

Dielectric and Dynamic Mechanical Behavior of Poly(vinyl Acetate) Containing Small Concentrations of Cholesteryl Additives

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Synopsis

Dielectric loss measurements at four temperatures and as a function of frequency are presented for the poly(vinyl acetate) (PVAc) systems containing small concentrations of cholesterol, cholesteryl acetate, cholesteryl oleate, cholesteryl nonanoate, cholesteryl benzoate, cholesteryl oleyl carbonate, *p*-methoxy benzilidene-*p*-*n*-butyl aniline, diphenyl ether, and cetyl acetate. For the first five systems, the α -relaxation temperature for pure PVAc was found to be increased in the presence of the said additives. The results of the dielectric depolarization spectroscopy at 1 kHz and the dynamic mechanical analysis also conform with these observations. It is inferred that the segmental motion in PVAc is hindered by these first five additive molecules through a specific dipolar interaction. These additives are therefore described as antiplasticizers to PVAc as they extend the glassy region over a wider temperature interval. The analysis of the dielectric data to give the dielectric decay function and the β parameter reveals that the two types of the additives, viz., plasticizers and antiplasticizers, can be distinguished by the opposite signs obtained for the ratio $\Delta\beta/\Delta C$, where C is the concentration. The analysis based on the WLF theory shows that the WLF reference temperature T^0 is higher than that for pure polymer if the additive is an antiplasticizer while the same is lower for the plasticizing additives. The apparent enthalpy of activation for the dielectric relaxation process is found to be higher in the case of additives which show antiplasticization of PVAc.

INTRODUCTION

There is ample evidence for antiplasticization of polymers caused by addition of small concentrations of certain additives through such work as creep measurements, stress-strain behavior, or velocity and absorption of ultrasound.¹⁻⁴ Such studies have indicated the suppression of the β -relaxation peak and an improvement in the mechanical strength of polymers in the glassy region. At the same time the glass transition temperature T_g is reported to be lowered by these workers.

It is well known that when a common plasticizer like dioctylphthalate (DOP) is added to poly(vinyl chloride) (PVC), at small concentrations of DOP, the β -peak in PVC is suppressed and the glass-transition temperature is lowered.⁵⁻⁷ The behavior is qualitatively described as due to the voids or free volume being occupied by the additive molecules when present in small amounts. This leads to closer packing and an increase in density and hence the motion responsible for β -relaxation is hindered.

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On the other hand, our earlier dielectric studies^{8,9} on poly(*n*-butyl methacrylate) (PBMA) containing small amounts of some cholesteryl compounds have clearly indicated a shift of α -relaxation region to higher temperature at a constant frequency. This effect was attributed to a hindrance in segmental motion of the polymer due to the presence of these additives. Such a behavior was observed for the first time and needs further investigation as to whether the phenomenon of shift of α -relaxation or glass transition region due to small concentration of these additives is applicable to other polymers.

In this work therefore, we present the results of our measurements on poly(vinyl acetate) (PVAc) containing small amounts of cholesteryl compounds and some other simple substances like cetyl acetate, diphenyl ether, and *p*-methoxy benzilidine-*p*-*n*-butyl aniline (MBBA).

EXPERIMENTAL

Materials

PVAc (BDH, $M_n = 45,000$) was dissolved in benzene and filtered through a G4 sintered crucible to remove any suspensions or gels before casting films. The polymer solution with a known concentration of the desired additive was allowed to dry at 50°C *in vacuo* for 3–4 weeks. Discs of 63 mm diameter were punched and used for dielectric studies while for dynamic mechanical analysis, rectangular pieces of dimensions 20 × 10 × 0.5 mm were punched. For every additive, films with three different concentrations in the range of 2–8% by weight were prepared as above and were used without further analysis for the composition.

All cholesteryl compounds were Aldrich chemicals and were used as received. Cholesterol (SISCO) was used after recrystallization from chloroform. Cetyl acetate was prepared by esterification of cetyl alcohol and acetic anhydride and the purity was checked by taking IR spectra.

Dielectric Bridge

Using a thermostatted three electrode stainless steel cell, capacitance and $\tan \delta$ were measured on a Rohde and Schwartz dielectric test bridge. The RC oscillator was calibrated by using a digital frequency meter (Yamuna) having a crystal-controlled time base. For each sample, measurements were made at four temperatures in the range of 40–75°C at 35–50 different frequencies in the range of 60 Hz to 300 kHz. The temperature of the cell was controlled to +0.05°C. The major error in the dielectric loss measurements was due to flow of the sample during measurements and amounted to a maximum of 5% in the worst cases.

Dielectric Depolarization Spectroscopy

A fixed frequency signal was applied to the dielectric sample having a resistance in series. The in-phase and out-of-phase current through the sample was monitored by measuring the voltage drop across the series resistance by means of a phase sensitive lock-in amplifier. The output of

the amplifier was fed to a recorder. The temperature of the sample was plotted on the X -axis of the recorder. The temperature was linearly increased at the rate of $0.8^{\circ}\text{C}/\text{min}$ using a temperature programmer. Thus the recorder trace obtained for in-phase current vs. temperature, directly represents the dielectric depolarization spectrum (vs. T). For an exact quantitative evaluation, a correction due to dc conductance is required.

Dynamic Mechanical Analysis

A dynamic mechanical analysis was carried out on DuPont Model DMA 981 dynamic mechanical analyzer, in the temperature range of 0 – 100°C . Details of procedure and calculations are given in our earlier paper.¹⁰

RESULTS

The dielectric data for a given system at different temperatures have been reduced to one master curve. A typical plot of the normalized dielectric loss (ϵ''/ϵ''_m) vs. $\log(f_m/f_m^0)$ for the system PVAc (pure) and PVAc + cholesteryl oleate is shown in Figure 1. These are used for the calculation of the dielectric decay function $\phi(t/\langle\tau\rangle)$ and the parameter β . The various parameters evaluated are given in Tables I and II.

The results of dielectric depolarization spectroscopy at 1kHz have been graphically given in Figures 2–7. For dynamic mechanical analyses, the samples were mounted in the horizontal mode of clamping to obtain high sensitivity of the instrument. This, however, permits the evaluation of loss modulus or $(\tan \delta)_{\text{mech}}$ only and the calculation of the storage modulus is not possible. From the recorder trace of damping signal vs. temperature, $(\tan \delta)_{\text{mech}}$ were calculated at different temperatures. The results are graphically shown in Figures 8–13. In all the Figures 2–13, the dotted curve indicates data for pure PVAc.

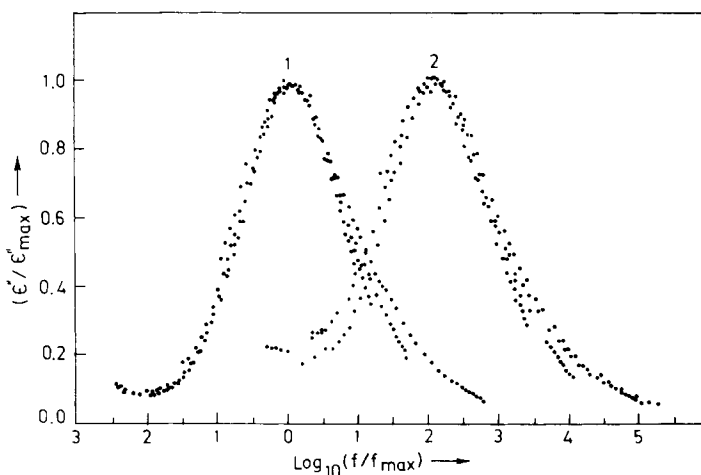


Fig. 1. Plots of $(\epsilon''/\epsilon''_m)$ vs. $\log_{10}(f/f_{\text{max}})$ for pure PVAc (1) and PVAc with 2.32% ChOl (2). Curve (2) is shifted by two decades for clarity.

TABLE I
 Dielectric Data for PVAc + Additive Systems

Additive	Concn (w/w %)	log (f_m)			$t(^{\circ}\text{C})^a$	$\Delta \log f_m / \Delta C$	β	$\Delta\beta / \Delta C$
		50	60	70				
—	0	1.125	2.05	2.93	59.5	—	0.53	
Ch	2.67	0.85	1.90	2.88	61.0		0.63	
	3.23	0.78	1.88	2.88	61.3	-0.17	0.63	+0.00
	4.50	0.45	1.63	2.73	63.4		0.66	
	5.27	0.23	1.45	2.63	64.5		0.63	
ChAc	1.9	1.00	1.93	2.80	60.9		0.65	
	3.0	0.88	1.78	2.68	62.4	-0.13	0.69	+0.01
	4.5	0.62	1.60	2.50	64.5		0.68	
ChNon	2.00	1.08	2.01	2.90	60.0		0.56	
	3.00	1.03	1.98	2.90	60.2	-0.08	0.57	+0.03
	3.90	0.88	1.86	2.80	60.4		0.61	
	1.81	0.73	1.80	2.82	62.0		0.61	
	2.32	0.58	1.68	2.70	63.0	-0.33	0.62	+0.03
ChBz	3.54	0.08	1.23	2.43	66.5		0.66	
	1.96	0.63	1.78	2.73	63.0			
	2.89	0.05	1.30	2.48	65.8	-0.31	—	—
ChOC	1.92	1.25	2.18	3.05	58.1		0.60	
	3.04	1.35	2.25	3.10	57.3	+0.07	0.60	-0.01
	4.20	1.45	2.33	3.15	56.3		0.57	
MBBA	1.86	1.25	2.18	3.03	58.0		0.53	
	4.45	1.73	2.58	3.18	53.5	+0.15	0.50	-0.02
DPE	1.42	1.20	2.10	3.00	58.9		0.56	
	3.76	1.25	2.15	3.00	58.4	+0.03	0.58	-0.01
	7.02	1.38	2.27	3.08	57.0		0.50	
CeAc	1.88	1.33	2.25	3.15	57.2		0.58	
	2.60	1.58	2.48	3.35	54.7	+0.2	0.56	-0.07
	3.10	1.80	2.60	3.43	52.6		0.50	

^a Temperature at which $\tan \delta$ is maximum at 100 Hz.

DISCUSSION

With the additives like diphenylether (DPE) and cetyl acetate (CeAc) which are isotropic liquids, *p*-methoxy benzilidene-*p*-*n*-butyl aniline (MBBA, a nematic liquid crystal), and cholestery oleyl carbonate (ChOC) (cholesteric

 TABLE II
 WLF Reference Temperatures and the Apparent Enthalpies of Activation of PVAc + Additive Systems

Additive	T^0 ($^{\circ}\text{C}$)	ΔH_a (60 $^{\circ}\text{C}$) (KJ/mol)
—	28	257.3
Ch	30	266.8
ChAc	31	271.7
ChNon	29.3	263.4
ChOl	31.7	275.5
ChBz	34.7	291.1
CHOC	26.8	251.9
MBBA	25.0	244.0
DPE	27.6	255.5
CeAc	23.5	237.8

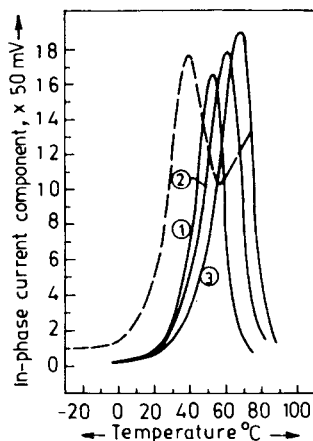


Fig. 2. Dielectric depolarization spectra (DDS). In-phase current vs. temperature; (---) PVAc; (1) PVAc with 2 phr Ch; (2) 4 phr Ch; (3) 6 phr Ch.

liquid crystal), the loss maxima are shifted to lower temperature than that in pure PVAc; the frequency at which the loss is maximum (f_m) is increased at a constant temperature as compared with that for pure PVAc. Thus, these additives behave as plasticizers for PVAc, reducing the glass transition temperature of the polymer. Dynamic mechanical analysis (DMA) results on the system PVAc + CeAc, given in Figure 8, are also indicative of plasticizing action of CeAc on PVAc.

On the other hand, the additives cholesterol (Ch), cholesteryl chloride (ChCl), cholesteryl acetate (ChAc), cholesteryl benzoate (ChBz), cholesteryl oleate (ChOl), and cholesteryl nonanoate (ChNon) behave quite differently. The dielectric loss maxima at a constant frequency for systems PVAc + Ch, +ChCl, +ChAc, +ChBz, +ChOl, and +ChNon are shifted to higher temperature as compared with that for the pure polymer. At a constant tem-

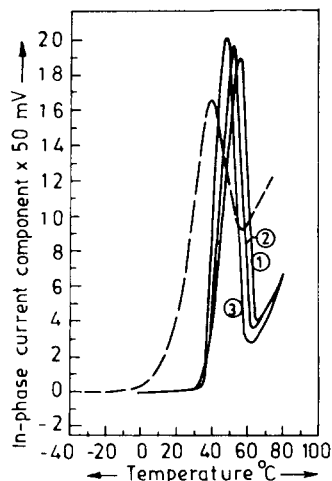


Fig. 3. DDS: In-phase current vs. temperature: PVAc CeAc. The in-phase current component plotted is in terms of the output of the lock-in-amplifier (mV); curves 1, 2, and 3 are for the additive compositions of 2, 4, and 6 phr, respectively; the dotted curve corresponds to pure PVAc.

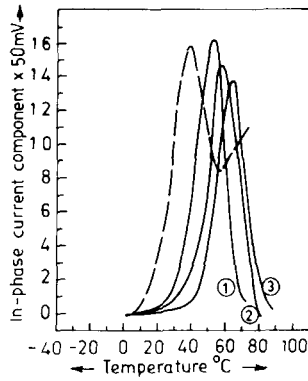


Fig. 4. DDS: in-phase current vs. temperature: PVAc ChAc. The notation is the same as for Figure 3.

perature, the frequency of loss maximum (f_m) is decreased in the presence of these additives. The dielectric depolarization spectra for these systems as given in Figures 2-7 markedly show the shift of the loss maxima towards high temperature and that the shift increases with concentration of the additive. The DMA results for the same systems are given in Figures 8-13 which are parallel to the dielectric behavior. The dielectric as well as dynamic mechanical spectra thus conclusively indicate the shift of the relaxation region of PVAc to the higher temperature due to the presence of these additives. This means that the said additives are capable of hindering the segmental mobility in PVAc. As a consequence, the α -relaxation or the glass-transition temperature is increased. From the Arrhenius plot of $\log(f_m)$, we find that the apparent enthalpy of activation ΔH_a for the dielectric relaxation process increases significantly for the systems PVAc + the said additives.

The hindrance to the segmental motion of PVAc caused by these additives like cholesterol and cholesteryl esters may be attributed to different reasons like the liquid crystalline nature of these additives, geometry of the additive

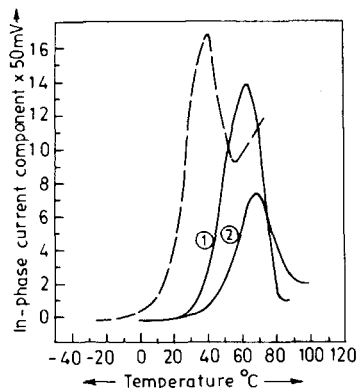


Fig. 5. DDS: in-phase current vs. temperature: PVAc ChBz. The notation is the same as for Figure 3.

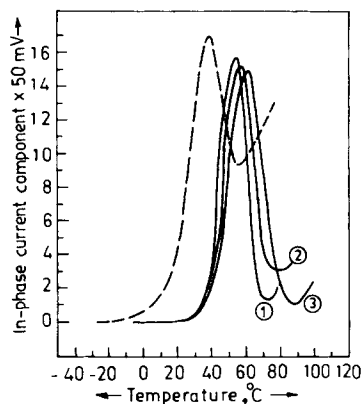


Fig. 6. DDS: in-phase current vs. temperature: PVAc ChNon. The notation is the same as for Figure 3.

molecules or to the specific dipolar interactions between the additive molecules and the polymer chain.

Of the reasons indicated above, we believe the liquid crystalline nature of the additive has no role to play because there is no correlation between the shift in the α -relaxation observed and the liquid crystalline transition temperature. Secondly, cholesterol is not a liquid crystal and yet it gives rise to a shift of the α -relaxation of PVAc to higher temperature; at the same time, cholesteryl oleyl carbonate (cholesteric liquid crystal) and MBBA (nematic liquid crystal) show plasticizing effect on PVAc. It is therefore reasonable to infer that the structure of these cholesteryl esters and cholesterol, in combination with the specific dipolar interaction with the acetate pendant groups of the PVAc chains, are responsible for the hindrance in segmental mobility of the PVAc chains. Our density measurements have not given any conclusive evidence for close packing due to occupation of

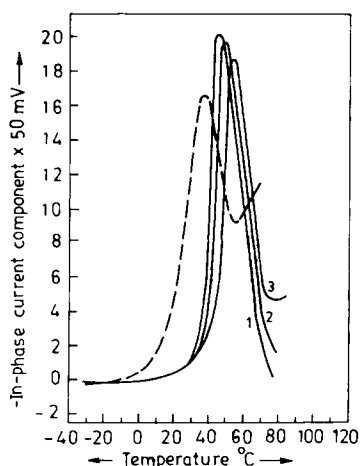


Fig. 7. DDS: in-phase current vs. temperature: PVAc ChCl. The notation is the same as for Figure 3.

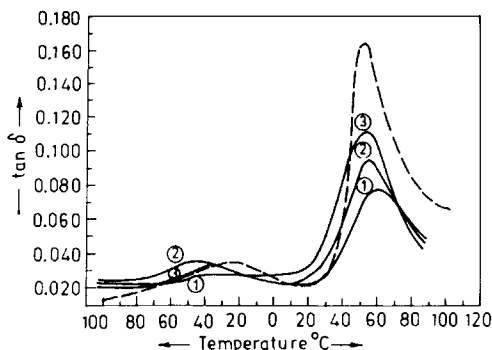


Fig. 8. DMA: $\tan \delta$ vs. temperature: (---) pure PVAc (1) PVAc with 2 phr CeAc; (2) 4 phr CeAc; (3) 6 phr CeAc.

voids in the PVAc by the additive molecules. Similarly, X-ray diffraction spectra of PVAc + additives do not indicate any changes in crystallinity compared to that of pure PVAc. The observed shift of the α -relaxation region of PVAc to high temperature therefore seems to be originating from the specific interactions between the additives and the PVAc repeat units. In PVAc, since the dipolar acetate group is a flexible pendant unit, the apparent enthalpy of activation for the dielectric relaxation process is quite small (~ 258 kJ/Mol) as compared to that in PVC (~ 560 kJ/mol), in which the C-Cl dipole is rigidly attached to the main chain. In the case of PVAc, therefore, a weak interaction of the polymer chain with the additive is sufficient to give rise to an efficient hindrance of the segmental motion. These additives therefore should be regarded as *antiplasticizers*, in the sense that, by shifting the α -relaxation to high temperature, the glassy region is extended over a wider temperature interval.

Dielectric Decay Function

Many systems do not obey the Debye relaxation process described by a single relaxation time or a Cole-Cole equation with symmetrical distribu-

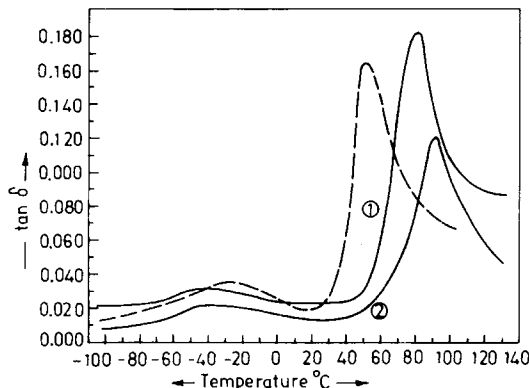


Fig. 9. DMA: $\tan \delta$ vs. temperature: PVAc ChBz. The notation is the same as for Figure 8.

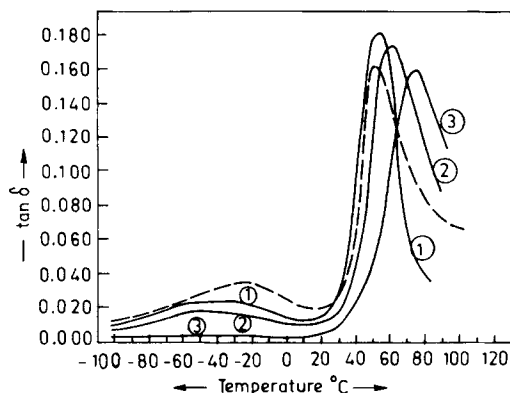


Fig. 10. DMA: $\tan \delta$ vs. temperature: PVAc ChCl. The notation is the same as for Figure 8.

tion of relaxation times. The shape of the loss curves for polymer systems may be expressed in terms of the natural nonexponential decay function¹¹

$$\phi(t) = \exp(-t/\tau)^\beta, \quad 0 > \beta > 1 \quad (1)$$

where β is an empirical parameter. The normalized loss curves as shown in Figure 1 may be utilized for the evaluation of the reduced decay function $\phi(t/\langle\tau\rangle)$ as described in detail in our previous work.⁹ A typical plot of $\phi(t/\langle\tau\rangle)$ vs. $\log(t/\langle\tau\rangle)$ for pure PVAc is shown in Figure 14, where most of the decay occurred in a short time as compared with the relaxation time. Another typical plot of $\log[-\log \phi(t/\langle\tau\rangle)]$ is shown in Figure 15, and the values of the parameters are given in Table I.

β Parameter

For non-Debye behavior, the value of the β parameter is less than unity. Sesabe and Moynihan¹² obtained a value of 0.58 for β at 62.5°C. Using the

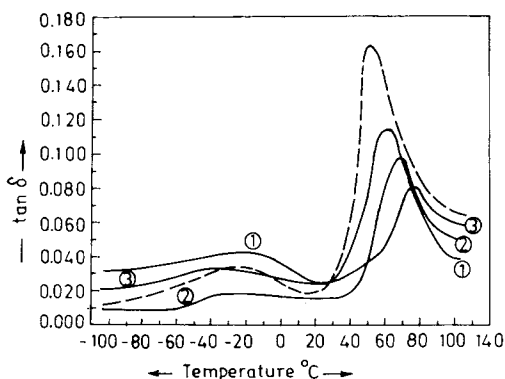


Fig. 11. DMA: $\tan \delta$ vs. temperature: PVAc ChAc. The notation is the same as for Figure 8.

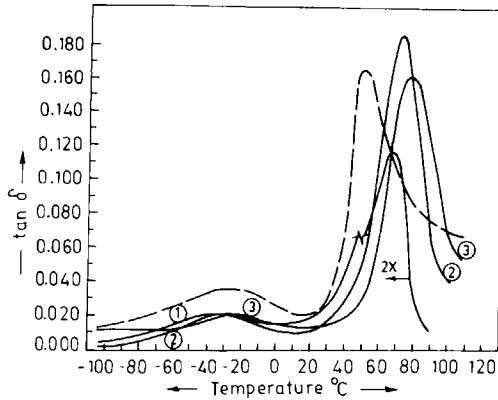


Fig. 12. DMA: $\tan \delta$ vs. temperature: PVAc ChNon. The notation is the same as for Figure 8.

data of Ishida et al.¹³, Williams et al.¹¹ obtained a value of 0.56 for β . Considering the errors involved in the evaluation from the normalized loss curves, our value of $\beta = 0.53$ for pure PVAc obtained in this work is in good agreement with the literature values quoted above. As the deviation of β from unity merely indicates a non-Debye behavior, from the magnitudes of β it is not possible to differentiate between a plasticizer and an antiplasticizer additive and both types of additives would cause a decrease of β , as seen from Table I.

Shape of Loss Curves

In the case of a pure polymer, the loss curves (ϵ'' vs. $\log f$) become narrower and symmetrical as the temperature is increased. The increased temperature causes increase in free volume, giving rise to increased mobility of the segments of the polymer chain. Naturally, addition of a plasticizer, which lowers the glass-transition temperature of a polymer, causes increase in free volume and hence the segmental mobility is increased. The loss curves for a plasticized polymer should therefore be narrower than that of the pure polymer. An antiplasticizer, on the other hand, which reduces the

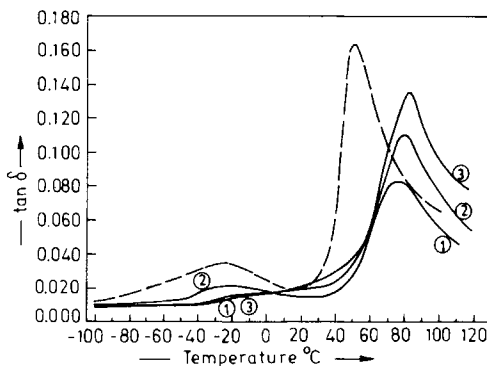


Fig. 13. DMA: $\tan \delta$ vs. temperature: PVAc Ch. The notation is the same as for Figure 8.

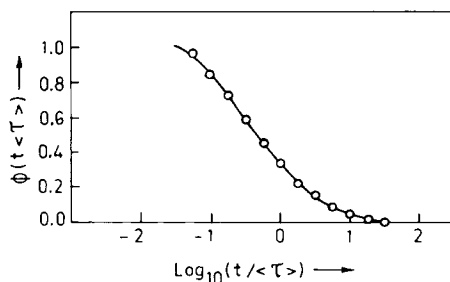


Fig. 14. Dielectric decay function for pure PVAc.

segmental mobility, is expected to give broader loss curves than that of the pure polymer. However, the present work reveals that any additive, be it a plasticizer or an antiplasticizer, causes the loss curves to broaden with increased asymmetry and hence the free volume model alone is inadequate to describe such a behavior. It may therefore be concluded that the additive molecules cause a change in mobility of the segments in the immediate vicinity and the segments which are away are less affected, thus creating a gradient of segment mobility and hence giving rise to a gradient of relaxation times over the given chain. As a consequence, β is less than unity and the broadening of the loss curves is irrespective of the nature of the additive—whether it is a plasticizer or an antiplasticizer. Shears and Williams¹⁴ and Baird and Sengupta¹⁵ have also reported similar observations.

The systems PVAc + DPE, +CeAc, +ChOC, and +MBBA show broadening of the loss curves, increased asymmetry with increasing concentration of additives and negative values of the ratio $\Delta\beta/\Delta C$. On the other hand, for systems PVAc + other additives, the loss curves, though broader than that for pure PVAc, are more symmetrical and the ratio $\Delta\beta/\Delta C$ is positive. Thus, though the shapes of the loss curves and the magnitudes of parameter do not reflect on the plasticizing or antiplasticizing behavior of the additive, the sign of the ratio $\Delta\beta/\Delta C$ does give a clue. At the same time, it is interesting to note from Table I that signs of the ratios $\Delta \log f_m/\Delta C$ are opposite in case of the two types of the additives.

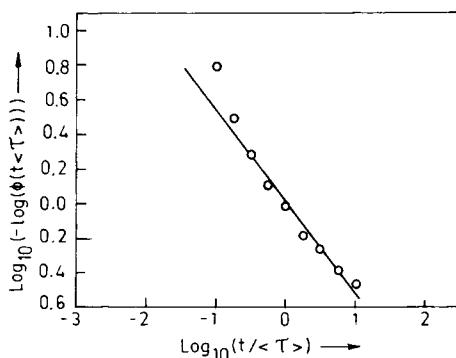


Fig. 15. Plot of $-\log\{-\log[\phi(t)/\langle\tau\rangle]\}$ vs. $\log(t/\langle\tau\rangle)$ for pure PVAc.

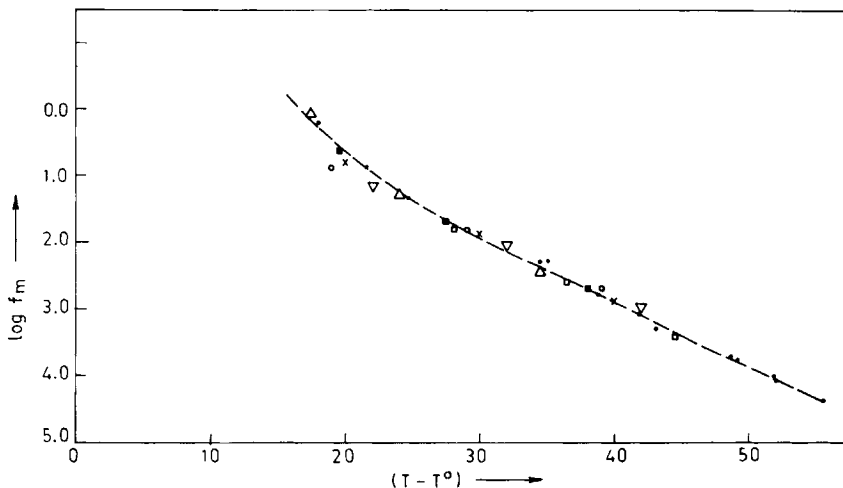


Fig. 16. Plot of $\log f_m$ vs. $(T - T_0)$: Pure PVAc, (∇) our results and (\bullet) from Refs. 12, 13, and 17; PVAc Ch; (\times) PVAc ChAc; (\circ) PVAc ChBz; (\triangle) PVAc CeAc; (\square) PVAc ChOl; (\blacksquare).

The WLF Equation

As our dielectric measurements by the bridge technique were restricted to four temperatures, it was not possible to obtain a good fit to evaluate the constants of the WLF equation¹⁶

$$\log a_T = -C_1 (T - T_0) / (C_2 + T - T_0) \quad (2)$$

Sasabe and Moynihan¹² have analyzed their data to give the constants of the WLF equation (2) as $C_1 = 16.2$, $C_2 = 65.7$ K and $T_0 = 304$ K.

Earlier extensive dielectric studies on PVAc are those of Mead and Fuoss¹⁷ and Ishida et al.¹³ Hence, together with the present data we have used the data of Mead and Fuoss, Ishida et al., and Sasabe and Moynihan to obtain the constants of the WLF equation. Through regression analysis, constants of the curve for $\log f_m$ vs. $1/T$ were obtained and were used to get $\log f_m(T_0)$, where T_0 is the reference temperature in the WLF equation. For pure PVAc, the constants of the WLF equation obtained were

$$C_1 = 19.0088$$

$$C_2 = 80.066 \text{ K}$$

$$T_0 = 301 \text{ K}$$

with a standard deviation of 0.0042 for the least squares fitting of experimental and calculated values of $\log f_m$. The apparent enthalpy of activation ΔH_a for the dielectric relaxation process can be calculated as

$$\Delta H_a(\text{WLF}) = 2.303RC_1C_2T^2 / \{C_2 + T - T_0\}^2 \quad (3)$$

and for pure PVAc it was found to be 257 KJ/mol at 60°C. The reference

temperature T_0 obtained as 301 K corresponds to the glass transition temperature of the polymer.

For the systems PVAc + additives, we assume that the constants C_1 and C_2 of eq. (2) have the same values as that for pure PVAc and that only the reference temperature T_0 would differ for each system at each concentration. In order to fit our experimental data for systems PVAc + additives to eq. (2), therefore, one needs to find out T_0 for the best fit. For this purpose it would also be necessary to evaluate $\log f_m(T_0)$ for obtaining the shift factor a_T . Due to limited experimental points at different temperatures, this was not possible. Hence instead of plotting the WLF curve $\log a_T$ vs. $(T - T_0)$, we have plotted $\log f_m$ vs. $(T - T_0)$ in Figure 16, where data of Sasabe and Moynihan, Mead and Fuoss, and Ishida et al. on pure PVAc are included. From our experimental values of $\log f_m$ on PVAc + additives, it is thus possible to evaluate $(T - T_0)$ and hence T_0 for the given system from the curve given in Figure 16. T_0 so obtained as an average of the data at 50, 60, and 70°C at a single concentration for each additive, together with the apparent enthalpy of activation $\Delta H_a(\text{WLF})$ at 60°C is given in Table II.

This analysis based on the WLF equation reveals two interesting features. First, the WLF reference temperature T_0 , i.e., the glass transition temperature is higher if the additive is an antiplasticizer and it is lower if the additive is a plasticizer, than that of pure PVAc. Secondly, ΔH_a is greater than that for the pure polymer in the case of the additives which act as antiplasticizers. This again is in support of the view that an antiplasticizer gives rise to a hindrance in the segmental mobility, which may be due to creation of an additional energy barrier for the relaxation process.

CONCLUSIONS

Dielectric loss measurements from the bridge technique, the dielectric depolarization spectra and the dynamic mechanical measurements on the systems PVAc + additives reveal conclusively that the α -relaxation region of PVAc is shifted to higher temperature by some of these additives, viz., cholesterol, cholesteryl acetate, cholesteryl oleate, cholesteryl nonanoate, and cholesteryl benzoate. These additives are therefore described as antiplasticizers for PVAc because (i) their behavior is opposite to that of a plasticizer, (ii) they give rise to an increase in the glass transition temperature—as inferred through the WLF analysis—, and (iii) they extend the range of the glassy region over a wider temperature interval.

The antiplasticizing behavior of these additives is a consequence of the specific dipolar interaction between these additive molecules and the repeat units of the PVAc chain; the liquid crystalline character of the additives has no role to play in the antiplasticization. The other additives used, viz., cholesteryl oleyl carbonate, MBBA, DPE, and CeAc act as plasticizers to PVAc.

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