

# The Effect of Moisture on the Dielectric Behavior of Poly(Vinyl Acetate)–Natural Rubber Blend

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## Synopsis

Dynamic dielectric analysis was used to analyze the miscibility of poly(vinyl acetate) and natural rubber and the effect of moisture on the dielectric properties of the polymer blend. Two separate dielectric relaxations were observed within the temperature range studied. The high-temperature relaxation was a result of the glass transition of poly(vinyl acetate), whereas the low-temperature relaxation was attributed to that of natural rubber. The peak temperatures of  $\epsilon''$  of the high-temperature relaxation decreased with increasing aging time, while the magnitudes of the  $\epsilon''$  peaks increased with increasing days of aging. The peak temperatures of  $\epsilon''$  of the low-temperature relaxation stayed constant, while the magnitudes of the  $\epsilon''$  peaks increased with increasing days of aging. This indicates that both polymers are responsible for the sorption of moisture; however, water is an effective plasticizer only for poly(vinyl acetate). Anomalous increases in the magnitudes of  $\epsilon''$ , especially in the low frequency sides, of the Argand diagrams were explained by Maxwell–Wagner–Sillar (MWS) polarization at component interfaces. The oscillator strength, relaxation time, and the two distribution parameters,  $A$  and  $B$ , calculated from the skewed circular arc equation, were affected with days of aging.

## INTRODUCTION

The application of dynamic methods is extremely useful in studying the viscoelasticities of polymers. By using dynamic measurements, in which the sample under investigation is subjected to an oscillatory electrical or mechanical field, the real part due to the energy stored and the imaginary part due to the energy dissipated during the cyclic stimulus can be separated and measured. Dynamic dielectric analysis (DDA) measures the dielectric relaxation which is the lag of the dipole behind an applied alternating electric field. Polymers with permanent dipole moments are, in some cases, more sensitive to the dielectrical response than to the mechanical one. For instance, the  $\beta$ -transition of poly(methyl methacrylate), which is due to the sidechain motion, has a greater response in dielectric loss than the  $\alpha$ -transition, which is due to the backbone motion, whereas the mechanical transitions reverse the case.<sup>1</sup> The DDA technique has also been successfully used in monitoring bonding processes<sup>2</sup> and characterizing organic coatings.<sup>3</sup>

Poly(vinyl acetate) has been used in a variety of applications,<sup>4,5</sup> e.g., adhesives, latex paints, paper coatings, etc., due to its low cost and good

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structural stability. Dynamic dielectric and dynamic mechanical properties of poly(vinyl acetate) have been studied.<sup>6-8</sup> Williams and Ferry<sup>7</sup> have shown that the electrical and mechanical shift factors of poly(vinyl acetate) are identical. Negami et al.<sup>9</sup> found that the glass transition of poly(vinyl acetate) followed a skewed circular arc equation and exhibited a range of distributions of dielectric relaxation time.

The characteristic extensibility of natural rubber has made it used widely in various industries.<sup>10</sup> However, the source has become scarce due to the cost of labor and the time consumed for the plant to grow. The blends of *cis*- and *trans*-poly(isoprene) have been found to be compatible with a dynamic mechanical test.<sup>11</sup>

The compatibility of poly(vinyl acetate) and natural rubber has not yet been studied with a dynamic method. Since the dynamic dielectric analysis is extremely sensitive to changes which involve dipole reorientations in polymeric matrix, the use of this technique to characterize polymer-water interactions should provide a unique understanding into the macromolecular origin.

In this paper the application of dynamic dielectric analysis to study the miscibility of poly(vinyl acetate) with natural rubber and the effect of moisture on the dielectric properties of the blend under 45% and 75% RH are presented. Their dielectric constant and loss data over a range of temperatures and frequencies are calculated and discussed.

## EXPERIMENTAL

### Materials

The poly(vinyl acetate) was blended with natural rubber at a ratio about 4:3. The number-average,  $\bar{M}_n$ , and weight-average,  $\bar{M}_w$ , molecular weights of poly(vinyl acetate) determined by gel permeation chromatography were  $8.56 \times 10^3$  and  $1.60 \times 10^4$ , respectively. The molecular weight distribution (MWD) of poly(vinyl acetate) was 1.87. The natural rubber used was the Jelutong with viscosity-average molecular weight  $\bar{M}_v$ , determined by the Mark-Houwink-Sakurada equation  $[\eta] = k\bar{M}_v^a$ . The values of  $k$  and  $a$  for natural rubber in toluene at 25°C are  $50.2 \times 10^{-5}$  dL/g and 0.667, respectively.<sup>12</sup> The calculated  $\bar{M}_v$  was  $1.8 \times 10^4$ .

The polymer blend also contained some other additives. However, their effects on the dielectric relaxation phenomena of poly(vinyl acetate) and natural rubber were limited to the polymer blend prior to humidity aging and were beyond the scope of this paper.

### Humidity Aging

The polymer blend of poly(vinyl acetate) and natural rubber was cut into small pieces (1-2 g each) and stored in desiccators with saturated salt solutions having a 45% or 75% relative humidity at room temperature. They were found to soften over a period of time, especially in the 75% RH chamber. Because the room temperature ranged about  $20 \pm 4^\circ\text{C}$ , the relative humidity in the desiccators could possibly vary  $\pm 5\%$  RH. The moisture gained for the blend at 45% RH on days 4, 10, and 19 were 0.15, 0.18, and 0.19% (w/w),

respectively, while that at 75% RH on days 4, 10, and 22 were 0.39, 0.47, and 0.54% (w/w), respectively.

### Dielectric Sampling

The polymer blend sample was taken from the desiccator after a desired aging time and immediately placed between two mechanically flattened aluminum foils. This sandwiched sample was put between two aluminum plates with a 1 mm thickness spacer having a 3 cm circular opening in the center. It was then put between a preheated (140°C) Carver Press and pressed at 5000 psi. An aluminum-sandwiched sample with a 2.54 cm diameter was cut after it was cooled to room temperature.

### Dielectric Measurements

The capacitance and the dissipation factors of the polymer blend were measured by the General Radio, Type 1610 B-2, capacitance measuring assembly. Real and imaginary parts of the complex dielectric constants,  $\epsilon'$  and  $\epsilon''$ , respectively, were calculated with a computer program using PDP-11 from the capacitance  $C_x$  and the resistance  $R_x$  of the condenser filled with unknown material and the capacitance  $C_0$  of the empty cell. The measurement involved the determination of impedance  $Z$  (voltage/current) of the circuit element formed by a cell containing the dielectric material:

$$Z = \frac{1}{i\omega C_x + 1/R_x} \quad (1)$$

The real and imaginary parts were then obtained:

$$\epsilon' = \frac{C_x}{C_0} \quad (2)$$

$$\epsilon'' = \frac{1}{\omega R_x C_0} \quad (3)$$

$$\tan \delta = \frac{1}{\omega R_x C_x} \quad (4)$$

## RESULTS AND DISCUSSION

Figure 1 shows the plot of dielectric constant,  $\epsilon'$  and dielectric loss  $\epsilon''$  vs. a range of temperatures between  $-50$  and  $+90^\circ\text{C}$  at 0.1, 1, 10, and 100 kHz for the natural rubber in the  $\alpha$ -relaxation region. One classical dielectric relaxation in which  $\epsilon'$  has a sigmoidal increase and  $\epsilon''$  goes through a peak during relaxation was found. The natural rubber used in this study was believed to contain about 20% *cis*-1,4-poly(isoprene) and 80% are other low-molecular-weight resins.<sup>13</sup> The dielectric relaxation observed was believed to be due to an  $\alpha$ -relaxation of the polymer rather than that of a low MW resin. Norman<sup>14</sup> has observed and reported that the dissipation factor,  $\tan \delta$ , went through a

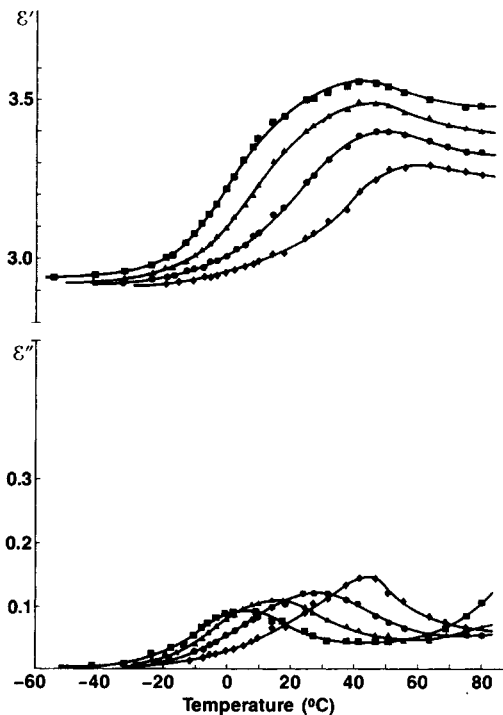


Fig. 1. Temperature dependence of  $\epsilon'$  and  $\epsilon''$  for the oxidized natural rubber: (■) 0.1 kHz; (▲) 1 kHz; (●) 10 kHz; (◆) 100 kHz.

maximum of about 0.0045 at  $-10^{\circ}\text{C}$  at a frequency of  $10^6$  Hz and at  $-55^{\circ}\text{C}$  at a frequency of 50 Hz for purified natural rubber. The magnitudes and the locations of the dissipation factor in this study were much higher than those reported by Norman. This dielectric relaxation arising from the natural rubber has been monitored and found<sup>15</sup> to further increase after purification. It is, therefore, concluded that this dielectric relaxation is due to the oxidized *cis*-1,4-poly(isoprene) of the natural rubber. The activation energy calculated from the Arrhenius plot of logarithmic  $\epsilon''$  peak transition frequency,  $\log f$  (maximum), vs. reciprocal of temperature for the oxidized natural rubber was 15.6 kcal/mol.

Figure 2 showed the plots of  $\epsilon'$  and  $\epsilon''$  versus temperature between  $-50$  and  $+100^{\circ}\text{C}$  at 0.1, 1, 10, and 100 kHz for the polymer blend at day 0 under room conditions ( $20 \pm 4^{\circ}\text{C}$ ,  $45 \pm 5\%$  RH). Two separate dielectric transitions have been noted. The high-temperature relaxation was attributed to the glass transition of poly(vinyl acetate), whereas the low-temperature relaxation was assigned to that of the oxidized natural rubber. The separation of these two dielectric relaxations also signified the immiscibility of poly(vinyl acetate) with natural rubber.

The peak transition temperature of oxidized natural rubber was lowered from  $5^{\circ}\text{C}$  (Fig. 1) to  $0^{\circ}\text{C}$  (Fig. 2) at a frequency of 0.1 kHz. Its dielectric oscillator strength,  $(\epsilon_0 - \epsilon_{\infty})_T$ , also was lowered from 0.70 (Fig. 1) to 0.15 (Fig. 2). This was due to dilution effect by the blending with poly(vinyl acetate).

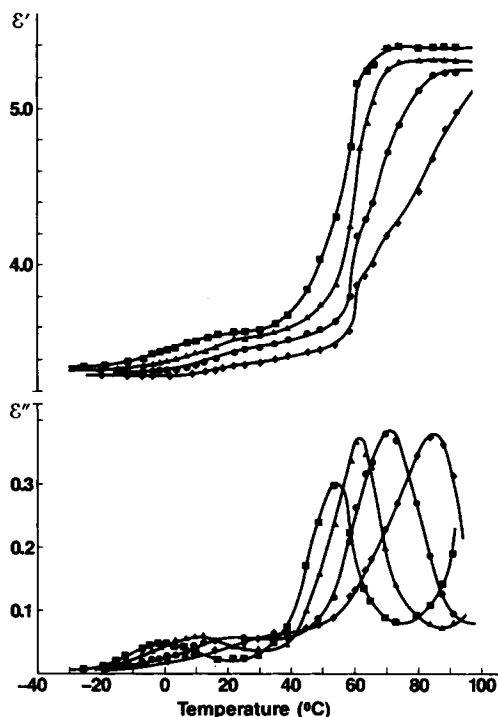


Fig. 2. Temperature dependence of  $\epsilon'$  and  $\epsilon''$  for poly(vinyl acetate)-natural rubber blend on day 0. (■) 0.1 kHz; (▲) 1 kHz; (●) 10 kHz; (◆) 100 kHz.

### Polymer-Water Interactions

Dielectric constants  $\epsilon'$  and dielectric loss factors  $\epsilon''$  were measured for the polymer blend stored under the conditions of 45% RH and room temperature on days 4, 10, and 19. Figure 3 shows the temperature plots of  $\epsilon'$  and  $\epsilon''$  at the four frequencies for the polymer blend stored under 45% RH on day 19. The  $\epsilon''$  peak transition temperatures of the high-temperature relaxation, were lowered slightly, e.g., from 54 to 52°C at a frequency of 0.1 kHz. The  $\epsilon''$  peak transition temperatures of the low-temperature dielectric relaxation, on the other hand, were essentially unchanged. However, the oscillator strength,  $(\epsilon_0 - \epsilon_\infty)_T$ , and the magnitudes of the  $\epsilon''$  of the high-temperature relaxation increased with aging. This was attributed to the sorption of polar water molecules by the carbonyl groups of poly(vinyl acetate) which, in turn, increased the effective dipole moment and made it more dielectrically lossy.

Dielectric data also were obtained for poly(vinyl acetate)-natural rubber blend stored under the conditions of 75% RH and room temperature on days 4, 10, and 22. Figure 4 showed the plots of  $\epsilon'$  and  $\epsilon''$  vs. temperature at the four frequencies for the polymer blend kept under 75% RH on day 22. Two dielectric relaxations were observed for the blend of the two immiscible polymers. It is noted that the  $\epsilon''$  peak transition temperatures of the low-temperature dielectric transition still remained about the same as the peak transition temperatures of the polymer blend on day 0, while the  $\epsilon''$  peak transition temperatures of the high-temperature dielectric transition were

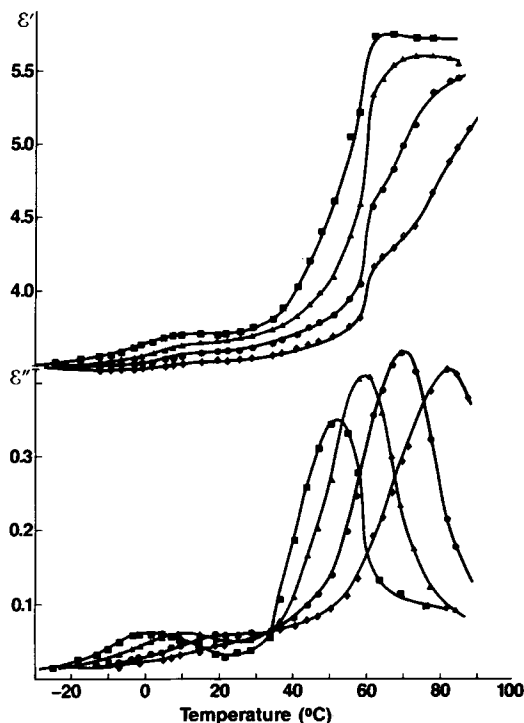


Fig. 3. Temperature dependence of  $\epsilon'$  and  $\epsilon''$  for poly(vinyl acetate)-natural rubber blend at 45% RH on day 19. (■) 0.1 kHz; (▲) 1 kHz; (●) 10 kHz; (◆) 100 kHz.

lowered at a much faster pace during the first few days of storage at 75% RH than at 45% RH. This possibly was due to the fact that water molecules were bonded more effectively to poly(vinyl acetate) than to natural rubber. The addition of water molecules to the carbonyl groups of poly(vinyl acetate) can isolate the polymer chain from its neighboring polymers, and it, in turn, decreases the hindrance and increases the backbone flexibility of poly(vinyl acetate). This behavior is similar to the internal plasticization effect of *n*-alkyl methacrylate polymers<sup>16</sup> whose  $\alpha$ -transition temperatures of the mechanical and dielectric relaxations decreased with increasing the length of *n*-alkyl group.

The magnitudes of  $\epsilon''$  peaks, however, increased with aging for the polymer blend kept under 75% RH. The oscillator strength of the low-temperature dielectric relaxation also displayed an increase with aging. The interaction of water with the active sites of the oxidized natural rubber was responsible for the increase of the  $\epsilon''$  peaks. The increases in the magnitudes of  $\epsilon''$  peaks as well as in oscillator strength signified that natural rubber was oxidized to a certain degree. The effectiveness of water on the  $\epsilon''$  peak temperatures of the high-temperature dielectric relaxation was limited to the first few days. Further storage under 75% RH did not cause any further decrease of the  $\epsilon''$  peak temperatures. It is concluded that the sorption and desorption of water molecules have reached thermodynamic equilibrium between the polymer and water. The oscillator strength  $(\epsilon'_0 - \epsilon'_\infty)_T$  and dielectric constants  $\epsilon'$  of the

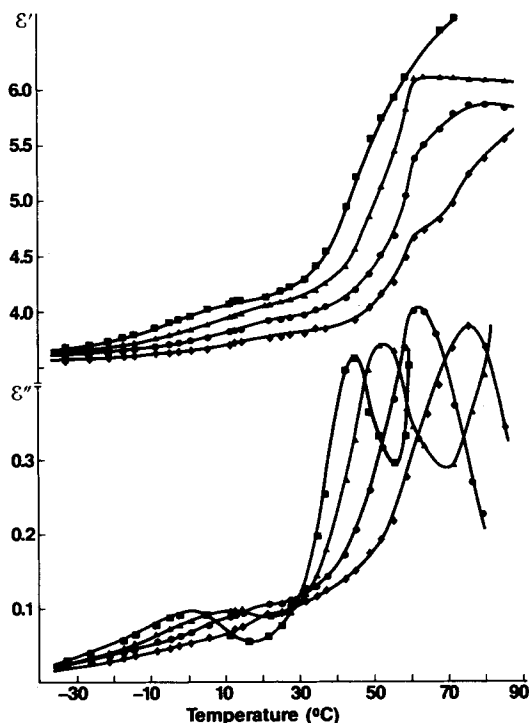


Fig. 4. Temperature dependence of  $\epsilon'$  and  $\epsilon''$  for poly(vinyl acetate)-natural rubber blend at 75% RH on day 22. (■) 0.1 kHz; (▲) 1 kHz; (●) 10 kHz; (◆) 100 kHz.

high-temperature dielectric relaxation, however, increased with aging under 75% RH. This is understandable, since the kinetic parameters of the  $\epsilon''$  peak temperatures of the high-temperature dielectric relaxation involved the backbone motion of poly(vinyl acetate); only the effective interactions caused by water molecules are counted. The oscillator strength and dielectric constants, on the other hand, are a measure of total bulk property.

Figure 5 shows the Arrhenius plots of  $\log f(\text{maximum})$  vs. reciprocal of temperature for the polymer blend kept under 45 and 75% RH, where  $f(\text{maximum})$  is the frequency of measurement at which  $\epsilon''$  reaches the maximum at certain temperature. In all cases, curvatures rather than linear relationships were observed. This indicates that Arrhenius equation is insufficient to describe the transition behavior of poly(vinyl acetate) in the blend.

### Relaxation Phenomena

The skewed circular arc equation (SCAE) derived from Havriliak and Negami is sufficient to describe most of dielectric relaxations at the glass transition. The equation<sup>8</sup> is written as

$$\epsilon^* = \frac{\epsilon_0 - \epsilon_\infty}{[1 + (i\omega\tau)^{1-A}]^B} + \epsilon_\infty$$

where  $\epsilon^*$  is the complex dielectric constant,  $\epsilon' - i\epsilon''$ ,  $\epsilon_0$  and  $\epsilon_\infty$  are the

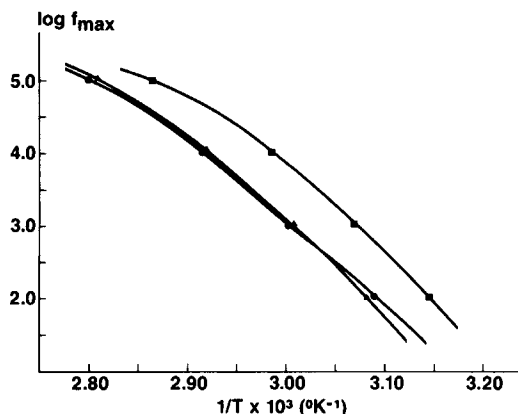


Fig. 5. Arrhenius plots of poly(vinyl acetate)-natural rubber blend: (●) day 0; (▲) day 19, 45% RH; (■) day 22, 75% RH.

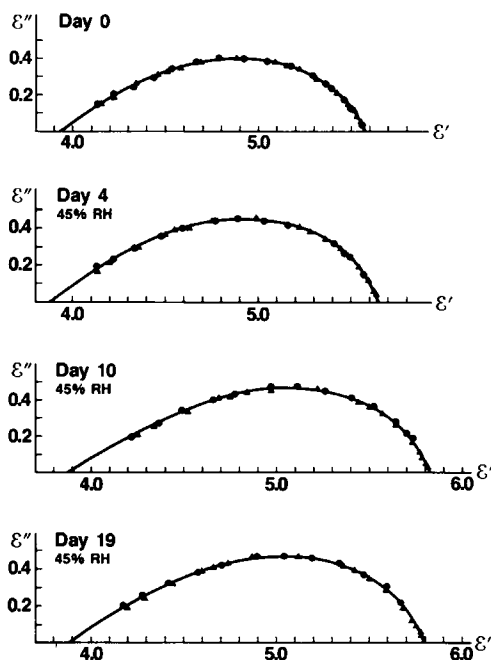


Fig. 6. Argand diagrams for poly(vinyl acetate)-natural rubber blend at 45% RH: (●) experimental; (▲) theoretical.

dielectric constants at zero and infinite frequencies, respectively,  $\tau$ ,  $1/(2\pi f_r)$ , is the dielectric relaxation time,  $f_r$  is the relaxation frequency, and  $A$  and  $B$  are distributed parameters that represent the breadth of the distribution of relaxation time and skewness on the high frequency side. The evaluation of parameters  $A$  and  $B$  was detailed elsewhere.<sup>8,9</sup> Figures 6 and 7 are the Argand diagrams in which dielectric loss  $\epsilon''$  was plotted against dielectric constant  $\epsilon'$  at 17 discrete frequencies for the polymer blend kept under 45 and 75% RH, respectively. These plots showed similar asymmetric arcs, which can be



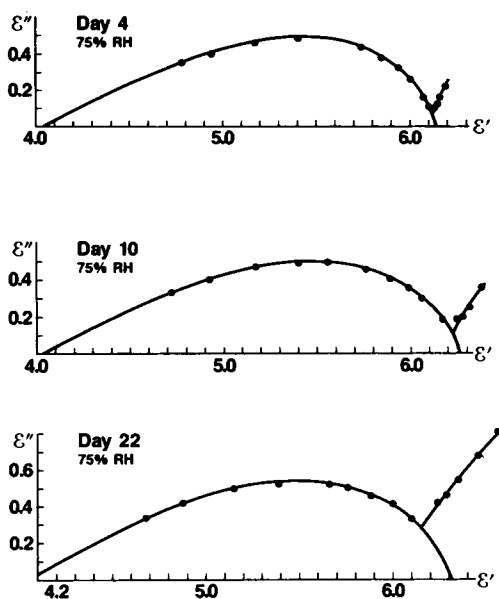


Fig. 7. Argand diagrams for the poly(vinyl acetate)-natural rubber blend at 75% RH.

TABLE I  
SCAE Characteristic Values of Poly(vinyl Acetate)/Natural Rubber Blend

	Days	Temp (°C)	$\epsilon_0$	$\epsilon_\infty$	$\tau \times 10^5$ (s)	A	B
45% RH	0	60.5	5.57	3.93	17.7	0.27	0.53
	4	60.2	5.65	3.88	14.5	0.23	0.51
	10	60.6	5.82	3.88	13.3	0.22	0.44
	19	60.8	5.79	3.88	15.9	0.21	0.45
75% RH	0	60.5	5.57	3.93	17.7	0.27	0.53
	4	60.0	6.14	4.05	3.98	0.15	0.35
	10	60.6	6.26	4.04	4.55		
	22	60.8	6.31	4.05	3.98		

represented by the SCAE-type relaxation. The SCAE characteristic values of the polymer blend were listed in Table I. The oscillator strength,  $\epsilon_0 - \epsilon_\infty$ , increased with aging in both cases. However, a more profound increase was found in the case of 75% RH than in 45% RH. This was due to the increase in the effective dipole moment of poly(vinyl acetate) with the addition of water molecules. It was also noted that the sorption of water led to a unique increasing overshoot in the magnitude of  $\epsilon''$  in the low frequency sides for the polymer blend kept under 75% RH. This was attributed to the Maxwell-Wagner-Sillars<sup>17</sup> (MWS) polarization which resulted from the phase separation on electrical charges accumulated in the polymer blend through the participation of water molecules which affect the rate of phase separation, crystallization, or other phenomena that result in interfaces where exchanges can accumulate.

Relaxation phenomenon takes place when a molecule proceeds from one equilibrium state to another. Increase in backbone flexibility facilitates, in general, the relaxation process and decreases the relaxation time. The SCAE characteristic values listed in Table I measured at about 60.5°C were mainly due to the relaxation process of poly(vinyl acetate) in the hydrated polymer blend. It was noted that the parameters *A* and *B* decreased with increasing days of aging as listed in Table I. It was difficult to evaluate parameters *A* and *B* with confidence for the polymer blend at 75% RH due to the interference of MWS polarization. The decrease of the mean relaxation time shown in Table I for the blend at both 45 and 75% RH indicates the increasing flexibility of polymer backbone. Increase in the temperature also increases the flexibility of polymer backbone and sidechain. Negami et al.<sup>9</sup> found that poly(vinyl acetate) with various molecular weights obeyed SCAE-type relaxation and its parameter *A* decreased as PVAc molecular weight increased.

The decrease of parameter *A* was attributed to the segment weight distribution. However, the parameter *A* of each individual poly(vinyl acetate), which decreased with increasing temperature can not be explained with the change of segment weight distribution. Polymer backbone and/or sidechain flexibility should be responsible for the decrease in parameter *A*. Ikada et al.<sup>18</sup> also found that parameter *A* of 2,4,6-heptanetriol triacetate, which represented the oligomer of poly(vinyl acetate), decreased with increasing temperature. Considering the change in backbone flexibility, the drop in the parameter *A* with increasing temperature is then understandable. This is in agreement with the findings of this paper that the decrease in parameter *A* of poly(vinyl acetate)-natural rubber blend is also an indication of backbone flexibility.

## CONCLUSIONS

Poly(vinyl acetate) and oxidized natural rubber were incompatible by observing two dielectric relaxations for the blend due to the separation of glass transitions of the two polymers. Both poly(vinyl acetate) and oxidized natural rubber were capable of sorbing moisture which makes both polymers more dielectrically lossy. However, the effects of the polymer-water interactions were different. Poly(vinyl acetate) could be plasticized by water molecules by lowering its dielectric transition temperatures, whereas oxidized natural rubber was not affected. The participation of water molecules also increased the effective dipole moment of both polymers but only increased the flexibility of poly(vinyl acetate) during its dielectric transitions. Its effectiveness of lowering dielectric transition temperatures was limited to the primary layer of water sorption of poly(vinyl acetate). Additional layers of water sorption did not affect its kinetic parameters, e.g.,  $\epsilon''$  peak temperatures and dielectric relaxation time, but its bulk properties, e.g., dielectric loss factor and oscillator strength.

The increase of the dielectric loss factors, especially in the low-frequency sides of the Argand diagrams of the polymer blend with increasing days of humidity aging was an evidence of MWS polarization due to the increase in the degree of heterogeneity. Its distribution parameters, *A* and *B*, were

affected by the sorption of water molecules. The breadth of relaxation,  $A$ , was also an indication of backbone inflexibility.

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