

Dielectric Relaxation and Electric Modulus Behavior in Poly(vinyl alcohol)-Based Composite Systems

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SYNOPSIS

The ultraviolet spectra of pure and lead salt–poly(vinyl alcohol) (PVA) composite films were studied at room temperature. Blending of PVA with lead acetate and lead nitrate cause a considerable change in the UV spectrum, indicating electronic structure modifications. The complex permittivity (ϵ^*) and the complex electric modulus (M^*) of the pure PVA and the PVA-based composite films were investigated between 300 and 400 K in the 100 Hz–100 kHz frequency range. The frequency dependence of the permittivity is influenced by the space-charge polarization. The interfacial polarization is manifested at high temperature and becomes important only above the PVA glass transition temperature and below 1 kHz. Dielectric properties of PVA–lead nitrate composite revealed that the salt is complexed with PVA through hydrogen bonding. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

One of the main uses of a dielectric properties study of polymeric materials is to obtain information on molecular motion and structural transitions. The dielectric behavior of a polymer is determined by the charge distribution and also by the statistical thermal motions of its polar groups. The study of relaxation behavior constitutes a powerful approach for obtaining information about the nature and types of molecular motions and the manner in which they are affected by chemical compositions, molecular structure, morphology, etc.¹ For polymers in the solid or in the viscoelastic state, the physical structure is of great importance in determining the dielectric behavior.^{2,3}

Dynamic and dielectric measurements, for studying molecular mobility in poly(vinyl alcohol) (PVA), have been done by several authors.^{4–7} According to dynamic mechanical study,⁴ PVA exhibits three relaxations in the same manner as do other semi-crystalline polymers: crystalline, primary, and local mode relaxations in the order of descending temperature. These three relaxation transitions have

been reported for atactic, syndiotactic, and isotactic PVA samples^{5,8} using a dielectric technique.

Recently, both basic and applied studies in polymer–admixture salts have been intensified since this new class of materials, which ranges from insulator to ionic solid conductors, may be tailored for a wide variety of applications. The solid-state properties of ion-containing polymers are determined largely by the association in a thermally reversible network of ionic groups in multiples and clusters.⁹ To obtain information about the structure–properties of these materials, dielectric loss measurements are currently used.^{10–12}

Therefore, the purpose of this article was to investigate the dielectric behavior of pure and some lead salt–PVA composite systems aimed at describing the extent to which the dielectric information may be used for a better understanding of the polymer–salt interactions in such composites. The results are correlated with those of the UV-absorption investigation.

EXPERIMENTAL

Materials

The atactic poly(vinyl alcohol) (PVA) used in this study was a commercial product, purchased from Polyscience, Inc.; the nominal molecular weight was

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78,000, and the saponification value was 99.7 mol %. Lead acetate and lead nitrate were supplied by BDH Chemicals, Poole, England.

Film Preparation

The composites were prepared by the mixed method,¹³ i.e., by dissolving the predetermined salt percentage and the PVA percentage (by weight) in distilled water. The mixture was stirred at room temperature for 24 h. The resulting solution was cast onto glass plates and dried under an air atmosphere at ambient temperature for 1 week and dried further in an oven regulated at 80°C for 24 h. Films containing up to 20 wt % lead salt and having a thickness ranging from 50 to 100 μm were obtained. The surfaces of the film were coated with a silver layer of about 150 Å thickness. No crystallization could be observed in any of the samples, as revealed by the polarizing optical microscope.

Measuring Techniques

The experimental techniques have been described elsewhere.^{3,14} Visible and ultraviolet (UV) absorption spectra of pure and PVA-lead salt composite films were measured at room temperature using a Perkin-Elmer-Lambda spectrophotometer. Dielectric permittivities were measured using a phase detector technique (look-in-amplifier Stanford-type SR 510 research system). The measurements were carried out in the frequency range from 100 Hz to 100 kHz under a controlled temperature that varied from 300 to 400 K. All measurements were carried out under a vacuum ($\sim 10^{-3}$ Torr) to avoid humidity effects in a cell designed especially to prevent stray capacitance.

RESULTS AND DISCUSSION

UV-Absorption Investigations

The UV absorption spectra of pure and the blend of PVA with $\text{Pb}(\text{CH}_3\text{COO})_2$ and $\text{Pb}(\text{NO}_3)_2$ are shown in Figure 1. As is clear for pure PVA spectra, four remarkable bands are observed, two sharp bands at 195 and 222 nm and broadening bands at 280 and 340 nm. On the other hand, blending of PVA with $\text{Pb}(\text{NO}_3)_2$ led to the disappearance of 195 and 222 nm bands with a sharp absorption edge at 265 nm, while on blending of PVA with $\text{Pb}(\text{CH}_3\text{COO})_2$, the formation of a sharp absorption

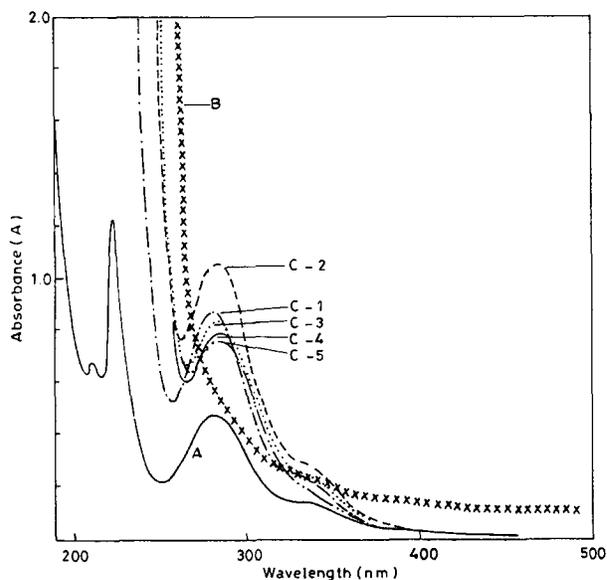


Figure 1 UV-visible absorption spectrum of (A) pure PVA, (B) 5 wt % $\text{Pb}(\text{CH}_3\text{COO})_2$ -PVA, and (C) $\text{Pb}(\text{NO}_3)_2$ -PVA: (1) 1 wt %, (2) 5 wt %, (3) 10 wt %, (4) 15 wt %, and (5) 20 wt % of $\text{Pb}(\text{NO}_3)_2$.

edge at 280 nm, without any absorption bands, resulted.

In the case of the $\text{Pb}(\text{NO}_3)_2$ -PVA system, the absorption at 280 nm increases as the lead nitrate concentration increases up to 5 wt % and then decreases with increasing the lead nitrate content to 20 wt %, as compared to the pure PVA (see Fig. 1). On the other hand, the absorption band intensity at 280 nm decreases, with a slightly shift toward a lower energy side, as the lead nitrate concentration increases. These results mean that on increasing lead salts more than 5 wt % led to increasing the aggregation of the nonreacted lead salts which acts as a defect center and reduces the absorption. Further, the disappearance of both 195 and 222 nm bands on treated PVA with both lead acetate and lead nitrate provides evidence for the formation of lead salt polymer complexes.

Dielectric Investigations

The complex dielectric constant,

$$\epsilon^* = \epsilon' - i\epsilon'' \quad (1)$$

is often used to describe relaxation processes in insulators. The dielectric permittivity ϵ' and the dielectric loss ϵ'' data measured at different fixed temperatures on pure PVA, PVA films doped with 5 wt % lead acetate, and lead nitrate salts are plotted

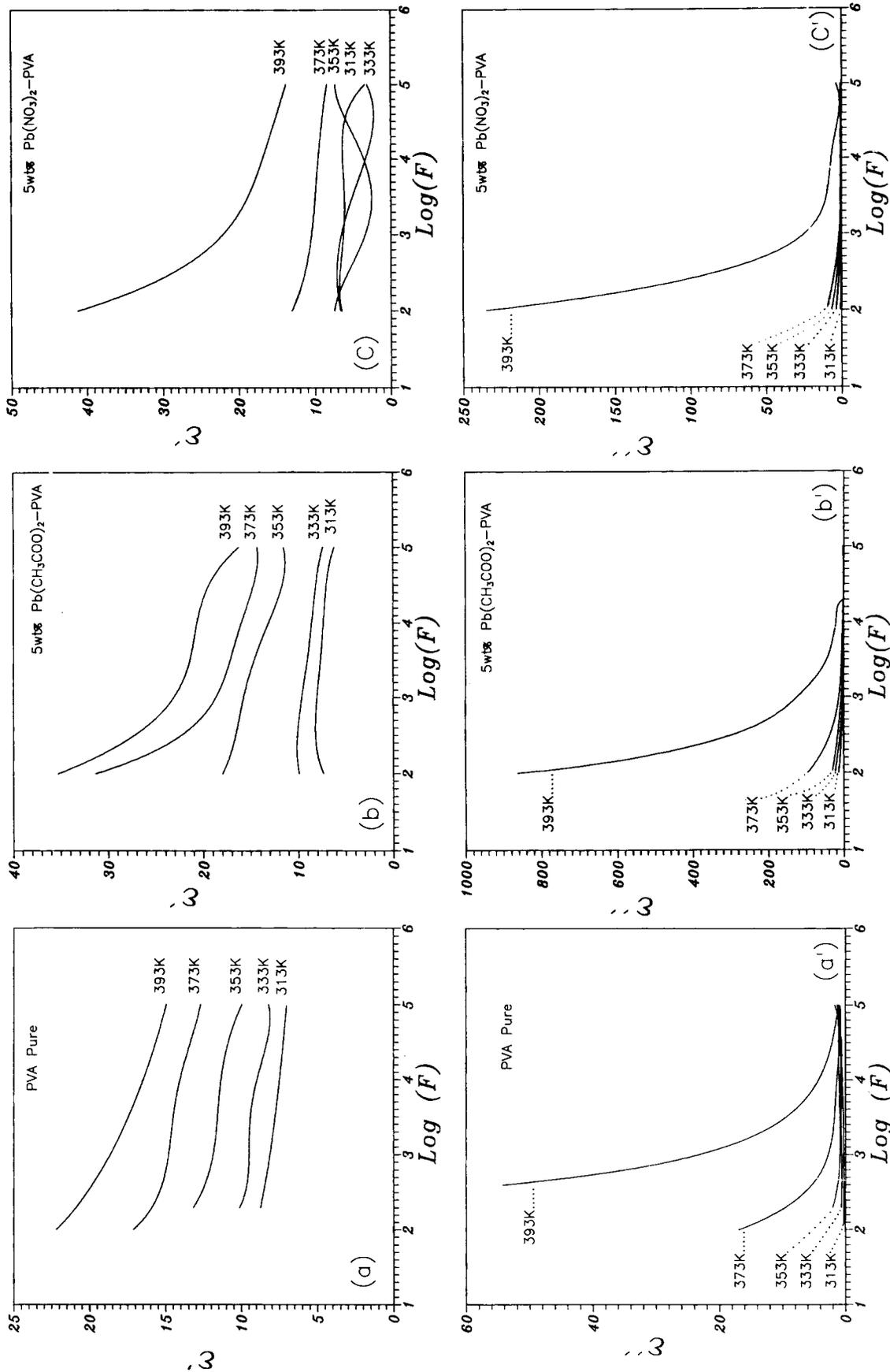


Figure 2 Dielectric permittivity ϵ' and ϵ'' as a function of $\log(F)$ at various temperatures, for pure and blended PVA films: (a,a') pure PVA; (b,b') 5 wt % $\text{Pb}(\text{CH}_3\text{COO})_2$ -PVA; (c,c') 5 wt % $\text{Pb}(\text{NO}_3)_2$ -PVA.

against frequency in Figure 2. The values of the dielectric constant ϵ' [Fig. 2(a)–(c)] and the dielectric loss ϵ'' [Fig. 2(a')–(c')] seem to decrease as the frequency increases and increase as the temperature increases. On the other hand, ϵ' and ϵ'' values depend on the salt type; they are lower in the case of the PVA–Pb(NO₃)₂ composite than in the case of the PVA–Pb(CH₃COO)₂ composite in comparing to the values of pure PVA. Further, ϵ' values seem to be large specifically at higher temperatures and frequencies. This is, of course, not the bulk dielectric constant but rather is due to the “free” charge motion within the material and is sometimes known as “space-charge polarization.”¹⁵ As shown in Figure 2, no definite relaxation modes could be clearly observed in salt-containing PVA.

Therefore, the complex electric modulus,

$$M^* = M' + iM'' \quad (2)$$

which is defined as the reciprocal of the dielectric constant ($M^* = 1/\epsilon^*$), has most frequently been employed in studies to investigate the relaxation processes in ionic conductors.

Hence, to resolve the dipolar and ionic natures of the relaxation processes, the real component of the complex electric modulus,

$$M' = \epsilon' / (\epsilon'^2 + \epsilon''^2) \quad (3)$$

and the imaginary component

$$M'' = \epsilon'' / (\epsilon'^2 + \epsilon''^2) \quad (4)$$

were calculated from the ϵ' and ϵ'' data.^{16,17} These values (M' , M'') are plotted vs. temperature for fixed measuring frequencies in Figure 3. On the other hand, Figure 4 shows the variation of M' and M'' with frequencies for fixed measuring temperatures. The M' vs. T and M'' vs. T curves of pure PVA and its composites show clearly relaxation peaks, but their structure features, peak positions, and peak intensities depend on the lead salt types, temperature, and frequency. In general, three relaxations can be characterized: These relaxations can be referred to low-, intermediate-, and high-temperature relaxations.

PVA has a polar side groups in its chain and dielectric primary relaxation and local mode relaxations have been reported.^{5,7} The lower and the intermediate relaxations are ascribed to torsional and segmental motion of the amorphous chains¹⁸ and will be designated as β - and α_g -relaxations, respectively. The higher-temperature relaxation is a non-

dipolar process due to the interfacial polarization or space charge polarization effects and will be designated as α_p -relaxation.

As Figures 3 and 4 illustrate, the relaxation processes become more clearly resolved on representing the data by the electric modulus. Investigation of M'' - T or M'' - $\log(F)$ curves of pure and Pb(CH₃COO)₂-PVA composite reveals that different positions of α_g and α_p peaks are observed at different temperatures and frequencies, i.e., a peak moves through the frequency “window” or temperature “window” as both the temperature and the frequency changes. On the other hand, the β -relaxation of PVA is located at about 320 K in M'' - T curves. It is seen, generally, that the composite of lead nitrate–PVA behaves somewhat differently.

These observations clearly suggest the persistence of the higher dipole moment segmental mobility (α_g -relaxation) in the crosslinked network, through H bonding of the lead nitrate–PVA composite. The occurrence of such localized motions seems to be common to all types of amorphous solids.¹⁹ The features of these localized motions are remarkably similar to those of the β -relaxation of pure PVA (as seen in the M'' - T curve), namely, that there is an increase in the height of the M'' peak with decreasing frequency (a decrease in the half-width). Hence, a second noncovalently bonded network structure, in addition to the covalent crosslinked network structure, of the polymer molecules must be considered. This second structure is attributed to the H bonding between the OH groups of PVA and the O atom of lead nitrate.

A more significant comparison is that of the data for the α_p -relaxation in pure and lead acetate-containing PVA. It is apparent from the plots (M'' - T) [see Fig. 3(b')] that the peak shape for salt-containing PVA is different from that of pure PVA [see Fig. 3(a')] and shifts over a wide temperature range. Further, as is clear in the M'' - T curve of pure PVA, the growth of at least one new peak, closely spaced to the original, is responsible for the shift. This α_p -relaxation has been associated mainly with aligned configuration of chain segments formed in the polymer during deformation treatment (complex formation).

It is believed that the loss peaks seen in the temperature domain are not true loss peaks; they are simply the result of two opposing effects; the increasing mobility of charge carriers or dipoles and the breakage of the hydrogen bond, and, hence, the decrease of the water content at the PVA–Pb(NO₃)₂ interfaces with increasing temperature. Only this interpretation can explain why the peaks do not

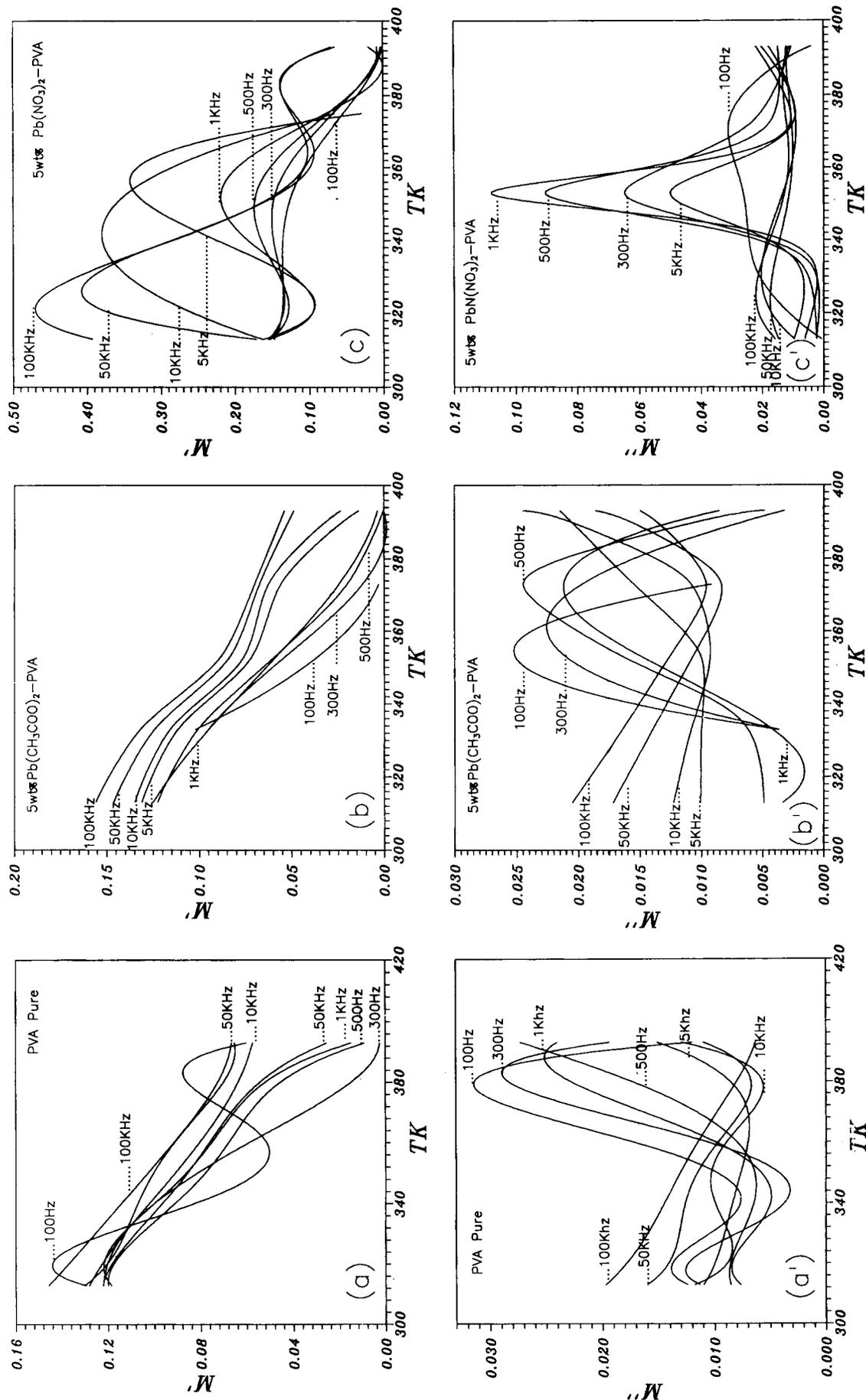


Figure 3 Variation of electric modulus M' and M'' with temperature (T) at various frequencies for pure and doped PVA films: (a,a') pure PVA; (b,b') 5 wt % $\text{Pb}(\text{CH}_3\text{COO})_2$ -PVA; (c,c') 5 wt % $\text{Pb}(\text{NO}_3)_2$ -PVA.

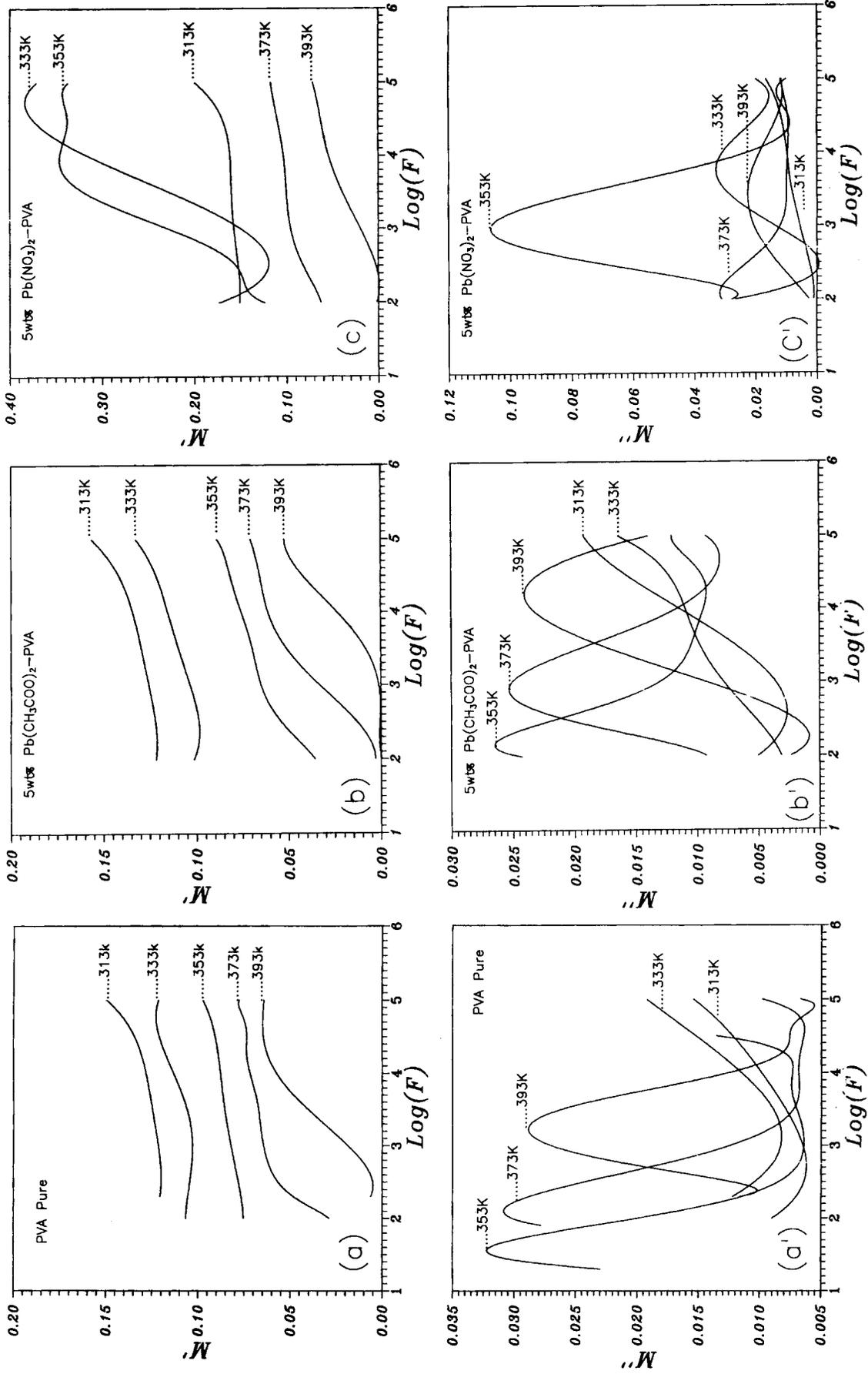


Figure 4 Variation of M' and M'' with $\log(F)$ at various temperatures for pure and doped PVA films: (a,a') pure PVA; (b,b') 5 wt % $\text{Pb}(\text{CH}_3\text{COO})_2\text{-PVA}$; (c,c') 5 wt % $\text{Pb}(\text{NO}_3)_2\text{-PVA}$.

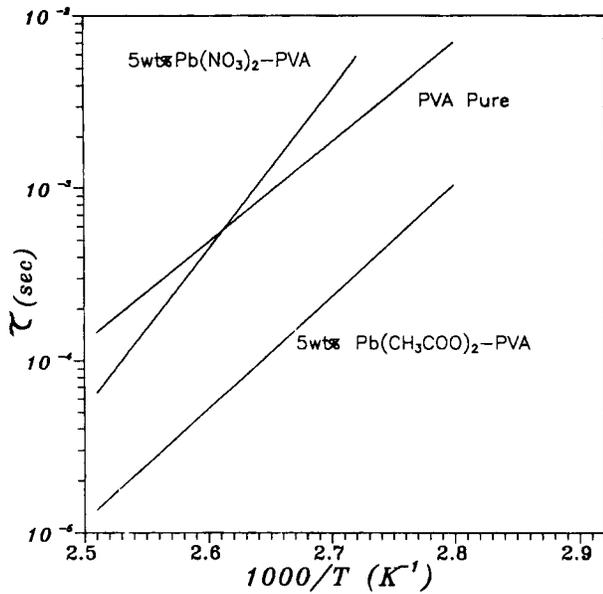


Figure 5 Plots of τ against reciprocal absolute temperature ($1/T$) for pure and blended PVA films.

change their position but only their height with varying frequency. This behavior may reflect the strong hydrogen bonding existing in the PVA-lead nitrate complex. It might be expected that hydrogen bonding in the film, involving the PVA chain, will determine the symmetry of the orientation distribution of the dopant. Further, hydrogen bond formation between the dopant and the polymer chains may influence the dielectric behavior of PVA-lead nitrate composite films.

c-Relaxation Characteristics

The transformation of the data to the electric modulus led to the resolving of the relaxation processes and enables one to evaluate the relaxation parameters, namely, the preexponential factor (τ_0) and the activation energy (E_a). The position of each peak indicates a characteristic rate of relaxation of that

particular structure and the height of its dielectric strength (or the magnitude of dipole moment and the number of molecules). Hence, it is of interest to evaluate the temperature dependence of the average relaxation times, τ , for M'' at various relaxation processes. The average relaxation time has been calculated using the formula

$$f_m = 1/2\pi\tau \quad (5)$$

where f_m is the frequency of the peak maximum.

Arrhenius plots for the transition of pure and doped PVA are shown in Figure 5. It is clear that the relaxation peaks (see Fig. 4) are non-Debye-like, being both broadened and of symmetry. The average activation energy, E_a , and the characteristic time, τ_0 , were evaluated from the plot $\ln \tau(T)$ vs. $1/T$ (see Fig. 5) using the Arrhenius equation²⁰:

$$\tau(T) = \tau_0 \exp(E_a/KT) \quad (6)$$

where K is the Boltzmann's constant. The preexponential factors (τ_0) and the activation energies (E_a) together with f_m for pure and PVA composites are listed in Table I. A higher activation energy was obtained for the lead nitrate/PVA blend, indicating the formation of the $\text{Pb}(\text{NO}_3)_2$ -PVA complex. Further, as seen in Figure 5, relaxation times are relatively high; the Maxwell-Wagner effect is expected. A mixture of two materials with different conductivities and permittivities always exhibits an additional dielectric polarization mechanism, the so-called interfacial or Maxwell-Wagner relaxation.²¹ In the present study, in the case of $\text{Pb}(\text{NO}_3)_2$ -PVA complexes (Fig. 4), the Maxwell-Wagner effect has been observed. The loss modulus increases from 333 to 353 K and decreases rapidly from 353 to 373 K, which is attributed to the charge buildup at the interface between the salt particles and the polymer matrix.

Table I Relaxation Parameters for Pure and Lead Salt-doped PVA

Material	Relaxation Parameters				
	f_m (s^{-1})			E_a (eV)	τ_0 (s)
	393 K	373 K	353 K		
Pure PVA	1.6×10^3	80.0	32.0	0.63	5.4×10^{-13}
5 wt % $\text{Pb}(\text{CH}_3\text{COO})_2$ -PVA	1.6×10^4	7.9×10^2	2×10^2	0.69	1.8×10^{-13}
5 wt % $\text{Pb}(\text{NO}_3)_2$ -PVA	2.5×10^3	1.3×10^2	1×10^3	1.03	3.0×10^{-17}

CONCLUSION

The UV-absorption study revealed that blending of PVA with both lead acetate and lead nitrate causes a remarkable change in its UV-spectrum, depending on both the concentration and the nature of the metal salt used, providing the formation of the lead salt-PVA complex.

A detailed dielectric relaxation study of pure and PVA composite films revealed the existence of three transitions: local, primary, and polarization relaxations. The nature of the salt, the temperature, and the frequency all influence the position and the intensity of the loss maxima. The high-temperature relaxation peak observed in the dielectric modulus loss curves of the composites has been assigned to the interfacial polarization (Maxwell-Wagner effect) in the low-frequency region.

It should be stated that the representation of the dielectric properties in terms of the electric modulus, M^* , is very sensitive, and the structure features of the relaxation peaks depend on whether the data are given in $M''-T$ or $M''-\log F$ plots. The low-frequency dielectric absorption of PVA-lead nitrate composites is most interesting and calls for a further detailed investigation.

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