Subglass Relaxations. Mechanical versus Dielectric Relaxation in Poly(vinyl acetate) and Its Ethylene Copolymers

Grant D. Smith, Fuguo Liu, Russell W. Devereaux, and Richard H. Boyd*

Department of Materials Science and Engineering and Department of Chemical Engineering, University of Utah, Salt Lake City, Utah 84112

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ABSTRACT: The complex shear moduli of poly(vinyl acetate) (PVAc) and two of its copolymers with ethylene have been measured in the subglass relaxation temperature region using a torsion pendulum. Previous dielectric relaxation data have been supplemented by additional measurements. The mechanical and dielectric relaxation features are in accord with similarities and differences expected on the basis of a previous interpretation of dielectric relaxation. For example, the copolymers both mechanically and dielectrically show two subglass relaxations, one related to the β subglass side-group reorientation relaxation in PVAc homopolymer and the other related to the γ subglass relaxation in PE. However, the relative strengths of the processes are quite different in the two types of relaxation experiments. The differences are consistent with the PE γ process being inherently strong mechanically but inactive dielectrically and the β process being active in both types of relaxation but being relatively weak in both cases due to a substantial site energy difference for side-group reorientation in the vinyl acetate moieties. Mechanical measurements were also made on poly(methyl acrylate) homopolymer (PMA). The β subglass process is, as was previously found to be the case dielectrically, considerably stronger than in the vinyl acetate polymers. This is consistent with the side-group reorientation site energy difference being smaller than in VA polymers, as was previously proposed. The effect of absorbed moisture on subglass relaxation in the VA polymers was studied dielectrically. Water was found to have a strong plasticizing action on the β subglass process but not on the γ. An additional relaxation, labeled β', was found in PVAc homopolymer between the glass rubber α relaxation and the β subglass process. It is speculated that it may be due to cis–trans isomerism of the ester groups.

Introduction

The pendent ester group has proven to be a useful model for elucidating subglass relaxations attributed to flexible side-group reorientation.[1-3] Both vinyl acetate and methyl acrylate polymers (PVAc and PMA), which differ only in the direction of attachment of the ester moiety, show such subglass processes. The details of the relaxation behavior in the two systems, however, are significantly different.[1,2] As studied by dielectric relaxation spectroscopy, the subglass process in PVAc is much weaker than in PMA. In the latter, its strength is an appreciable fraction of the total relaxation strength, which includes the glass–rubber relaxation. The weakness of the PVAc process relative to that in PMA has been attributed to a greater site energy difference for side-group reorientation in the former.[3] In copolymers of vinyl acetate with ethylene (VA/E), the subglass behavior is complex. There are two poorly resolved broad subglass processes in isochronal temperature scans. The higher temperature one (β) has been attributed to the side-group reorientation and the lower temperature one (γ) to the effect of main-chain subglass motion in the PE segments on the side-group dipoles. That is, nearby main-chain motions associated with the PE subglass γ process cause excursions of the rigid side groups and make the γ process dielectrically active. In methyl acrylate/ethylene (MA/E) copolymers there is but one subglass process. The side-group reorientation and ethylene segment main-chain subglass motions appear to take place isochronally in the same temperature region.

One of the purposes of the present work was to study the same processes via mechanical relaxation, that is, to determine if the above interpretation of subglass processes is consistent with differences in relative strengths to be expected in mechanical relaxation compared to the dielectric case. Previous work on mechanical relaxation in VA/E copolymers was concerned only with the glass transition region and above.[4] Another purpose was to study the vinyl acetate polymers via dielectric relaxation at lower frequencies than previously employed and thus with significantly improved resolution in isochronal temperature scans. Additionally, the presence of absorbed moisture has an effect on the dielectric relaxation in PVAc[5] homopolymer, and a study of this was made in the polymers considered. Finally, an additional relaxation process is found between the α glass–rubber relaxation region and the β side-group rotation process. It has been previously reported only as a possible artifact in mechanical relaxation.[6,7] At the low frequencies employed in the present study it is found to be well resolved and well characterizable dielectrically and is designated as the β' process.

Experimental Section

The polymers studied were from the same source, Scientific Polymer Products, as those used previously.[1,2] They included PVAc homopolymer and two copolymers with ethylene. One of the latter was 20 mol % VA and is the same polymer as previously designated[2] VA40 on the basis of its nominal weight percent VA (43.4% by analysis). Here it is designated "VA×0.20" on the basis of its mole fraction, a more transparent indicator of its molecular composition. The other copolymer used, nominal 70 wt % VA, was found to be 41 mol % VA by C, H, and O analysis (Galbraith Laboratories, Knoxville, TN) and is designated "VA×0.41". The latter sample was not studied by us before, and it is of higher ethylene content than the other copolymers previously considered. A poly(methyl acrylate) homopolymer (PMA) from the same source was also studied.

Dielectric measurements were made on the VA copolymers using a time domain dielectric spectrometer (TDS) made by the IMASS Co. of Hingham, MA. Compression-molded specimens were coated with evaporated gold, and a guard ring was scribed. The TDS instrument permits lower frequency measurements and hence improved peak resolution compared to our previous work.[1,2] After preparation, all samples were kept in a desiccator until used.

As PVAc homopolymer is known to absorb ~4% water when immersed in pure water,[5,8] the effect of small amounts of moisture absorbed in transferring an initially dry specimen into the dielectric cell in starting a run was investigated. This was done as follows. A sample was removed from the desiccator and allowed

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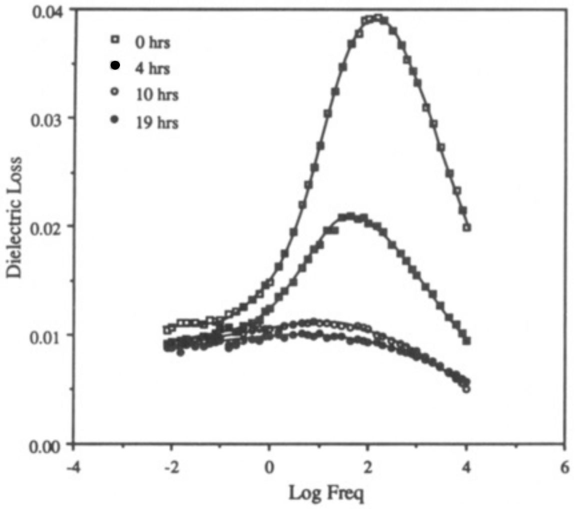

Figure 1. Dielectric loss vs frequency in PVAc homopolymer at 180 K as a function of purge time in the measuring cell (with a dry-N_2 stream) at room temperature.

to equilibrate to ambient atmospheric moisture for several days. The specimen was then supported in its measurement configuration in a small closed chamber within the larger temperature-controlled chamber associated with the TDS. The smaller chamber could be purged with dry nitrogen that is thermally equilibrated with the outer chamber by flowing through a long copper coil situated in the latter. The sample was then purged in a dry-nitrogen atmosphere in the dielectric cell at room temperature for a specified time period before cooling and data acquisition. After return to room temperature the process was repeated for increasing lengths of purge time until no noticeable change in dielectric behavior occurred. This is illustrated in Figure 1 for a PVAc homopolymer. Specimens for which the purge time was sufficient to achieve this condition of no change are referred to as "dry" in the ensuing data displays. Samples that were desiccator dried but exposed to ambient atmosphere while being placed in the dielectric cell or torsion pendulum with no special precautions or extended room temperature purge are referred to as "ambient". Comparing the results in Figure 1 with previously reported data[2,9] for the β relaxation in PVAc homopolymer indicates that those presumably ambient specimens were approximately equivalent to the 4-h purge of Figure 1.

Measurements of the complex shear modulus were made using a torsion pendulum. It is the same as the one previously described[10] but modified for automated operation.[11] By varying the inertia arms and the sample width, the effective frequency of a run could be selected from a range of a factor of approximately 10. In accomplishing multiple-frequency runs, samples for each frequency were cut as parallel strips from the same compression-molded specimen. Three frequencies were studied for each polymer except for PMA where two were employed. Run characteristics are summarized in Table I. All of the mechanical samples were run in the ambient condition described above.

Results and Discussion

Representative relaxation data are illustrated mechanically by the complex shear modulus of ambient PVAc homopolymer in Figure 2 and dielectrically for dry VAx0.20 copolymer in Figure 3. A composite of the mechanical data for all three specimens, PVAc homopolymer, VAx0.20, and VAx0.41, is presented in Figure 4 and for the dielectric data in Figure 5. Although the principal purpose of this investigation was to compare the mechanical and dielectric processes, it is important to understand the effect of absorbed moisture on the relaxations, and this is taken up first.

Effect of Absorbed Moisture on Relaxation. Figure 6 compares the dielectric loss of the three dry polymers of Figure 5 with the same polymers measured in the ambient condition. The cursory observation is that the β process loss peak, previously associated with side-group rotation, is increased in height and displaced to lower temperature isochronally on absorption of some moisture. Although the increase in peak height could indicate that relaxation of water itself takes place, the displacement to lower temperature suggests that plasticization by the water is involved. In fact, the increased peak height turns out to be a manifestation of the isothermal sharpening in the frequency domain that accompanies the plasticizing action of the water. This is illustrated in Figure 7 via Argand plots for PVAc homopolymer. Cole–Cole[12] circular arcs are drawn, although it is to be noticed that for the moisture-containing ambient specimen some systematic deviations are present. In any event, it is apparent that the process is much broader in the dry specimen than in the ambient one. The two Cole–Cole width parameters are 0.17 dry vs 0.34 ambient, based on unity for a single relaxation time. However, it is also to be noticed that the relaxation strengths as represented by the $\epsilon_r - \epsilon_u$ interval on the ϵ' abscissa are nearly identical.

Another observation is that the γ region in the two copolymers is relatively unaffected by the presence of water. Although not well illustrated in Figure 6, the effect of moisture on the α glass–rubber relaxation may be noticed as a shift in the steeply rising high-temperature portion of the loss curves to lower temperature in the homopolymer and the VAx0.41 copolymer. The amount of moisture absorbed by the VAx0.20 sample is too small to have much effect in this connection.

In summary, the effect of water absorption on the subglass processes seems to be described as a plasticizing action on the reorientation of the polar side groups connected with the β process but with little effect on the aliphatic main-chain-related γ process. This is consistent with the water molecules being concentrated at the polar groups and reducing the effective intermolecular barriers to side-group reorientation but not contributing to relaxation themselves in this region. Because of the isothermal frequency-domain sharpening action of the water and because of the extremely broad character in the dry specimens, the β loss peaks are actually better observed in the ambient condition. This is very apparent in the dry VAx0.41 sample dielectric data in Figures 5 and 6b where the labeling of the location of the very poorly resolved β process is indicated by a dashed line.

Comparison of Mechanical and Dielectric Relaxation. It is seen in the mechanical data of Figure 4 that, as in the dielectric case, PVAc homopolymer possesses a β relaxation but no γ one. In the two copolymers the γ process is present, and in the VAx0.41 VA/E copolymer the β process is observed but is not apparent in the VAx0.20 sample. The VAx0.41 copolymer forms a good basis for rationalizing all of these observations. In Figure 8 the shear loss modulus is compared to the dielectric loss for this polymer, both cases being in the ambient condition. There it is seen that the γ process is very prominent mechanically but the β process is only a higher temperature shoulder. Dielectrically the situation is reversed; the γ process is a very weak shoulder on the more prominent β peak. The γ process is a strong relaxation mechanically in polyethylene ($G''_{max} = \sim 8 \times 10^7$ Pa in 40% crystalline BPE[13]), much stronger than the β process peak associated with side-group rotation in PVAc homopolymer (2×10^7 Pa, Figure 4). Thus it is not surprising that the γ process predominates quickly over the β one as ethylene units are introduced into PVAc. Conversely, in the dielectric case relaxation is associated with polar units and thus directly with the side-group reorientation. The γ dielectric activity is attributed to the more indirect action of reorientation of nearby methylene sequences in causing polar group angular excursions

Table I
Sample Characteristics for Torsion Pendulum Runs

			sample dimen, mm				temp, K	
sample and run[a]	VA, mol %	frequency,[b] Hz	length	width	thickness	MI,[c] g mm^2	min	max
VA-lf	100	0.49–0.27	51.1	2.88	0.280	77500	85	306
VA-mf	100	2.2–2.1	51.1	2.88	0.280	3613	105	220
VA-hf	100	3.5–3.3	51.0	10.00	0.236	3613	86	310
VAx0.20-lf	20	0.29–0.20	52.0	5.06	0.219	95300	89	255
VAx0.20-mf	20	1.50–1.20	53.4	10.08	0.151	3613	88	251
VAx0.20-hf	20	3.02–2.05	53.0	10.19	0.255	3613	85	256
VAx0.41-lf	41	0.39–0.27	53.0	1.90	0.337	88560	92	257
VAx0.41-mf	41	0.92–0.63	51.0	5.98	0.391	92600	90	261
VAx0.41-hf	41	4.33–3.05	54.1	5.81	0.380	3613	97	265
MA-lf	100 MA	0.33–0.25	51.2	5.01	0.178	81900	88	290
MA-hf	100 MA	2.51–1.97	51.1	9.98	0.182	3613	89	292

[a] lf = low-frequency. mf = medium frequency. hf = high frequency. [b] Range from the lowest temperature measurement to the high-temperature end of the subglass region. [c] Moment of inertia.

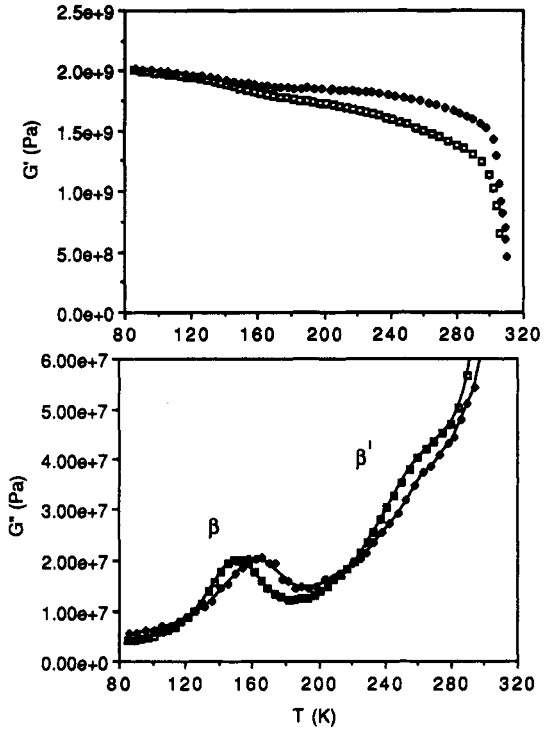

Figure 2. Complex shear modulus (G', upper curves; G'', lower ones) versus temperature for PVAc homopolymer. "Ambient" sample (transfer of an initially dry sample into the apparatus in open atmosphere, no prolonged purge). High (filled points) and low (open squares) frequency runs of Table I.

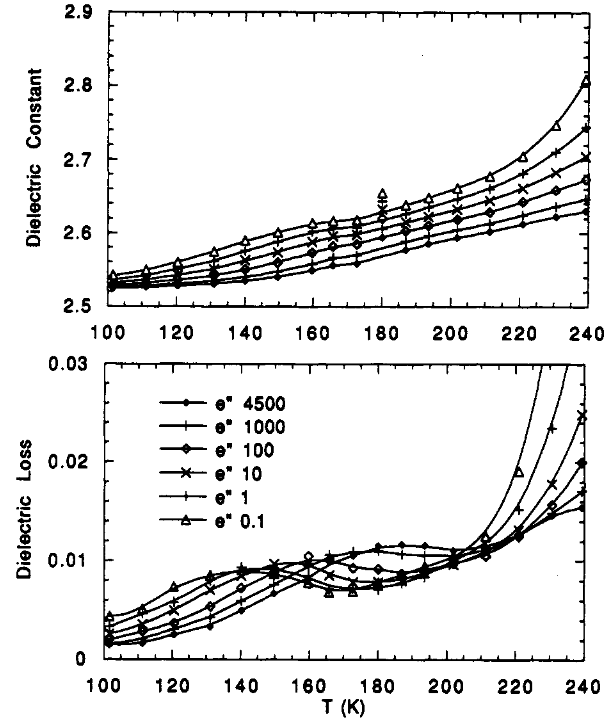

Figure 3. Dielectric constant (upper plot) and loss (lower plot) at the indicated frequencies (Hz) versus temperature for dry VAx0.20 homopolymer.

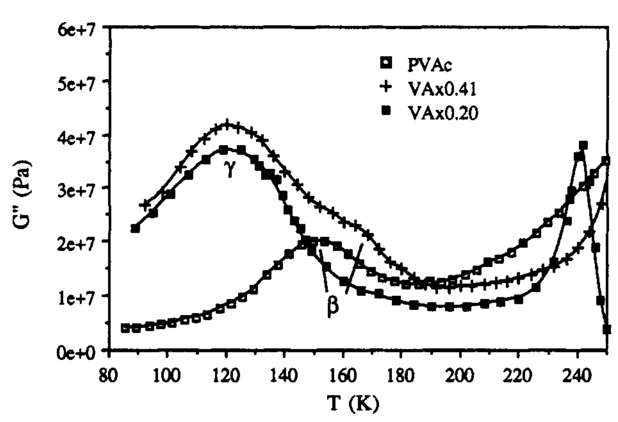

Figure 4. Comparison of shear loss modulus versus temperature (low-frequency runs) for ambient PVAc homopolymer, 41 mol % copolymer VA/E (VAx0.41) and 20 mol % VA/E copolymer (VAx0.20) samples.

without internal rotation of the groups. Thus, the high concentration of polar units in VAx0.41 is sufficient to ensure dominance of the dielectric β process.

A comment on the relative peak heights for the mechanical γ processes shown in Figure 4 is of interest. Assuming that peak heights are reflective of relaxation strength, it is seen that the γ processes in the VAx0.41 and VAx0.20 copolymers are of comparable intensity even though the latter polymer has more methylene units. This is probably ascribable to the fact that the former is totally amorphous while the latter contains significant crystallinity and that the γ process is attributable morphologically[14] to the amorphous phase.

Loss maps for the mechanical and dielectric data for the three VA polymers are displayed in Figures 9–11. Arrhenius parameters for the processes are given in Table II. Data for the mechanical[15] and dielectric[16] γ processes in branched polyethylene (BPE) are also included in Figures 10 and 11 and in Table II. BPE is the appropriate comparison with PE for the copolymers since both are made by the high-pressure free-radical method and are branched. The similarity in time–temperature behavior for the γ processes in the VA/E copolymers with BPE is to be noticed. The plasticizing action of water on the β processes is also apparent as isochronal shifts to lower temperature.

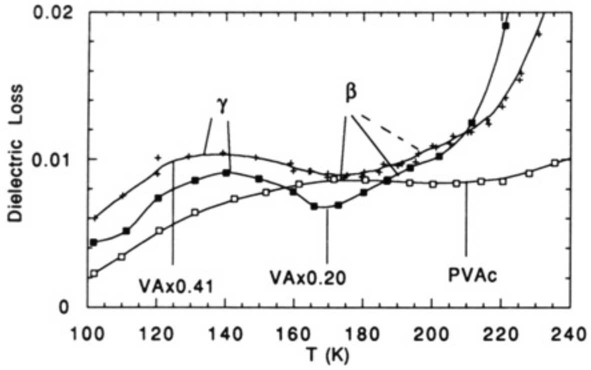

Figure 5. Comparison of dielectric loss for dry PVAc, VAx0.41, and VAx0.20 samples. Isochronal scans at 0.1 Hz versus temperature.

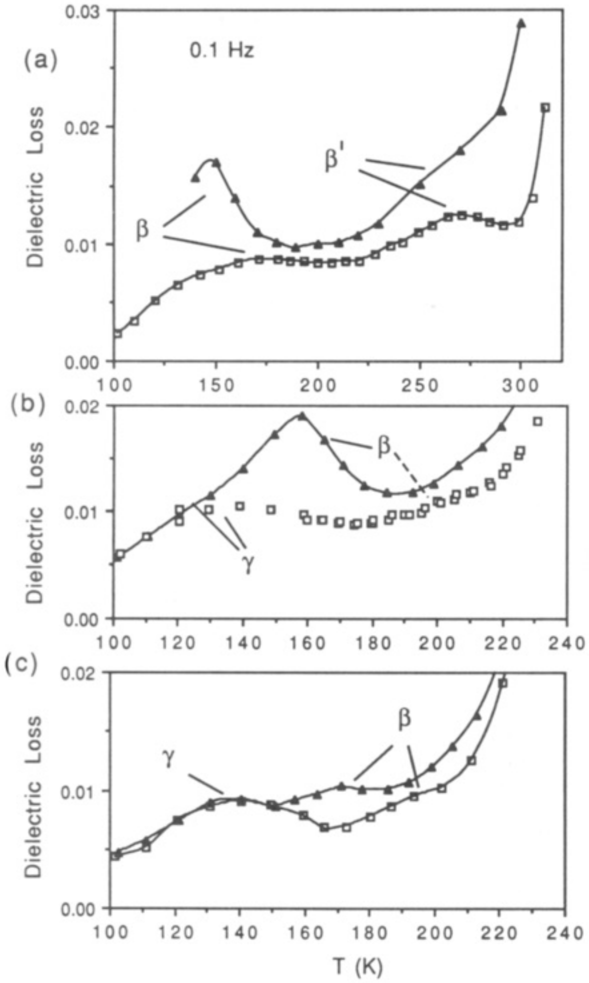

Figure 6. Effect of moisture on dielectric relaxation. Comparison of dielectric loss in dry (open squares) and ambient transfer (filled points) samples of (a) PVAc homopolymer, (b) VAx0.41, and (c) VAx0.20 copolymers. Isochronal scans at 0.1 Hz versus temperature.

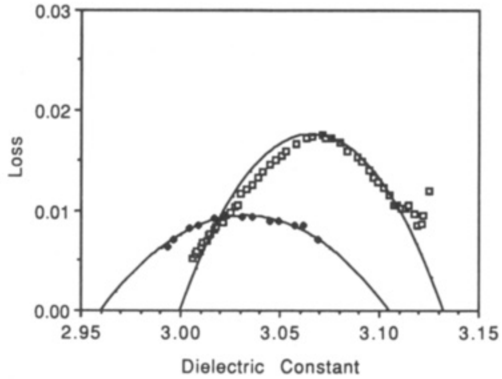

Figure 7. Effect of moisture on dielectric relaxation. Argand diagrams for the β dielectric relaxation process in PVAc homopolymer (filled points, dry specimen at 187 K; open squares, ambient transfer specimen at 160 K). Curves are Cole–Cole circular arc function fits. Width parameters are given in text.

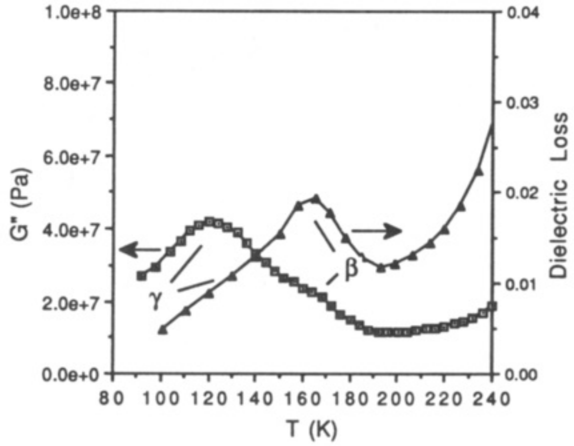

Figure 8. Comparison of mechanical loss modulus, G'' (left-hand ordinate, squares), with dielectric loss (right-hand ordinate, filled triangles) in VAx0.41 copolymer. Both are ambient specimens. The frequencies of the isothermal scans are similar, 0.45 Hz dielectrically, for a low-frequency sample and ~0.3 Hz mechanically (see Table I).

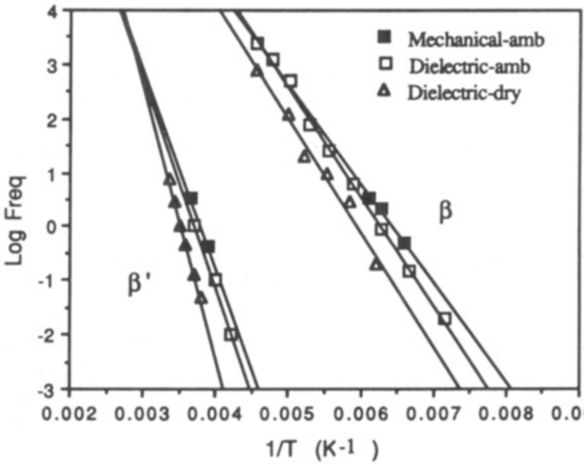

Figure 9. Loss map, log f_{max} (isochronal) versus $1/T$, for PVAc homopolymer.

The shear modulus and loss of PMA homopolymer is shown in Figure 12. The mechanical results, in common with the previous dielectric results,[1] show the presence of but one subglass process. This is the same situation that is found in PVAc (excluding the β' process). However, the β process strength as indicated by the loss peak height and especially by the increment in the modulus is much greater in PMA than in PVAc. This is consistent with the dielectric findings[1] where the much weaker β process in PVAc as compared to PMA was attributed to[1,2] and explained by[3] a higher intramolecular site energy difference for side-group reorientation in PVAc. This same feature would also decrease the mechanical strength in VA compared to MA in a site model interpretation.

The inherent weakness of the VA β process both dielectrically and mechanically is also evident in the VAx0.20 data in Figures 4–6. Mechanically in Figure 4 the β process is no longer observable even though there is still a substantial VA content. Dielectrically in Figures 5 and 6 the β and γ processes are of comparable strength even though the β process is directly associated with the polar

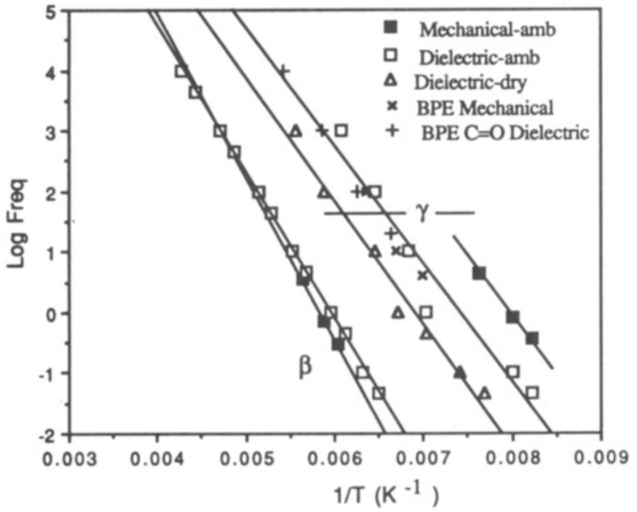

Figure 10. Loss map, $\log f_{\max}$ (isochronal) versus $1/T$, for VAx0.41 copolymer. "BPE Mechanical" is $G''_{\max}$ data for branched polyethylene from ref 15. "BPE C=O Dielectric" is for lightly oxidized BPE, from ref 16.

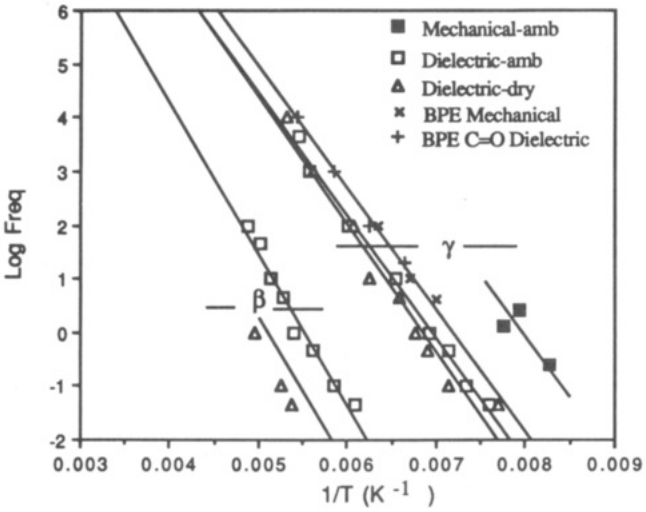

Figure 11. Loss map, $\log f_{\max}$ (isochronal) versus $1/T$, for VAx0.20 copolymer.

group reorientation and the γ activity is rather indirect as explained above.

β' Process. A relaxation feature not previously seen dielectrically in these systems is evident in both the mechanical and dielectric scans for PVAc homopolymer, Figures 2 and 6a. It is a shoulder on the low-temperature side of the large glass–rubber relaxation α peak, and it becomes increasingly well resolved at decreasing frequency, especially dielectrically (Figure 13). We have designated this process as β'. Mechanically, a process in the same temperature region has been reported in PVAc but attributed to the possible presence of impurities.[6] It is observed here only in the PVAc homopolymer and not in the copolymers. Since it appears only at low frequency next to the glass–rubber α peak, the lack of observation in the copolymers is simply attributable to their lower T_g values. The strong α peak would clearly mask the β' process if the latter were present. Dielectrically, the process becomes better resolved as the moisture content of the homopolymer is reduced, as shown in Figure 6a. This is due to the shifting of T_g to higher temperature as moisture content is reduced, a phenomena noted also in other investigations.[5,8] The reliable observation in specimens of quite different origin (those studied here and in ref 6) would seem to preclude its origin as an artifact such as being due to impurities.

Table II
Arrhenius Parameters[a] and Activation Energies for Mechanical and Dielectric Subglass Processes

specimen	method	process	A	B	ΔH, kcal/mol
VA-amb[c]	mechanical	β'	−3669	13.9	17[a]
VA-amb[c]	dielectric	β'	−3877	14.4	17.8[a]
VA-dry[d]	dielectric	β'	−5026	17.7	22.9[b]
VA-amb	mechanical	β	−1819	11.7	8.3[a]
VA-amb	dielectric	β	−2004	12.6	9.2[a]
VA-dry	dielectric	β	−2514	13.3	11.5[a]
VAx0.20-amb	mechanical	γ	−1594	12.7	7.3[a]
VAx0.20-amb	dielectric	β	−2830	15.6	12.9[a]
VAx0.20-dry	dielectric	β	−3170	15.7	14.5[a]
VAx0.20-amb	dielectric	γ	−2278	15.8	10.4[a]
VAx0.20-dry	dielectric	γ	−2371	16.3	10.9[a]
VAx0.41-amb	mechanical	β	−2689	15.7	12.3[a]
VAx0.41-amb	dielectric	β	−2415	14.3	11.0[a]
VAx0.41-dry	dielectric	β	−2550	11.9	11.7[a]
VAx0.41-amb	mechanical	γ	−1693	13.5	7.7[a]
VAx0.41-amb	dielectric	γ	−1949	14.4	8.9[a]
VAx0.41-dry	dielectric	γ	−2035	14.1	9.2[a]
BPE[e]	mechanical	γ	−2703	23.8	12.3[a]
BPE (C=O)[f]	dielectric	γ	−2272	16.3	10.4[a]

[a,b] $\log f_{\max}$ (a, isochronal; b, isothermal) = $A/T + B$. [c] amb = ambient atmosphere transfer to apparatus, see text. [d] Dry, see text. [e] From ref 15. [f] From ref 16.

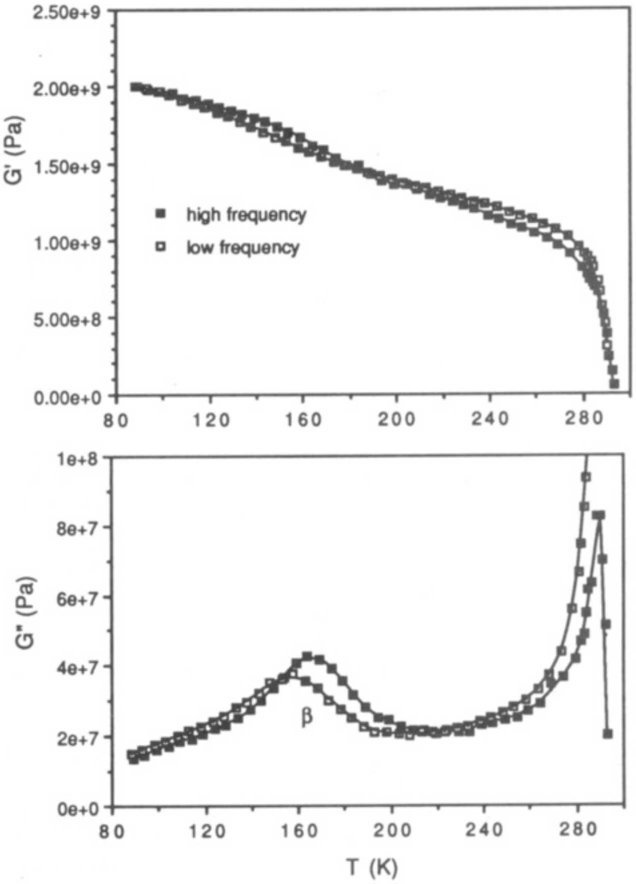

Figure 12. PMA homopolymer. Complex shear modulus (G', upper curves; G'', lower ones) versus temperature. Ambient sample. High (filled points) and low (open squares) frequency runs of Table I.

Figure 14 is an Argand plot for the dielectric β' process at several temperatures. The Cole–Cole circular arc equation was fit to the data, and the fits are shown in the figure. Parameter values, along with the relaxation strength $(\epsilon_r - \epsilon_u)$, are given in Table III.

The question then arises as to the origin of the process. The following is admittedly speculative. The reorientation of the ester group associated with the β process has been considered as due to rotation about the carbon–

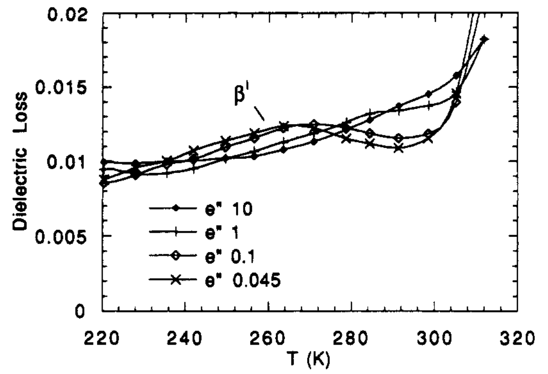

Figure 13. Dielectric loss in the β' region for dry PVAc homopolymer. Isochronal scans at the indicated frequencies (Hz).

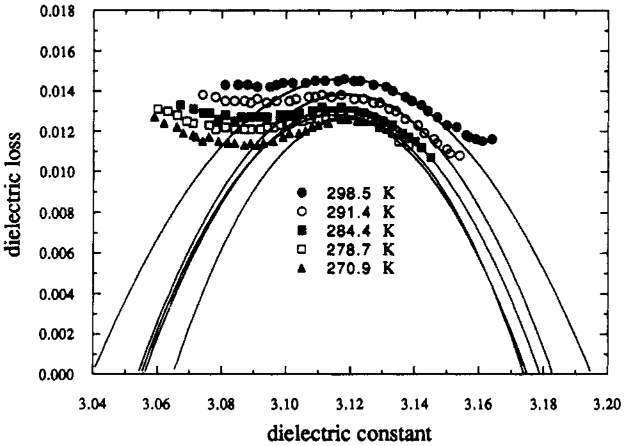

Figure 14. Argand plots for the dry PVAc dielectric β' process. Curves are Cole–Cole circular arc function fits. The associated parameters are given in Table III.

oxygen bond in VA systems or C(sp^3 main chain)–C(sp^2) in the MA case. This is no doubt correct. However, it is worth considering the possibility of rotation about the ester –C(sp^2)–O– bond, or in other words cis–trans isomerization of the ester group, as the source of an additional relaxation process. There is strong preference, probably on the order of several kilocalories per mole, for the trans configuration of the ester group C–C(sp^2)–O–C bond over the cis.[17] The barrier for interconversion is not known precisely. We have parametrized it in a molecular mechanics ester force field[18] as 14 kcal/mol. Based on experimental values for the torsional fundamental in methyl formate, this is probably a bit low.[18] Thus, the experimental activation energy for the β' process, ~22 kcal/mol, Table II, is consistent with this, especially if some intermolecular contribution is assumed. The several kilocalories per mole energy difference in energy between the trans and cis conformations should lead to a fairly strong temperature dependence of the relaxation strength or, more appropriately, to strong temperature dependence of the correlation factor of the Kirkwood–Onsager equation.[19] Explicitly, the strength defined as the difference in relaxed and unrelaxed dielectric constants, ϵ_r and ϵ_u, is related to the correlation factor, g_p, of the polar units of number density N_p and moment μ_0 through

$$\epsilon_r - \epsilon_u = \left(\frac{\epsilon_u + 2}{3}\right)^2\left(\frac{3\epsilon_r}{2\epsilon_r + \epsilon_u}\right)\frac{1}{3kT\epsilon_0}(N_p g_p \mu_0^2) \qquad (1)$$

Strong temperature dependence of g_p through $(\epsilon_r - \epsilon_u)T$ does prevail, as can be concluded from Table III. Invoking a value of $\mu_0 = 1.8$ D[18] and utilizing the room temperature density of 1.2 g/cm^3 along with the experimental values of $\epsilon_r - \epsilon_u$ in Table III leads to the experimental values of g_p calculated from eq 1 listed in Table IV.

Table III
Cole–Cole Parameters for the PVAc Dielectric β' Process

temp, K	α	ϵ_u	ϵ_r	$\epsilon_r - \epsilon_u$	τ, s
270.9	0.290	3.065	3.174	0.109	1.12
278.7	0.268	3.055	3.175	0.120	0.28
284.4	0.269	3.056	3.179	0.123	0.16
291.4	0.269	3.054	3.183	0.129	0.064
298.5	0.260	3.050	3.191	0.141	0.025

Table IV
Calculated and Experimental Correlation Functions for the Strength of the β' Relaxation

	correlation factor, g_p	
temp, K	exptl[a]	calc[b]
270.9	0.012	0.0110
278.7	0.014	0.0128
284.4	0.015	0.0143
291.4	0.016	0.0162
298.5	0.018	0.0183

[a] Determined from the ϵ_u and ϵ_r values of Table III using eq 1. [b] Calculated using eq 2 with the energy difference ΔU = 3020 cal/mol and the reorientation angle γ = 120°.

Assuming a two-site model with energy difference ΔU, the correlation factor is given by[3,19,20]

$$g_p = 2(1 - \cos\gamma)\frac{\exp(-\Delta U/kT)}{(1 + \exp(-\Delta U/kT))^2} \qquad (2)$$

where γ is the angle through which the dipole reorients. Assuming the dipole lies along the C=O bond,[18,21] cis–trans isomerism results in a value of γ = 120° for ideal sp^2 hybridization angles. Using this angle and adjusting ΔU to 3020 cal/mol gives the calculated values listed in Table IV. The agreement is seen to be very good. Achieving this agreement in absolute values as well as relative temperature dependence with a single adjustable energy difference parameter that is very reasonable in magnitude lends some credence to the interpretation of the process as cis–trans isomerism.

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References and Notes

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Registry No. PVAc (homopolymer), 9003-20-7; VAc/ethylene (copolymer), 24937-78-8; PMA (homopolymer), 9003-21-8.