

A dielectric study of poly(vinyl acetate) using a pulse-probe technique

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Abstract There is considerable literature available that describes our understanding of the viscoelastic properties of polymers subjected to mechanical stresses or deformations. What we refer to here as a pulse-probe technique is one method that is commonly used to study the time-dependent behavior of materials in histories, e.g., temperature-jump or step-deformations, that exhibit fading memory responses. In the linear case the behavior is well understood in the context of Boltzmann superposition ideas. However, there is only limited work available that investigates the dielectric response of materials within this same context. In the present study, we present an investigation of the dielectric behavior of poly(vinyl acetate) (PVAc) using a two-step pulse-probe technique. Time domain dielectric experiments were performed in the vicinity of the glass transition temperature. After establishing the linear response function in single-step experiments, two types of pulse-probe experiments were performed. In one, the time duration t_1 of the first step in the probe was varied. In the second case, the magnitude of the field E_1 applied to the sample for the first step was varied. We not only demonstrate the existence of the memory effect in the dielectric response, but also find that the responses are consistent with the linear Boltzmann superposition principle. Evidence of deviations from linear superposition at the highest electric fields is also presented.

Keywords Dielectric spectroscopy · Pulse-probe method · Boltzmann superposition · Poly(vinyl acetate) (PVAc) · Nonlinear spectroscopy

Introduction

Dielectric spectroscopy is normally performed in the frequency domain and in the linear response regime [1–3]. It is used as a tool to characterize materials and often the results of dielectric response in the linear regime are compared with mechanical and rheological measurements. The pulse-probe technique is one method used to study time-dependent responses in temperature jumps [4] and nonlinear mechanical or rheological measurements [5–8]. In this study, we present results from time domain dielectric spectroscopy experiments in which we explore the limits of linearity in poly(vinyl acetate) (PVAc). In particular, we used a pulse-probe method. The way in which the experiments are carried out is similar to the single- and double-step strain or stress experiments commonly used in nonlinear viscoelasticity investigations [5–8].

Dielectric properties such as dielectric compliance and modulus are analogous to mechanical properties such as shear compliance and modulus [9]. The equivalents to mechanical stress and strain in a dielectric measurement are the dielectric stress (applied electric field) and the dielectric strain (polarization). The equation relating the time-dependent dielectric compliance $\varepsilon(t)$ to the applied field ΔE and the polarization ΔP is [9]

$$\varepsilon(t) = \frac{\Delta P(t)}{\Delta E \varepsilon_0} \Leftrightarrow \frac{\text{Dielectric strain}}{\text{Dielectric stress}} \quad (1)$$

where ε_0 is the dielectric permittivity of vacuum. Importantly, Eq. 1 is valid in ideal situations in which the field is applied instantaneously, i.e., a step-pulse measurement and does not decay with time. Here, we found that the time decay of ΔE is small enough that the errors introduced by treating the data as ideal constant dielectric stress experiments are negligible.

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In the present study, we use time domain dielectric spectroscopy, a method pioneered by Mopsik et al. [10–12] to investigate the dielectric responses of small molecule liquids and polymers. The method has been extended by Richert and Wagner [13] through the development of time domain modulus spectroscopy to investigate dynamic heterogeneity in small molecule glass formers and polymers. These studies were confined to the linear domain and the responses were well explained using classic descriptions such as the Kohlrausch–Williams–Watts (KWW) [14, 15] and modified KWW [16] functions to describe the time-domain responses and the Vogel–Fulcher–Tammann [17–19] expression to describe the temperature dependence of the relaxation or retardation times near to the glass transition temperature.

As noted above, linear dielectric spectroscopy is generally used in the frequency domain rather than the time domain. Frequency domain measurements, however, have also been used to study the nonlinear dielectric response of materials. For example, Furukawa and Matsumoto [20] studied the nonlinear dielectric response of PVAc by obtaining the first and third harmonics in the frequency domain in samples subjected to increasing electric field. This is similar to the attempts by Davis and Macosko [21] to use modified Boltzmann superposition [22, 23] to study the nonlinear viscoelastic behavior of polymers subjected to large mechanical deformations. A similar study has recently appeared from Wilhelm's group in which Fourier transform rheology is used to characterize the higher harmonics of the extremely nonlinear rheological response of polymers and other complex fluids [24, 25]. In addition, mixed mode experiments have been carried out in which large amplitude sine waves are followed by single-step small probes or time-domain measurements to examine the nonlinear response of glass-forming liquids and polymer melts and solutions. For example, Schiener et al. [26] established the dielectric hole burning method using experiments on supercooled propylene carbonate and Shi and McKenna [27] developed a mechanical hole burning experiments using a polyethylene melt and a polystyrene solution as example systems. Richert and Weinstein

[28, 29] have studied the nonlinear dielectric behavior of supercooled liquids by subjecting them to several cycles of sinusoidal waves of high amplitude followed by a wait time and a small step (time domain) probe.

Prior to this study, there have been only limited reports in the literature of using the pulse-probe technique to study the dielectric behavior of materials. Bohmer et al. [30] used the pulse-probe technique to study the dielectric responses of super cooled liquids. They observed the memory effect similar to that observed in thermal and mechanical measurements [4, 5]. An interesting early study from the 1890s by Hopkinson reports a memory effect in simple glasses subjected to reversing polarity. This work was cited by Whitehead in a 1927 treatise [31]. There, the Boltzmann superposition principle [22] was used to predict the same.

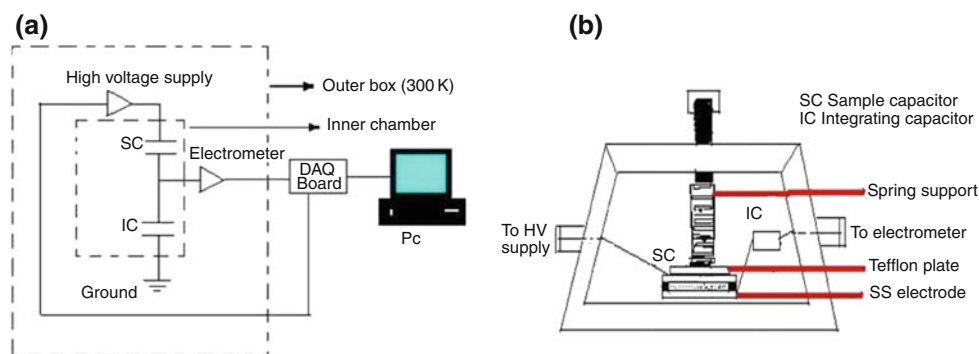
In the present investigation, we test the limits of Boltzmann superposition [22] for the dielectric response of PVAc in pulse-probe experiments. For this, we have performed single-step time domain response and two-step (pulse-probe) measurements having different amplitudes and durations in the vicinity of the glass transition. This is the first of a series of work to be later extended to study the nonlinear dielectric time-domain response using the modified Boltzmann superposition principle [21, 23] and the pulse-probe method as developed here.

Experimental

Dielectric experiments were performed using a time-domain dielectric spectrometer built at Texas Tech University. A schematic of the experimental setup is shown in Fig. 1a. The system consists of a high-voltage supply (TREK model 610), electrometer (Keithley model 6514), sample capacitor (two steel plates with the polymer film in between), integrating capacitor, and DAQ board interfaced with the computer via LABVIEW®.

PVAc of molecular weight 157000 g mol⁻¹ purchased from Scientific Polymer Products, Inc. was used for the experiments. The glass transition temperature T_g of this PVAc as previously measured by our group using DSC at a

Fig. 1 **a** Schematic of time domain dielectric spectrometer and **b** sample holder setup built at Texas Tech



cooling rate of 10 K min⁻¹ was reported to be 303.6 K [32]. The sample was made by placing the pellets between thin brass sheets placed between two thick brass plates and then pressed at 333 K in a platen press. After that, the sample is cut into a circular section to fit the electrode plate, then held tight using a spring support and annealed at 338 K (above the *T_g*) before performing the experiments. The loaded spring setup helps to establish and maintain good contact between electrodes and polymer. The figure for the sample support setup is given in Fig. 1b. PVAc films of thickness 185 ± 10 μm were used for the single-step isothermal measurements to examine the time-temperature superposition behavior of the PVAc. The same film thickness was used for two-step pulse-probe experiments in which the first step duration *t*₁ was varied. Films of 112 ± 8 μm thickness were used for the experiments in which the electric field *E*₁ was varied. The sample was cut into size and placed into the dielectric cell for measurement.

Methods of analysis

The dynamic response of many liquids can be described by the stretched exponential or so-called KWW function shown in Eq. 2 [14–16, 33]. However, because the shape of the dielectric compliance response shows a sigmoidal-like shape, it can be necessary to apply a modified KWW function [16] as shown in Eq. 3 to capture the full response. Furthermore, when there is a longtime process such as the viscosity in viscoelastic creep measurements [34] or the conductivity in dielectric creep, it may be necessary to add an additional term as in Eq. 4.

$$\varepsilon(t) = \varepsilon_1 * e^{(t/\tau)^\beta} \tag{2}$$

$$\varepsilon(t) = \varepsilon_1 + \varepsilon_2 * (1 - e^{-(t/\tau)^\beta}) \tag{3}$$

$$\varepsilon(t) = \varepsilon_1 + \varepsilon_2 * (1 - e^{-(t/\tau)^\beta}) + \frac{t}{\tau_c} \tag{4}$$

where $\varepsilon_1, \varepsilon_2, \tau, \tau_c,$ and β are fit parameters. Here τ is the retardation time and τ_c is the conductivity term. We find that Eq. 3 describes the recoverable part of the dielectric compliance and the full response of $\varepsilon(t)$ is well described by Eq. 4. This separation of Eq. 4 into a recoverable term and a conductivity term is used subsequently.

To test the validity of Boltzmann superposition for the two-step dielectric response, we used the Boltzmann equation as rearranged by Riande et al. [35] and implemented numerically by our group [32]:

$$\Delta P(t) = \varepsilon_g E(t) + \int E(t - t') \frac{d\varepsilon(t')}{dt'} dt' \tag{5}$$

Hence, ΔP is the predicted dielectric strain, $E(t)$ the applied dielectric stress for the two-step test in the experiment analyzed, ε_g the dielectric compliance at zero time, and $\varepsilon(t)$ is the modified KWW (Eq. 3) fit to the single-step, recoverable, linear dielectric compliance response.

Results

Single-step response

Isothermal measurements of the dielectric response (compliance) for the PVAc were performed in a temperature range of 303 to 333 K and the data are shown in Fig. 2a. The solid lines in Fig. 2a are the fits to the data at each temperature using the modified KWW function with conductivity contribution given in Eq. 4. Similar studies on PVAc have been performed by various groups [1, 13, 36]. The reason for using Eq. 4 is to separate the effect of dc conductivity from the dielectric compliance response and also to examine the time-temperature superposability of the dielectric response separate from the dc conductivity. The fit parameters for Eq. 4 for the 308 K reference temperature are given in Table 1. The β parameter obtained at the reference temperature was kept fixed for fitting the data at the remaining temperatures. We observed an increase in

Fig. 2 a Isothermal measurement and **b** master curve for PVAc with 308 K as reference temperature

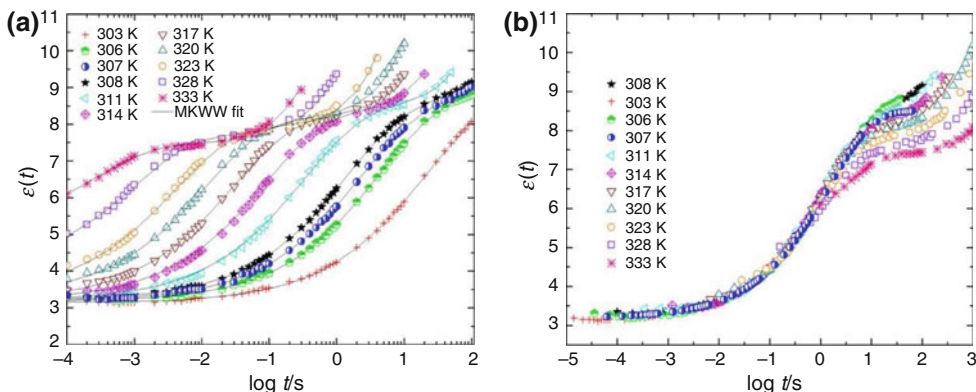


Table 1 Fit parameters for Eq. 4 at 308 K

ε_1	ε_2	β	τ/s	τ_c/s
3.21 ± 0.0096	5.34 ± 0.017	0.5 ± 0.005	1.43 ± 0.03	164 ± 5.25

Errors represent standard error of estimate on the fit parameters

the ε_1 parameter and decrease in ε_2 parameter with increasing temperature for the above-used function as shown in Fig. 3. Both the conductivity term and retardation time decreased with increasing temperature.

Figure 2a shows that, with increasing temperature, the curves shift to shorter times. We attribute the steep rise after the secondary plateau to the dc conductivity [9, 13]. Richert and Wagner [13] used two KWW functions to capture the entire spectrum of data in their study on dielectric modulus. As noted above, we have used a term similar to the viscosity term in linear viscoelasticity but for the conductivity added to a modified KWW function to fit our data (see Eq. 4). Figure 2b is the master curve for the data of Fig. 2a with 308 K as the reference temperature. The data at the longer times do not superimpose and we hypothesize this to be due to the domination of dc conductivity over dielectric response.

The retardation time τ and the conductivity term τ_c obtained from Eq. 4 for the isothermal measurements of PVAc shown in Fig. 2a are plotted as a function of inverse temperature in Fig. 4. The data are fitted using the VFT function given in Eq. 6 [37]. The fit parameters are given in Table 2. The fit parameters for the dielectric retardation time and the dc conductivity term are different which explains the spread of the dielectric response at longer times in Fig. 2b.

$$\log \tau = -A + \frac{B}{(T - T^0)} \tag{6}$$

where A , B , and T^0 are fit parameters.

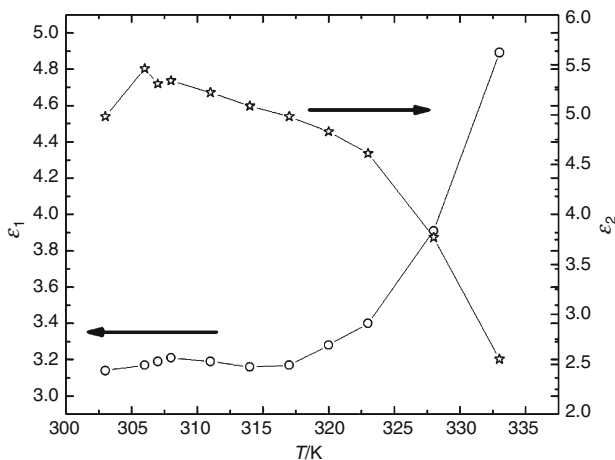


Fig. 3 Equation 4 parameters ε_1 and ε_2 as a function of temperature

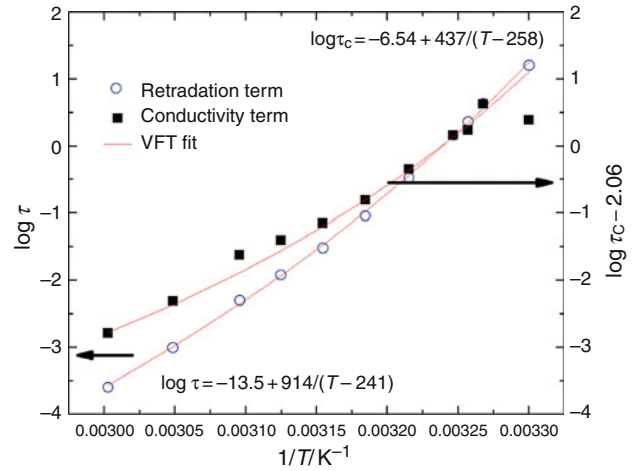


Fig. 4 Dielectric retardation time τ and dc conductivity τ_c term plotted as a function of inverse temperature. The solid lines represent the VFT fits

Table 2 A , B , and T^0 from VFT fits for the retardation time and the dc conductivity term versus temperature obtained by fitting the data in Fig. 2a to Eq. 4

Time constants	A	B/K	T^0/K
$\log \tau$	13.5 ± 0.95	914 ± 87	241 ± 4.8
$\log \tau_c$	6.54 ± 0.85	437 ± 110	258 ± 9.8

Errors represent standard error of estimate on the VFT fit parameters

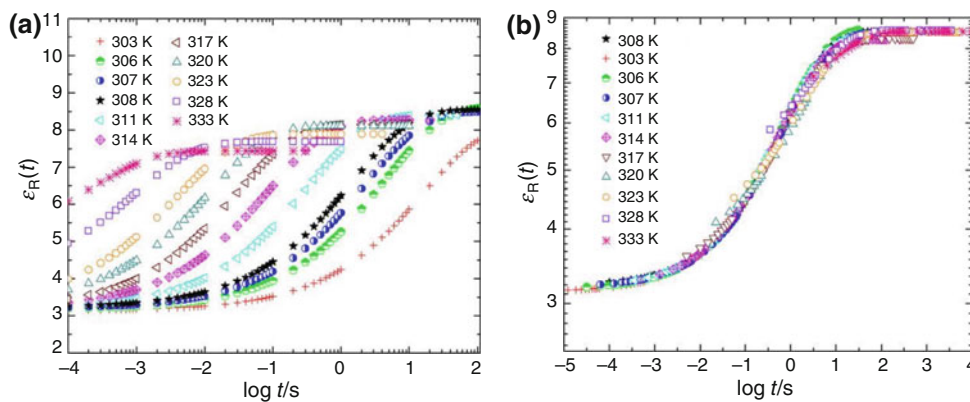
To confirm the above hypothesis, the recoverable dielectric compliance (which is the difference between the dielectric compliance and the conductivity term) was estimated using Eq. 7.

$$\varepsilon_R(t) = \varepsilon(t) - \frac{t}{\tau_c} \tag{7}$$

where $\varepsilon_R(t)$ is the recoverable dielectric compliance.

For each fit of Eq. 4 to the data of Fig. 2a $\varepsilon_R(t)$ was determined and the recoverable dielectric compliance response functions are plotted in Fig. 5a. In fact, these are described by the modified KWW function presented in Eq. 3. Figure 5b gives the master curve for the recoverable compliance data with 308 K as the reference temperature. We also observed softening-like behavior of the secondary plateau with increasing temperature. This can be explained by the increase in ε_1 and decrease in ε_2 parameters of Eq. 4 with temperature as shown in Fig. 3. In Eq. 4 the parameter ε_1 is related to the glassy (short time) response and ε_2 is related to the transition toward the longtime plateau response. This kind of softening behavior with increasing temperature is also observed for dielectric responses in the frequency domain in the literature [9]. By shifting the curves vertically for the higher temperature data in addition to the horizontal shift, we obtain a reasonable time temperature

Fig. 5 **a** Dielectric recoverable compliance and **b** master curve for PVAc with 308 K as reference temperature



superposition. In Fig. 6 we compare the horizontal shift factor data for the dielectric recoverable compliance with Plazek’s recoverable creep compliance data [38] and Richert’s (digitized) dielectric modulus [13] data. The results are in good agreement with Richert’s dielectric data. Somewhat surprisingly, the data of Fig. 6 show that the dielectric response seems to follow Plazek’s terminal dispersion data rather than the softening dispersion data. A similar sort of behavior has also been observed by Zorn et al. [12] in their study on polybutadienes.

Two-step (pulse-probe) response

Prior to performing a two-step experiment, we checked the effects on the dielectric compliance due to the small drift in the dielectric stress (ΔE in Eq. 1) as a function of time. We used the Boltzmann equation given in Eq. 5 to obtain the true compliance data for the single step as implemented by our group previously [32]. We observed that there is no significant difference between the apparent and true

compliance for the above material, indicating that the effect of the time varying dielectric stress is very weak. The comparison is shown in Fig. 7. Hence, we have used the data as obtained for the experiments without the additional use of the full Boltzmann equation.

The dielectric compliance response of PVAc in the variable duration first step, two-step pulse-probe experiments is shown in Fig. 8. The experiments were performed at 302.8 K. The electric field-jump is made from 10.8×10^5 to $5.4 \times 10^5 \text{ V m}^{-1}$ at varying jump times t_1 of 0.25, 0.5, and 1 s. In all the cases, we see a typical nonmonotonic memory response similar to what is observed in thermal [4] and mechanical responses [5] to stepwise histories. In Fig. 9, two-step pulse-probe responses after decreasing the field from E_1 to $44.6 \times 10^5 \text{ V m}^{-1}$ for different values of E_1 are shown. This is a ‘down-jump’ experiment. As the down-jump magnitude increases the memory effect lasts for longer times.

When the response is linear, we expect Boltzmann [22] superposition to hold. To test this for the two-step pulse-probe experiments, we applied Eq. 5, using the single-step response function determined above (recoverable part) and the experimentally applied fields for each step, to calculate

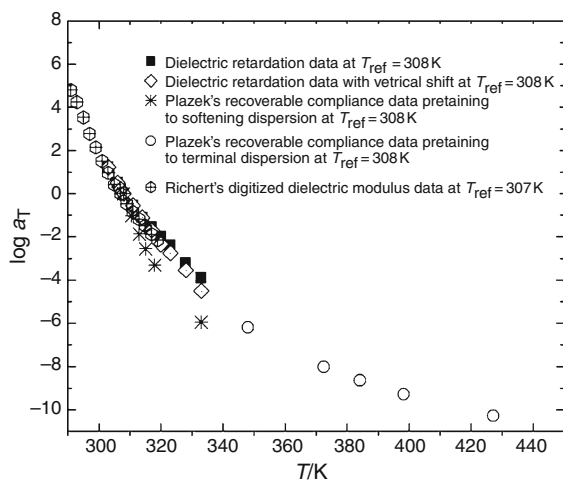


Fig. 6 Time–temperature shift factors as a function of temperature for PVAc. Comparison of current dielectric results with literature reports for dielectric [13] and mechanical [37] behaviors

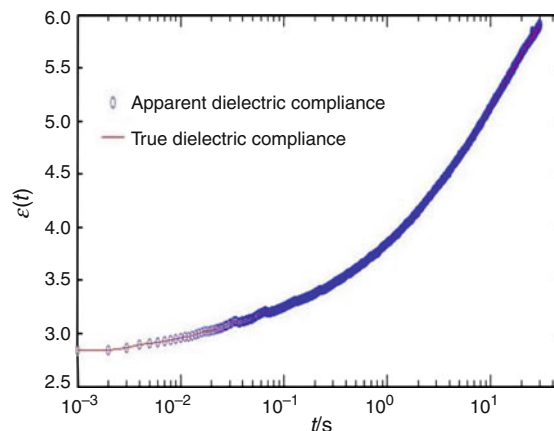


Fig. 7 Comparison of apparent dielectric compliance with true dielectric compliance for an applied electric field of $5.4 \times 10^5 \text{ V m}^{-1}$

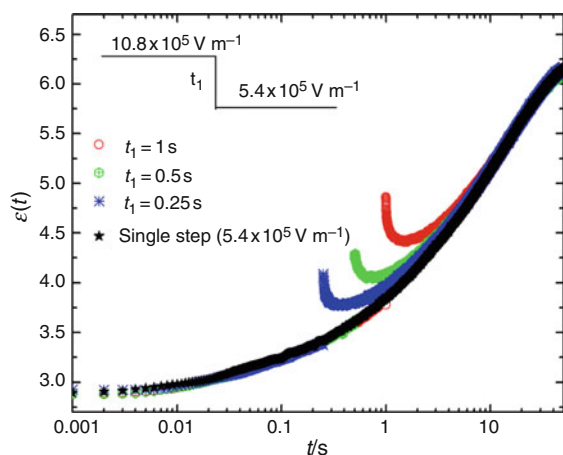


Fig. 8 Dielectric compliance response in two-step pulse-probe experiments with varying time duration t_1 of the first step

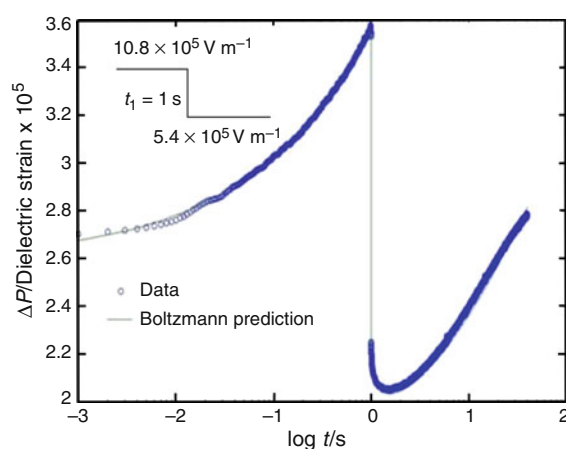


Fig. 10 Dielectric strain response for the 1 s jump of Fig. 8. The solid line represents the Boltzmann prediction

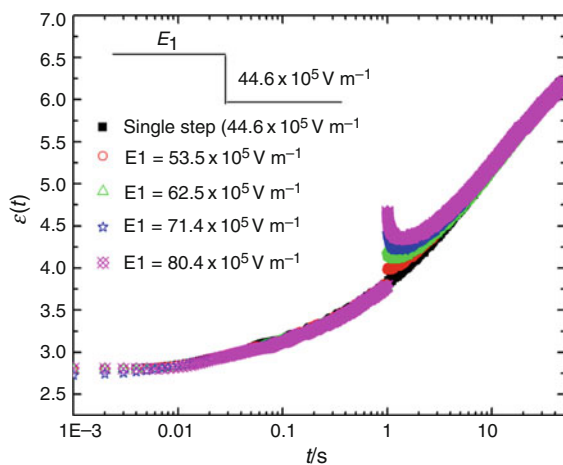


Fig. 9 Dielectric compliance response in two-step pulse-probe experiments with varying electric field E_1 of the first step

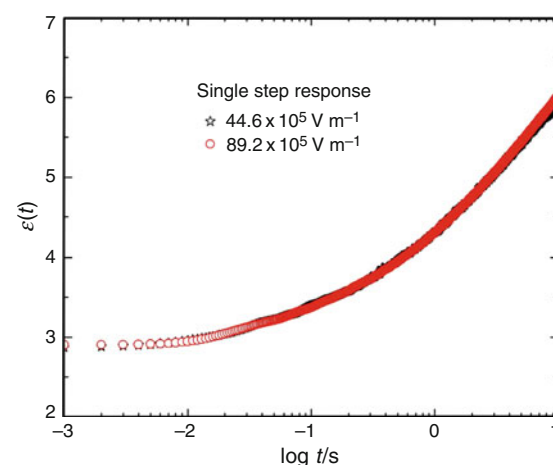


Fig. 11 Single-step responses for applied electric field of 44.6×10^5 and 89.2×10^5 V m^{-1}

the expected second step response. Equation 5 was solved using a MATLAB program based on a numerical integration method used previously by our group [32]. Comparison of the dielectric strain response from the experiment for the 1 s jump depicted in Fig. 8 with the Boltzmann prediction is shown in Fig. 10. The results are in good agreement, confirming that the dielectric response of the two-step pulse-probe is in the linear regime for the above experimental conditions.

On the other hand, for the largest down-jump investigated, that from 89.2×10^5 to 44.6×10^5 V m^{-1} , the outcome is different although the single-step response at this applied field is in good agreement with Boltzmann superposition (see Fig. 11). As shown in Fig. 12 the Boltzmann superposition prediction deviates from the observed second step response showing evidence of nonlinear behavior. For comparison, Richert and Weinstein observed nonlinear behaviors in small molecule liquids at a

high applied electric field [27, 28] in frequency domain spectroscopy.

Discussion

Time-domain dielectric spectroscopy has been used to characterize the linear response of PVAc. We found that the response was well fitted using Eq. 4, which is basically the modified KWW function (Eq. 3) plus an additional term for conductivity. This is equivalent to the use of a viscosity term in creep compliance determinations in linear viscoelasticity [34]. The conductivity and the retardation terms show different temperature dependences which explain the spread of data at longer times. Richert and Wagner [13] also observed this kind of behavior in their dielectric relaxation work on PVAc. By subtracting the conductivity term, we obtain the dielectric recoverable

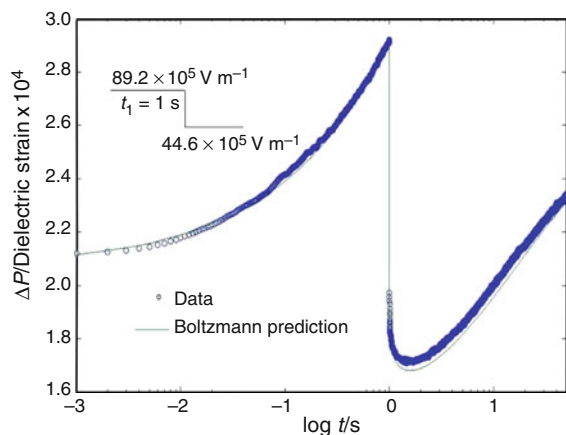


Fig. 12 Two-step dielectric compliance response (jump from 89.2×10^5 to $44.6 \times 10^5 \text{ V m}^{-1}$) with linear Boltzmann prediction showing deviation from linear behavior

compliance of the material which is analogous to the recoverable creep compliance in linear viscoelasticity [34, 38].

The recoverable dielectric compliance plotted as a function of time in Fig. 5a clearly shows a softening-like behavior with increasing temperature similar to that for frequency response data reported in the literature [9]. This can be attributed to the change in ε_1 and ε_2 parameters which are related to glassy and longtime plateau responses, respectively. The recoverable dielectric compliance is found to follow time–temperature superposition with ε_1 and ε_2 changing with temperature. To our knowledge, other workers have not explicitly written the dielectric compliance in an equivalent fashion (directly analogous to the creep compliance in mechanics; Eq. 4). The temperature shift factors for the dielectric recovery are found to be the same as those determined by Richert and Wagner [13] for dielectric modulus. Surprisingly, the dielectric shift factors seem to follow the terminal shift factors determined by Plazek [38] in shear experiments and differ from the mechanical segmental shift factors. This is a surprise because the type B dipole in PVAc should reflect molecular motions that are local rather than long chain motions related to the terminal relaxations.

Two-step pulse-probe experiments were performed to test the limits of linearity in PVAc. We observed the classical memory response similar to that observed by others for dielectric behavior [30, 31] and in volume recovery after temperature jumps [4] and in two-step mechanical experiments [5]. The experiments demonstrate that memory depends on both the time duration of the first step and the magnitude of the field jump. We observed that for small jumps, Boltzmann superposition is valid. For larger jumps, we find deviations from linearity as observed by the over prediction of the memory response by Boltzmann superposition in spite of the fact that the single step

response at the same field magnitudes were in the linear regime as evidenced in Fig. 11. This suggests that the two-step pulse-probe method may be a sensitive approach in dielectric spectroscopy to delineate the linear to nonlinear transition in behavior.

Conclusions

Time-domain dielectric spectroscopic measurements were performed on a PVAc polymer near to its glass transition temperature. Time–temperature superposition of the response was not strictly valid due to the existence of different shift factors for the recoverable portion of the dielectric compliance and for the conductivity contribution to the response. The shift factors agree with those for dielectric modulus measurements [13] and terminal relaxation response in mechanical measurements [38] reported in the literature. A modified KWW function with an additional term for the dc conductivity was able to capture the entire experimental regime with the retardation time τ for the recoverable compliance term and the conductivity contribution τ_c showing different temperature dependence.

A two-step pulse-probe technique was used to study the dielectric behavior of PVAc in the context of the Boltzmann superposition. We observe a memory effect similar to those observed in mechanical [5] and thermal responses [4]. The memory effect observed was in quantitative agreement with linear Boltzmann superposition for small applied fields. Evidence of nonlinearity is observed when the polymer was subjected to higher electric field. This nonlinear dielectric response is currently under further investigation.

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