluster population, i.e. subunits, moving as rigid bodies. An individual cluster element will participate in the motions of all sizes of subunit from that of the element moving as an independent dipole up to that of the whole cluster, with the index n measuring its

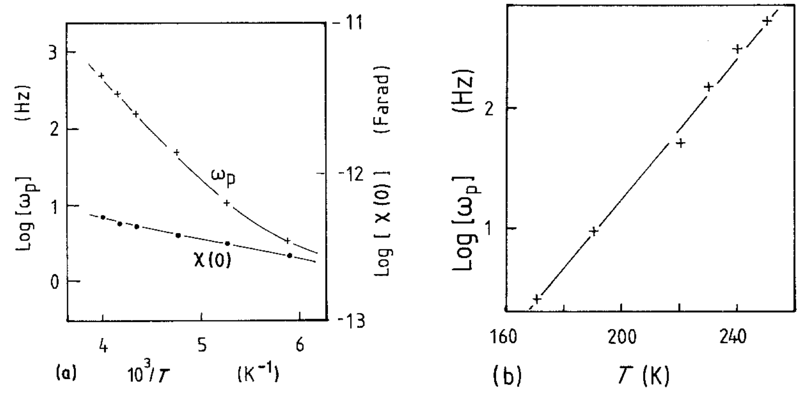

Figure 11 (a) Arrhenius plot of the relaxation rate and magnitude of response for the β' process. (b) A plot of the logarithm of the relaxation rate in the β' process as a function of linear temperature.

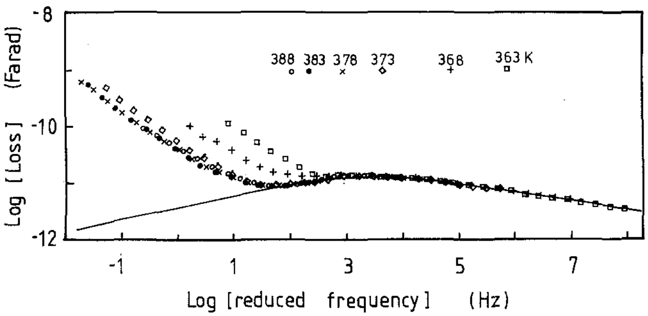

Figure 12 Spectral response of the α' process in unplasticized PVC. The plot is scaled at 378 K and the parameters used for curve fitting from Equation 2 are given in Table I.

mean degree of correlation with the displacements of the other cluster elements. This is a scaling picture [21], and n can alternatively be defined in terms of the degree to which properties such as the susceptibility and local mode structure are replicated when the scale is varied within the cluster size. The influence of interactions between clusters is to cause such cluster properties as size and number of elements to fluctuate dynamically, thereby generating a steady-state distribution of clusters in dynamic equilibrium [22]. The index m ($\equiv p$) measures the degree to which elements in different clusters can correlate their motions, and defines the shape of the steady-state cluster distribution.

The theoretical expressions of Equations 2 and 3 are the result of combining these processes so that in the former case interactions between clusters fluctuate the relaxing cluster [9], and in the latter case intra-cluster relaxations reduce the coherence of charge displacements transported between clusters [15].

5.1. α-type responses

In this subsection we discuss the amorphous α-response [19, 20] which we have designated α in the plasticized material and α' in the unplasticized sample. The characteristic feature of this type of response is the slowing down of the relaxation rate as the glass transition is approached from above, as shown in Figs. 6a and 13a. This behaviour has been observed [18, 23] to obey the power-law form, Equation 4, with temperature-independent parameters r and T'_g. It has been analytically shown that the commonly used WLF equation [24] is an approximation to Equation 4 with a region of validity centred about the chosen reference temperature, T_r. As a result r and T'_g can be approximately identified with the WLF constants c_1 and $(T_r - c_2)$ respectively, evaluated at T_r.

The general significance of Equation 4 is that it defines the relaxation dynamics of the system at different temperatures on the approach to rigidity ($\omega_p = 0$) at T'_g, with the parameter r describing the sharpness of the approach. It is not implied by this that the state of the system defined by T'_g is actually accessible in practice, merely that the system approaches this state. Therefore the question as to whether the glass transition as defined calorimetrically has predominantly a kinetic origin [25] or thermodynamic origin [26] is left open in this formalism. The advantage is that use of a glass transition temperature T_g which cannot be precisely defined is avoided in favour of a precisely defined if unrealizable state at T'_g.

In terms of our relaxation model the most important aspect of Equation 4 is that it defines a form of scaling for ω_p. This can be seen by

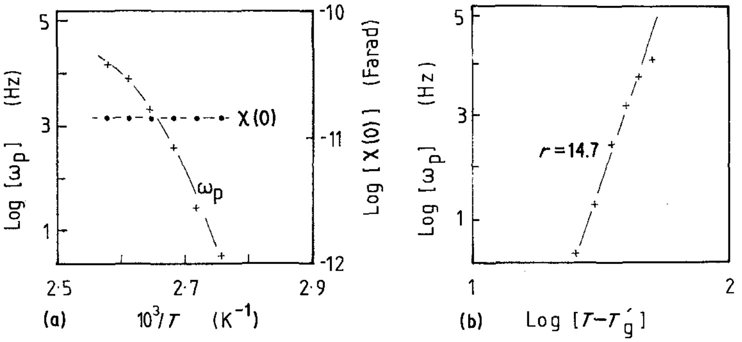

Figure 13 (a) Arrhenius plot of the relaxation rate and magnitude of response for the α' process. (b) Log/log reduced-temperature plot for the α' process. T'_g was taken as 338 K.

setting $T - T_g' = \varepsilon$ and noting that the ratio

$$\frac{\omega_p(b\varepsilon)}{\omega_p(\varepsilon)} = b^r \qquad (5)$$

is dependent only upon the scaling factor b. It has been noted that inverse viscosities [18, 27] (η^{-1}) and also, in some cases, the effective radius of gyration [27] (R^{-1}) obey similar power laws in this region. We can therefore take ε to be a controlling variable for a single cluster factor that determines all three properties [21]. The original derivation of the WLF equation [24] would suggest the cluster-free volume as the likely candidate for this factor; however, it would seem more appropriate to use the configurational entropy [26]. This property can be related to ω_p, η^{-1} and R^{-1} through the number of configurations available to the cluster [21]. Furthermore it has recently been shown that the cluster model of relaxation can be formulated in terms of the evolution of configurational entropy as a specified configuration relaxes [2, 18].

In the cluster model the susceptibility at frequencies $\omega > \omega_p$, given by

$$\chi'(\omega) \propto \chi''(\omega) \propto \chi(0)(\omega/\omega_p)^{n-1} \qquad (6)$$

is contributed by the motion of cluster subunits. Since the amplitude $\chi(0)$ is usually a weak function of temperature for the α-responses and in this particular case effectively temperature-independent, it would seem reasonable to assume that the "susceptibility" of a given subunit is also independent of ε. Under these circumstances the frequency to be assigned to a given subunit must have a *fixed proportionality* to the cluster relaxation rate ω_p. This is a fundamental departure from the type of dynamic scaling applicable to ferro-electrics [28] or reptation [21], where the subunit frequency is determined solely by the number of elements it contains. However, in the present context it receives a simple physical explanation if it is accepted that the approach to T_g' is characterized by a reduction of alternative configurations, with the reduction being appropriately scaled for each subunit. In this way the scale-replication index n will be maintained invariant of ε as is observed experimentally.

In the case of the commercial PVC considered here n is 0.86, which is much larger than is normal in the α-response of polymers. We suggest that this value of n implies an intra-cluster structure in the form of a near-regular three-dimensional mesh, in which the framework is formed by chain crossings or incipient entanglements. The irreducible element of the cluster would then be the unit mesh-cell. On scaling the mesh size the degree of reproducibility would be 0.86 up to the cluster boundary, which may be determined by entanglements that are already formed, or simply by loss of reproducibility. In the latter case the cluster is equivalent to the "blob" as defined by de Gennes [21] and can be regarded as the primitive element for a reptating chain of blobs which generates the viscous flow appropriate to this phase. If the array of blobs is ideal we would expect a Gaussian distribution of blob sizes, and this is in fact close to the cluster distribution density as implied by the values of m observed, i.e. 0.15 and 0.19 [22]. However, it should be noted that this refers to a steady-state dynamic situation rather than a static one, and thus the blobs do not behave as perfect hard spheres.

Extraction of the plasticizer has increased T_g', increased r dramatically and m slightly whilst leaving n unchanged. The amplitude $\chi(0)$ has also been slightly increased. It therefore appears that the plasticizer molecules occupied the intra-cluster mesh in the same scale proportions as the mesh itself. Their extraction would cause the mesh size to collapse while retaining its scaling proportions. If we assume T_g' to be the temperature at which the mesh becomes rigid, thereby preventing all relaxations except those within the irreducible cluster element, then T_g' can be expected to increase as observed. The increase in r may be attributed to the decrease in free volume or configurational entropy per cluster; its physical origin, however, lies in the increased ε-dependence of the contraction of the mesh as it approaches T_g', due to the removal of the more mobile plasticizer molecules. We note that the extrapolation of Figs. 6a and 13a gives an intersection of 416 K, a temperature lying just below the normal melting range of 420 to 460 K. Finally, the increase of the shape parameter m is likely to be the result of non-uniform inter-cluster stresses. These would arise because the plasticizer in the inter-cluster regions is not in proportion to that within the cluster, and thus its removal does not retain the inter-cluster scale. The resulting distribution density is therefore extended to include a wider range.

5.2. The β response

In terms of the model we have presented, this response originates with the motions within an irreducible element of the α-response cluster. The dipoles involved are thus the same as those relaxing in the α response, contributing a fraction of their strength [19, 20] to displacements along a different route. Although potentially observable at higher temperatures, they become the only means of relaxation below the glass transition as we have described.

We can apply our cluster model to this type of response by taking the subunits to be fractionally sized segments of the unit mesh-cell which now comprises the whole cluster. The value of n observed was very close to unity, which suggests a structure in which different scale subunits are highly self-similar and very different from a polar configuration [29]. One of the possibilities is therefore that of a spirally coiled chain. The shape parameter m is small, and in the plasticized material very small, showing that the fluctuations in number of elements or length available to a particular cluster are very weak.

In the plasticized material the amplitude $\chi(0)$, when the β response is well established in the glass phase, is only weakly temperature-dependent. If we assume that this implies that the subunit susceptibilities are also temperature-independent, then from Equation 6 ω_p must be a fixed fraction of the frequency assigned to a particular subunit. Writing ω_p in the form

$$\omega_p = v_0 e^{\Delta S/k} e^{-\Delta/kT} \qquad (7)$$

where ΔS is the activation configuration entropy, this result can be rationalized if each subunit contributes a scaled proportion to the ground-state configuration entropy of the whole cluster [30]. Equivalently we could say that the probability of finding a relaxation path via a fixed activated state increases in proportion as the scale of the subunit decreases. This interpretation clearly has an affinity with that of the α process when it is understood that in the glassy state ΔS will be essentially temperature-independent.

Extracting the plasticizer has resulted in an activated amplitude, and a non-Arrnehius behaviour for ω_p. Since the value of n is unchanged we expect the same chain morphology to exist on this scale, but within a much more tightly constraining mesh. Increase of the shape parameter m reflects the much greater fluctuations in chain sizes caused by increased local stresses. The mechanism determining ω_p has the temperature dependence of an activated tunnelling process, and has been identified in a number of polymeric systems [18]. It appears to occur when the environmental steric hindrance to relaxation is sufficiently high that the relaxing system chooses paths of reduced probability, involving a number of co-operative adjustments of the steric hindrance which lower the energy barrier. In these terms the word "tunnelling" should be understood to apply to a free-energy barrier, rather than in its quantum-mechanical sense. For this reason we should choose the tunnelling mass to be that of a proton travelling 0.18 nm, which suggests a chain twisting and is similar to that of other examples [18]. The activation of the response amplitude is sufficiently well established to indicate that as the temperature is lowered the maximum sized subunit of the cluster that can relax as a rigid body is progressively reduced. Thus the behaviours of $\chi(0)$ and ω_p are consistent with one another and with a physical picture in which the mesh tightens about a coil, forcing it to relax in subunits which must adjust their configurations locally to fit the cage constraints.

5.3. The γ relaxation

This relaxation originates solely with polar plasticizers [2–5]. In the present case it is observed only in the glass phase with a low activation energy, but a value of n close to that for the α-response scale. We therefore suggest that it is the plasticizer molecules occupying the α-scale clusters, which we already know scale in the same manner as the cluster and free volume, that give rise to this response. A relaxation response can be expected only below T_g' when molecular transport becomes impossible, and even here a low activation energy would not be unreasonable. In this case the plasticizer system acts like a softer image of the α clusters in which it is embedded, which can accomodate configurational relaxation below the temperature at which its polymer cage becomes rigid. The loss of molecular transport is indicated by m, which shows that almost no fluctuations occur in cluster size.

5.4. Electrical transport

Molecular transport in the plasticizer system can be expected to occur at temperatures above the T_g' of the *plasticizer*, which will lie below the rigidity temperature of the polymer mesh. If the plasticizer molecules can support charge transfer as in this case, molecular transfers across cluster boundaries can transport a charge displacement by means of co-operative local configuration adjustments throughout the cluster array. This is the basis of the quasi-d.c. [31] or low-frequency dispersion behaviour [15] (Process A) observed above 278 K in the plasticized PVC and shown in Fig. 7. Further confirmation of this interpretation lies in the fact that the effective cluster ionization rate, ω_c of Fig. 8b, scales with ε in an almost identical manner to that of the relaxation rate of the α process, and that the intra-cluster scaling indices n for both processes are identical. The index p, which defines the perfection of the transport process through the cluster array, has a value of 0.65 which is close to that expected, 2/3, for the non-classical diffusion of a charge packet through a disordered three-dimensional system [32].

Above 323 K this process converts to one exhibiting a bulk d.c. conductivity in series with a barrier capacitance, as shown in Fig. 9b. It seems to us that around this temperature the charges, which are presumably electrons on the carboxyl group, significantly populate a conduction band. The low-frequency dispersion method of transport is thus effectively circumvented and a bulk conductivity ensues. Because of the interfacial effects the charges build up a barrier layer at the electrodes, and the frequency dispersion in this barrier layer capacitance ($\sim \omega^{-1/2}$) originates with classical charged-particle diffusion.

Above 363 K, Fig. 9c shows that the activation energy of the bulk conduction increases. A comparison with the conductivity of the deplasticized sample shows that this can be attributed to an intrinsic conductivity, with the charge transport most probably being associated with the viscous motions of the chain. The increased activation energy in this latter case is therefore a natural consequence of the increased barrier to such motions resulting from a tightening of the large-scale polymer matrix following plasticizer removal. It should be noted that no sign of either of the transport processes attributed directly to the plasticizer system appears in the deplasticized material. Neither is there any evidence for a barrier capacitance in this material.

6. Summary

The dielectric behaviour of a commercial PVC which has been reported here has been shown to be consistent with a general picture of the polymer morphology in which there exist three size scales. Within each scale there is a strong self-similarity between volume elements of different size up to a finite maximum, which then defines the minimum volume element for the grosser scale of organization. Above the glass transition all three levels of organization may respond, giving the viscous behaviour and the α and β responses. The approach to the glass transition is characterized by a reduction in configurational entropy, or free volume, in the intermediate level which is scaled in proportion for any volume element chosen within this level. Below the glass transition a constant excess configurational entropy is available, distributed in proportion to the size of volume elements of the most local scale. These elements form a cluster hierarchical system and give rise to the β response. Through this approach the plasticizer molecules have been shown to occupy volume elements of the intermediate level, in proportion to their total occupancy on this level. Their effect on the α response is to alter the way the configurational entropy scales with ε. In addition, plasticizer molecular transport in this case gives rise to an anomalous electrical transport process. At lower temperatures the molecular transport becomes impossible and a loss peak (γ) response ensues.

A system morphology consistent with this picture is suggested in terms of a polymer mesh; however, it should be noted that this is probably not unique, and it should be regarded as a stimulus to further work rather than a definitive model.

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