Investigation of the Diffusion of Di-*n*-hexyl Phthalate in Rubbery Poly(vinyl chloride) Using Electrical Impedance Spectroscopy

Deyan Wang, R. F. Storey, and Kenneth A. Mauritz*

Department of Polymer Science, University of Southern Mississippi, Southern Station Box 10076, Hattiesburg, Mississippi 39406-0076

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ABSTRACT: Electrical impedance spectroscopy was used to monitor the diffusion of the plasticizer di-*n*-hexyl phthalate in poly(vinyl chloride) films above the glass transition temperature. In the isothermal experiment, the initial plasticizer concentration was greatest at the film surfaces and lowest in the middle and then readjusted toward a more uniform profile across the film thickness as the system moved toward equilibrium at constant plasticizer content. Curves of the imaginary part of the complex impedance vs frequency, at constant temperature, show peaks that shift to higher frequencies with increasing diffusion time. The frequency at peak maximum increased linearly with diffusion time at constant temperature. Plots of imaginary vs real parts of the complex impedance appear as well-defined depressed semicircles from which a distribution-of-relaxation-times parameter can be extracted. Altogether, the results reflect an average increase in polymer chain segmental mobility as well as a decrease in microstructural heterogeneity owing to a redistribution of the free volume throughout the sample as the plasticizer advances from the surfaces toward the middle of the film.

Introduction

Mauritz, Storey, and co-workers reported on the progressive development of a general predictive mathematical model for the above-T_g diffusion of large molecules in polymers that recognizes their complex shapes in preferred conformations as well as their interactions with the host polymer. As the penetrant size increases, its translatory motions within the available free volume become increasingly sensitive to its shape. In the present context, a molecule is considered to be "large" if its volume greatly exceeds that of a chain segment of the host polymer but is not large enough to be a macromolecule. Our ultimate goal is to fill the nebulous gap between theories for the diffusion of small molecules in rubbery polymers and macromolecular self-diffusion.

The reader is directed to refs 1–5 for the numerous details of this model. Some of the major features factored into an equation for the diffusion coefficient, *D*, include the following: (1) theoretical conformational analysis is used to determine penetrant molecular shape-dependent parameters; (2) given the spontaneous creation of an adjacent pocket of free volume, the penetrant displacement is only a fraction of its dimension in a given direction; (3) a reverse solvation model accounts for explicit polymer–penetrant interactions.

It is significant that the evolution of the model was guided and its validity checked against extensive experimental gravimetric studies of the diffusion of numerous phthalate and adipate plasticizers in poly(vinyl chloride) (PVC) in our laboratory.[6,7] We established a large reference database involving linear and branched plasticizers over a considerable range of molecular weights which demonstrated the sensitivity of *D* to penetrant size and shape. The more compacted (branched) molecules were seen to diffuse slower than extended (linear) molecules of the same chain carbon number, in accordance with our theory. These studes were conducted as a function of temperature so that diffusion activation energies could be extracted. We monitored, via light microscopy, the kinetics of uptake of dialkyl phthalates (DAP's) by PVC particles at various temperatures above and below unplasticized T_g.[8] Diffusion time regimes were identified based upon the physical states of the polymer in relation to its glass transition. Experimental T_g vs plasticizer content relationships were determined for these systems using DSC.[9] It was seen that plasticizing efficiency (i.e., slope of T_g vs weight percent plasticizer lines) decreases with increasing molecular weight for both linear and branched DAP's. For a given molecular weight, branched DAP's have higher efficiencies than the linear structures. We rationalized this in terms of the additional free volume created by the inefficiency of packing chains about large penetrants. The DSC scans also implied an increasing degree of *microstructural heterogeneity* presumably in the form of plasticizer pooling with increasing concentration. The average nearest-neighbor environment about a penetrant should become increasingly populated with other penetrant molecules in addition to polymer chain segments, with increasing concentration.

The following work is a continuation of the effort to provide experimental feedback that suggests incorporation of significant mechanistic and structural factors into the model to enhance its accuracy and range of applicability.

In short, the kinetics of the uptake of the plasticizer di-*n*-hexyl phthalate (D*n*HxP) in PVC was monitored through progressive changes in the electrical impedance spectra as the plasticizer concentration profile shifted from being nonuniform toward being uniform across the film thickness.

Finally, this work has practical relevance as PVC is one of the most broadly-applied plasticized polymers that is produced in enormous quantities. The most important industrial issues related to the work in this paper are the polymer/plasticizer dry-blending process and long-term plasticizer permanence in finished articles as each is concerned with the molecular migration of plasticizer, respectively, into or out of PVC.

Experimental Concept

Imagine that the flat surfaces of a thin circular sample (film) of unplasticized PVC are exposed to a plasticizer, D*n*HxP, at a temperature > T_g for a time short enough so that the equilibrium liquid uptake of the polymer has not yet been attained. The sample is totally submerged in a large reservoir of this liquid. In this preequilibrium state, a nonuniform D*n*HxP concentration profile exists

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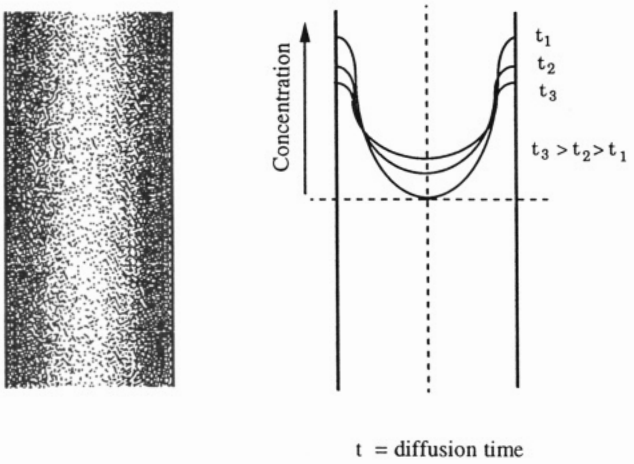

Figure 1. Hypothetical plasticizer concentration profile across a polymer film thickness and the evolution of the profile with increasing time for the condition of constant plasticizer content.

across the film thickness, as roughly illustrated in Figure 1. In the early stages of the experiment, the concentration is greater at the two surfaces than at the center. Since the film is thin in relation to its diameter, liquid sorption around the edge is assumed to be negligible. As the uptake proceeds, the concentration profiles emanating from each surface move inward and eventually overlap at the center where the concentration progressively increases. If the experiment is allowed to continue for a "long time", the concentration profile becomes flat, reflective of a condition of sorption equilibrium. The experiment in this work concerns removing the film from the plasticizer bath before equilibrium sorption is attained, removing excess plasticizer from the surfaces, and then placing the film between, and in contact with, two parallel-plate electrodes in a temperature-controlled cell that is wired to an electrical impedance analyzer. The impedance analyzer measures the electrical impedance, $Z^* = Z' - iZ''$ ($i = \sqrt{-1}$), of the film as a function of the frequency, f, of a weak sinusoidal voltage applied across the plates. Both the plasticizer sorption and subsequent impedance determinations are conducted isothermally and each at the same temperature above T_g for the unplasticized PVC. As this section is concerned with an abstract discussion of molecular mechanisms, the exact details of the experiment, as executed, are reserved for the following section.

Having rapidly transferred a given plasticizer-soaked (and wiped-dry) film to the impedance test cell, Z' and Z'' vs f are obtained as a function of time. While D*n*HxP no longer enters the film at this stage, we still refer to the time as "diffusion time" because the plasticizer continues to migrate inward under continually-decreasing concentration gradients at all points in the thermodynamic drive toward swelling equilibrium. The impedance response as a function of diffusion time can provide useful information regarding the shifting time scale of the long-range chain segmental motions that are operative at these temperatures, the energetics associated with these motions, and the microstructural heterogeneity that must result from a nonuniform distribution of plasticizer.

This mixed system is simple to the degree that the usual equivalent electrical circuit representation consisting of a resistor (R) and capacitor (C) in parallel is appropriate in the mathematical analysis. The actual experimental results will show this to be true. Z'', for this model, is equal to $1/2\pi fC$. When conditions within the polymer are such that C is at a minimum, the ability of the polymer to *store* energy is at a minimum; i.e., a *molecular relaxation* is occurring. For a given temperature, there will be a frequency, $f_{\max}$, at which Z'' is at a maximum and a *relaxation time* defined as $\tau = (2\pi f_{\max})^{-1}$ will be a measure of the time scale during which macromolecular rearrangements occur. For $T > T_g$, these rearrangements are associated with the long-range chain segmental mobility as usually portrayed by the Rouse model.[10]

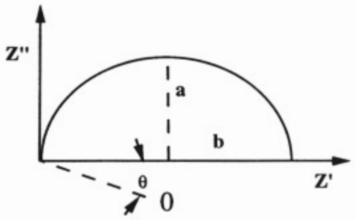

Figure 2. Hypothetical plot of the imaginary (Z'') vs real (Z') part of the complex electrical impedance, at constant temperature, for a single relaxation process. The point O is the center of the semicircle, and θ is related to the distribution of relaxation times. $r = a/b = (1 - \sin\theta)/\cos\theta$.

As plasticizer molecules invade a given microscopic region of the polymer, the local free volume increases and the "local T_g" is thereby depressed. Within the context of this experiment, one might imagine a gradient of free volume, and therefore a gradient of T_g, existing across the film thickness in such a way that it is highest in the middle and monotonically decreases toward the more plasticizer-rich surfaces. It might also be anticipated that this compositional and microstructural heterogeneity produces rather broad distributions of relaxation times so that the measured values of $f_{\max}$ are averages over the film thickness. $f_{\max}$ is consequently expected to shift to higher values with increasing diffusion time at a given temperature. In contrast with simple gas molecules, the diffusion of large plasticizer molecules in rubbery polymers is more interactively coupled with the motions of the host polymer chains. Furthermore, the distribution of relaxation times is expected to finally narrow with diffusion time as the plasticizer concentration profile becomes more uniform.

Z', equal to R, is the "loss" component of the impedance response. Z' vs f graphs should be monotonically decreasing with an inflection point at $f_{\max}$. The frequency increases to the point where the time scale of the measurement approaches the natural motional time scale of the chain-attached dipoles. In this way, the displacement current across the plates increases, resulting in a greater conductance = R^{-1}.

Given the above set of conditions, plots of Z'' vs Z' should be semicircles whose centers are depressed below the horizontal (Z') axes (see Figure 2), the amount of depression being a measure of the degree of compositional and microstructural heterogeneity over the macroscopic dimensions of the sample.

The concepts developed above provide the basis for the interpretation of our experimental results.

Experimental Section

Materials. D*n*HxP and compounded PVC were generously supplied by the Exxon Chemical Co. The unplasticized PVC films were compression molded from a commercial suspension-polymerized PVC resin (Exxon Chemical Co., grade 369) which was described in detail in a previous publication.[8] The PVC resin was compounded with 2.0 phr of Mark 7101 stabilizer and 0.2 phr of stearic acid. Circular disks (diameter 2.54 cm) were stamped from the PVC film (nominal thickness 0.010 cm) using a machined die.

Procedure. A disk was totally immersed in a beaker of D*n*HxP liquid, held, for example, at the constant temperature of 85 °C until the plasticizer content reached about 43% by weight.

Table I
Weight Percent of DnHxP in PVC at Indicated Temperatures

T, °C	85	90	95	100
wt %	43.3	42.5	42.5	44.1

The temperature 85 °C is just above T_g for unplasticized PVC. The sample was surface-blotted dry and then weighed. The cited weight percent uptakes refer to the percent of the final (PVC + DnHxP) mixture. Then, the film was placed between, and in close contact with, the two flat, parallel, circular electrodes of an in-house-designed electrical impedance test cell that is temperature-controlled (isothermal) by means of a circulating oil system. The temperature of the cell was always set at the temperature of the plasticizer bath to preserve thermal equilibrium. The sample was transferred from bath to cell as quickly as possible.

The electrodes in the cell were connected to a PC-controlled Hewlett-Packard HP4192A impedance analyzer capable of performing electrical measurements in the frequency range 5 Hz to 13 MHz. The signal voltage was set at 100 mV in order to bring the impedance parameters within the measurable range of the instrument. It was established that the current–voltage response is linear about this voltage. Therefore, concepts relating to the theory of linear dielectric response are applicable. Measurements were immediately taken across this entire frequency range and subsequently every 15 min for 60 min. As it is difficult to establish an "absolute zero time" for the impedance measurements, the results are somewhat relative in this sense. The experiment was also conducted at higher temperatures, namely, 90, 95, and 100 °C. The actual weight uptakes for these samples are listed in Table I. Since the largest deviation in plasticizer content among these values is only 1.6%, it is reasonable to assume that the initial concentration profiles do not considerably differ.

Results and Discussion

In practice, the real and imaginary parts of the complex admittance, Y^*, were determined over the instrumental frequency range and Z^* was calculated as $1/Y^*$. Z'' vs f curves are displayed in Figure 3a–d for the constant temperatures 85, 90, 95, and 100 °C. In each figure, curves are illustrated for various indicated diffusion times. Very distinct peaks that monotonically shift to higher frequencies with increasing diffusion time are seen in these figures. We attribute this shifting behavior to the downward evolution of a spatially-averaged glass transition temperature. As the plasticizer concentration profile advances inward from the film surfaces, increasingly more free volume is created in regions invaded by DnHxP molecules. The measured relaxation time is an average over the macroscopic ensemble consisting of all the long sequences of chain segments that are participating in the α process throughout the heterogeneous medium.

Owing to the difficulty in initiating the impedance measurements for all temperatures at exactly the same time, curves cannot be strictly compared at the same diffusion time at different temperatures. On the other hand, a comparison of the *rates* at which the peak positions change in time, $\partial f_{\max}/\partial t$, for the various temperatures, is quite meaningful, especially if the $f_{\max}$ vs diffusion time plots are linear. It is seen in Figure 4 that such linearity does in fact exist and that the slope, therefore, provides a distinct and unique parameter that characterizes the rate of increase in the *average* time scale for long-range chain segmental mobility under this condition of plasticizer diffusion. The slope is observed to steadily increase with increasing temperature. Of course, at "long times" the system will reach a condition of equilibrium wherein the concentration of the plasticizer is uniform and directional (inward) diffusion ceases. Then, $f_{\max}$ will have attained its maximum asymptotic value. The fact that $f_{\max}$ increases uniformily implies that the plasticizer concentration profiles, while shifting inward, to be sure, did not significantly change over the observational time frame.

A coefficient of diffusion, $D_{\rm av}$, can be defined as an average over the PVC volume, $V_{\rm PVC}$, as well as over the experimental time frame, $t_{\rm exp}$:

$$D_{\rm av} = (t_{\rm exp} V_{\rm PVC})^{-1} \int D \, dt \, dV \qquad (1)$$

$D_{\rm av}$, in effect, is the sort of diffusion coefficient determined in our earlier experimental plasticizer uptake studies. On an instantaneous basis, D will decrease along a direct line from a film surface toward the middle, owing to a gradually decreasing degree of polymer plasticization. Also, space–time-averaged D will increase with increasing temperature. Therefore, D will increase with increasing $\partial f_{\max}/\partial t$, in consideration of Figure 4. $\partial f_{\max}/\partial t$, itself, is a space–time-averaged quantity. One might inquire as to how D explicitly depends on $\partial f_{\max}/\partial t$.

Consider the following rather general analysis. According to the most basic concept of diffusion, $D \propto \delta^2/\Delta t$, where δ in this case is meant to be a space–time average of the plasticizer molecular hopping displacement occurring in a time Δt at a given fixed temperature. A prefactor of $^1/_6$ is usually present for totally-random, three-dimensional diffusion. One can write $v = \delta/\Delta t$ as the average speed of site-to-site molecular hopping so that $D \propto v\delta$. If the rate at which the plasticized polymer chains exchange conformations on a long-range basis (above T_g), which is proportional to the quantity $f_{\max}$, depends on v in direct proportion, then one can write $D \propto (f_{\max}\delta)\delta$. Differentiating D with respect to time yields

$$\partial D/\partial t \propto f_{\max}[\partial(\delta^2)/\partial t] + \delta^2(\partial f_{\max}/\partial t) \qquad (2)$$

Equation 2 provides a relationship between D and $\partial f_{\max}/\partial t$. However, since all of the quantities in this equation are a function of temperature, an explicit solution is not evident. For example, both $f_{\max}$ and δ depend on temperature. An increase in temperature will increase the free volume content, which in turn increases both $f_{\max}$ and δ.

We measured the diffusion coefficient for DnHxP in PVC as a function of temperature in earlier experiments.[6] While the experimental conditions and plasticizer contents for these earlier experiments were not the same as those for the impedance experiments in this work, the trends in D with temperature should be reasonably comparable. Figure 5 shows D from this earlier study plotted against $\partial f_{\max}/\partial t$ at corresponding temperatures. The graph, albeit of a limited number of available points, appears somewhat linear. In view of eq 2, if D were, for example, directly proportional to $f_{\max}$ (rather than to its time derivative), one might conclude that the first term is insignificant and that δ is practically independent of temperature within the experimental time frame. The last assertion might be supported by our earlier statement regarding the relative constancy of the concentration profile over the experimental period.

A somewhat equivalent concept supporting the notion that $D \propto f_{\max}$ consists of the following. Consider the application of Fick's first law to any point in the film during the approach to thermodynamic equilibrium. The flux of DnHxP molecules (net unidirectional number of molecules per unit time passing through a unit perpendicular area, at a given time and temperature) is directly proportional to the DnHxP concentration gradient at that point, the constant of proportionality being the (local) diffusion coefficient. However, if one assumes the concentration

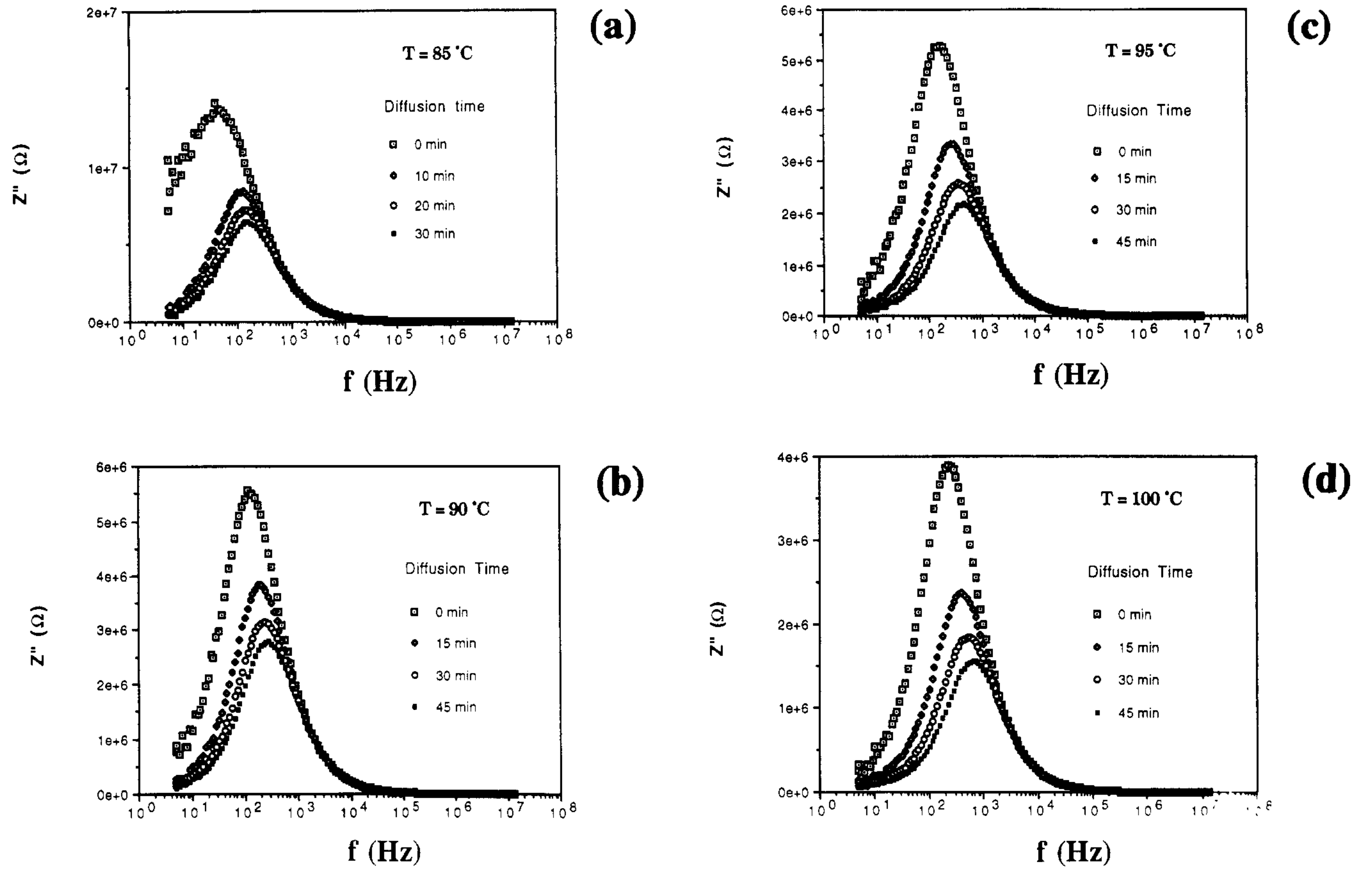

Figure 3. Z'' vs f for the constant temperatures of (a) 85, (b) 90, (c) 95, and (d) 100 °C for the indicated diffusion times.

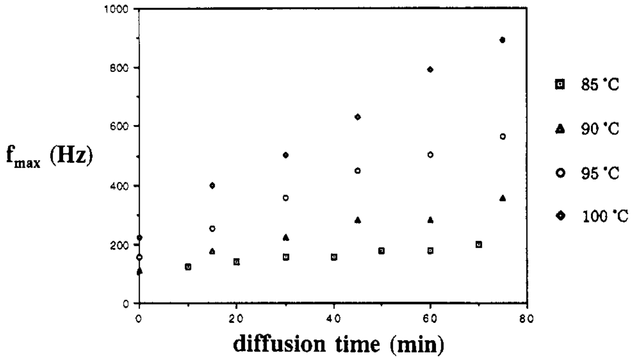

Figure 4. f_{max} vs diffusion time (t) for the indicated constant temperatures.

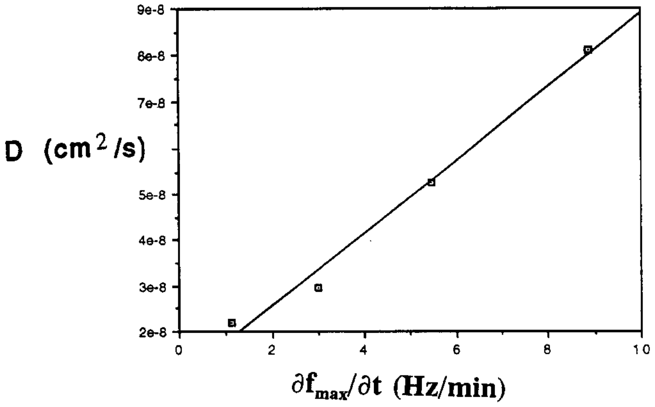

Figure 5. Diffusion coefficient vs df_{max}/dt for various above-T_g temperatures.

gradient to be effectively constant over experimental times, then the flux is directly proportional to the diffusion coefficient. Furthermore, it is reasonable to assume that the plasticizer flux is strongly coupled to the polymer chain dynamics so that the flux is directly proportional to f_{max}. In this crude analysis, D can be seen as being directly proportional to f_{max}.

However, this is apparently *not* the case, and a satisfactory theoretical interpretation of the graph of Figure 5 remains to be found.

Z'' vs Z' plots were constructed for each of the test temperatures. These plots are shown in Figure 6a–d for the indicated diffusion times. On the whole, the plots are seen to be rather distinct, reasonably-shaped semicircles, again reflective of a strong relaxation process. The greatest deviation from this description understandably exists for the condition of zero diffusion time at 85 °C, which is rather close to the unplasticized glass transition state.

The centers of these semicircular arcs can be tortuously located by mathematically fitting circles to all of the corresponding data points in the usual way. When the center lies on the Z' axis, the physical process is characterized by a single relaxation time, and when the center falls below this axis, there is a distribution of relaxation times, the distribution being broader the more the semicircle is depressed downward. Having located the center, the angle θ, depicted in Figure 2, is determined and considered to be a distribution-of-relaxation-times parameter. We, on the other hand, have chosen to quantify the distribution of relaxation times by computing the ratio, r, of the height $= a$ (i.e., the distance of the maximum point on the semicircle, from the Z' axis) to the half-width $= b$ (i.e., half the distance between the Z' intercepts of the semicircle) of the arc. If r is 1, then there is but a single relaxation time. Furthermore, it can be shown that

$$r = (1 - \sin\theta)(\cos\theta)^{-1} \qquad (3)$$

r decreases as θ increases from 0 to $\pi/2$. For a single relaxation time, $r = 1$.

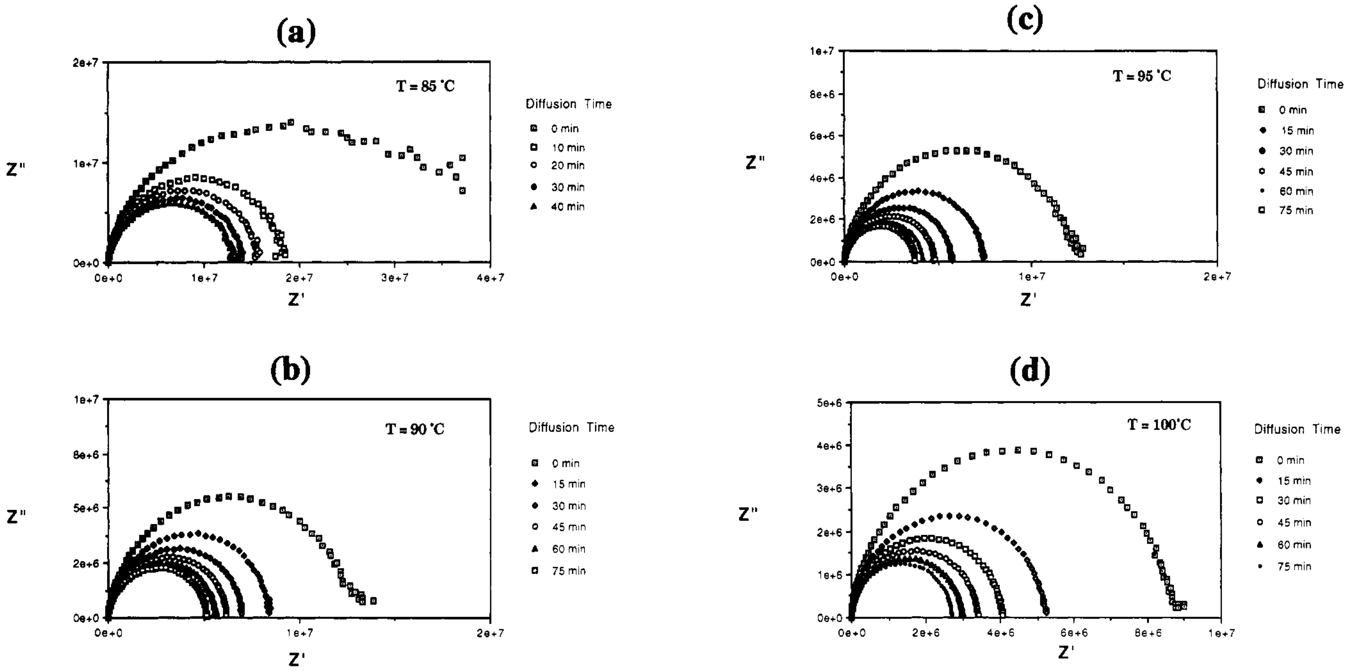

Figure 6. Z'' vs Z' plots for indicated diffusion times at constant temperatures of (a) 85, (b) 90, (c) 95, and (d) 100 °C.

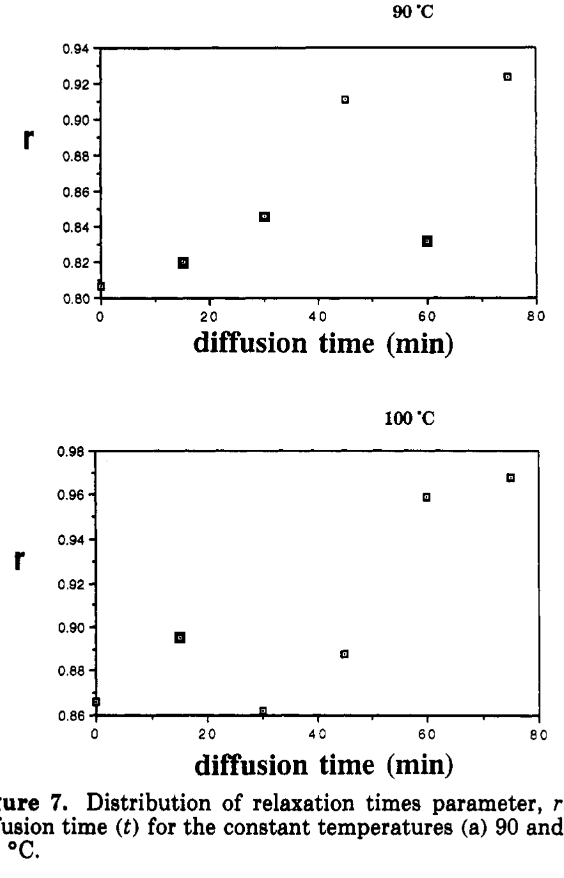

Figure 7. Distribution of relaxation times parameter, *r*, vs diffusion time (*t*) for the constant temperatures (a) 90 and (b) 100 °C.

An upward progression of *r* with diffusion time for 90 and 100 °C is seen in Figure 7. Although the data fluctuate, on the whole there is a clear indication of the evolution of an increasingly greater degree of microstructural homogeneity. In crude molecular terms, as the plasticizer concentration profile becomes more uniform across the film thickness, the distribution of free volume becomes uniform as well. Therefore, the molecular environments about the relaxing elements are increasingly similar. At higher temperature, plasticizer diffusion is faster and higher values of *r* are seen over the range of experimental times.

Conclusions

It has been demonstrated in this work that electrical impedance spectroscopy can be used to monitor the above-T_g isothermal diffusion of a plasticizer, in this case, di-*n*-hexyl phthalate, in PVC films. The films, having been totally submerged in a plasticizer reservoir, were removed from the liquid before the D*n*HxP gradients across the film thickness became uniform, i.e., before swelling equilibrium was attained. The observation of dynamic impedance spectra attests to a preequilibrium condition. The diffusion process causing the redistribution of plasticizer during the approach toward thermodynamic equilibrium was of interest in this study. The main difference between this approach in contrast to direct diffusion studies is that here the emphasis is on the motions of the polymer chains rather than on the motions of the penetrant molecules.

Isothermal Z'' vs f plots show relaxation peaks that shift to higher frequencies with increasing diffusion time. This primary relaxation was associated with the long-range polymer chain segmental mobility that is activated at the glass transition (α process). The steady shift of this peak to higher frequencies indicates increasingly shorter motional time scales of the polymer chains. In turn, this enhanced chain segmental mobility over the macroscopic ensemble was attributed to the progressive redistribution of free volume throughout the sample domain. The frequency at peak maximum was seen to increase linearly with diffusion time at a constant temperature. As the temperature increased, the slopes of these lines increased.

Isothermal Z'' vs Z' plots are distinct semicircles whose centers are depressed below the Z' axis, indicating a distribution of relaxation times. A distribution of relaxation times parameter was extracted from the degree of semicircle depression. The general trend of this parameter with diffusion time portrays a situation consisting of a continually decreasing degree of microstructural heterogeneity as the distribution of free volume becomes more uniform.

To be sure, these studies are but exploratory in nature and similar experiments with phthalates of different chain lengths and various degrees of chain branching, as well as with other large plasticizers, need to be performed in the future to establish relaxation trends with penetrant molecular structure.

In a more general sense, the results of this investigation reinforce the concept that electrical impedance spectroscopy is a tool that can monitor the time evolution of polymer chain dynamics in the presence of diffusing, plasticizing molecules.

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Registry No. PVC (homopolymer), 9002-86-2; D*n*HxP, 84-75-3.