

# Dielectric Studies on the Miscibility in Poly(vinyl acetate)/Poly(ethyl methacrylate) Blends

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## SYNOPSIS

The glass transition relaxations of different blends of poly(vinyl acetate) and poly(ethyl methacrylate) have been investigated by dielectric relaxation spectroscopy in the frequency range from 20 Hz to 1 MHz. The obtained results suggest that the poly(vinyl acetate)-rich blends show immiscibility between the two components, whereas the poly(ethyl methacrylate)-rich blends show partial miscibility. The results obtained by differential scanning calorimetry and the analysis of the Maxwell–Wagner–Sillars effect seem to confirm the dielectric relaxation results. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

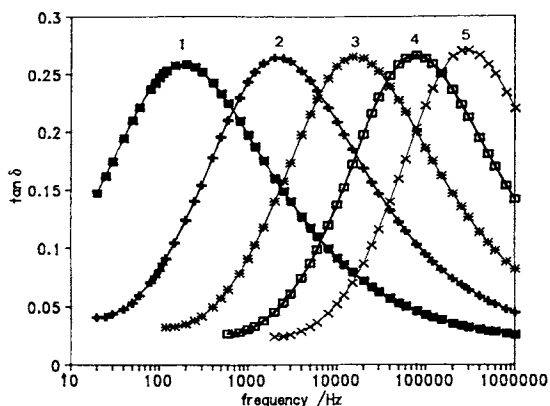
Polymer blends have been the subject of extensive studies both in industry and at university laboratories. The technological interest of the research on miscible polymer blends comes from the possibility they offer for engineering the properties of polymeric materials. In fact, blending two or more polymers allows new materials whose properties can be tailored to become superior to those of the constituent homopolymers. Polymer blends are metastable systems tending continuously to phase separation. For this reason, the search for criteria and methods to suppress incompatibility is an investigation with important practical applications.

Despite the numerous studies published about this subject, many aspects of polymer miscibility are far from being understood. The generally accepted miscibility criteria is the exhibition of optical clarity and of a single glass transition.<sup>1,2</sup> Phase-separated samples exhibit two distinct glass transitions. Many techniques have been used to study polymer miscibility, namely differential scanning calorimetry, mechanical relaxation, dielectric relaxation, nuclear magnetic resonance, and thermally stimulated currents. Because each component brings to the blend

a separate contribution to the overall properties, which depends more or less on the nature of the other component, the dynamics of polymer blends are understandably more complicated than that of the individual components. In fact, blending alters the molecular dynamics of both components, and the extent of this modification is such that the individuality of the components is sometimes difficult to observe. The dynamic characteristics of the  $\alpha$ -relaxation are thus significantly different in the blend, when compared with the pure polymers.<sup>2,3</sup> These modifications of the glass transition relaxation induced by blending (modification of the components mobilities, broadening of the distribution of relaxation times) are believed to be connected to the presence of concentration fluctuations or to the existence of compositional microheterogeneities due to the different segmental environments.<sup>1,4–7</sup> The study of the molecular dynamics in blends can thus give important information about the factors affecting the glass transition relaxation. Moreover, by varying the composition of miscible blends, we can study the modification of the chain dynamics due to interchain interactions.

In the present work, we study the miscibility in poly(ethyl methacrylate)/poly(vinyl acetate) (PEMA/PVAc) blends by dielectric relaxation spectroscopy. The study was carried out between 50 and 140°C, which covers the glass transition regions of both pure polymers. The obtained results were

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**Figure 1** Loss factor ( $\tan \delta$ ) as a function of the frequency for pure PVAc at different temperatures: 1–50°C, 2–60°C, 3–70°C, 4–80°C, and 5–90°C.

compared with those corresponding to the pure polymers,<sup>8,9</sup> and the conclusions were confirmed by the analysis of the differential scanning calorimetry (DSC) thermograms.

## EXPERIMENTAL

PVAc was an Aldrich product (catalogue no. 18,949-9) with a weight-average molecular weight ( $M_w$ ) of 120,000. PEMA was also from Aldrich (catalogue no. 18,335-0) and had an  $M_w$  of 340,000. The polymers were used as received.

The pure polymers and their blends were prepared by solution casting in a common solvent (dichloromethane, high-performance liquid chromatography grade, from Aldrich) followed by evaporation. The films were heated for several days in a vacuum oven at 43°C to eliminate most of the remaining solvent.

The dielectric measurements were performed using a Hewlet-Packard 4284-A impedance analyzer

(frequency range from 20 Hz to 1 MHz). The samples were placed between the electrodes of a three-terminal parallel plate capacitor described elsewhere.<sup>10</sup> The quantities  $\epsilon' \cdot C_0$  and  $\epsilon'' \cdot C_0$  (where  $C_0$  is the geometric capacitance of the cell and  $\epsilon'$  and  $\epsilon''$  are, respectively, the relative permittivity and the dielectric loss) were directly measured as a function of the frequency. The loss factor ( $\tan \delta = \epsilon''/\epsilon'$ ) was calculated from the measured quantities and used to compare the behavior of the pure polymers and blends.

DSC thermograms were obtained with a Setaram calorimeter DSC-121 in a heating mode run using a scanning rate of 10 K/min.

The experiments were repeated several times and with different samples to check the reproducibility of the results.

## RESULTS AND DISCUSSION

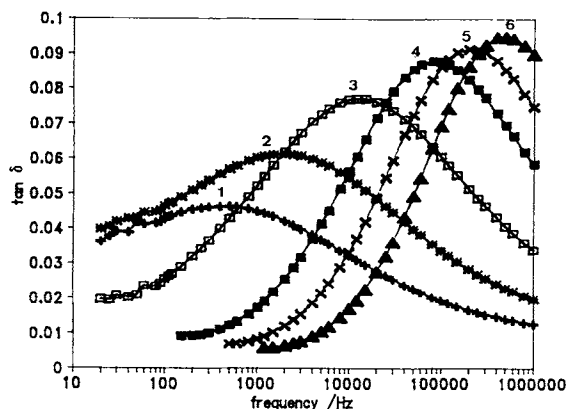
We present a selection of the results obtained on the pure polymers (based on measurements of  $\epsilon'' \cdot C_0$  and  $\tan \delta$ ) and compare the  $\tan \delta$  results with those obtained for three blends of different composition (25, 50, and 75% w/w in PEMA). We chose  $\tan \delta$  to compare the different data because this quantity is independent of the thickness of the sample (and consequently of the capacitance of the empty cell,  $C_0$ ).

### The $\alpha$ -Relaxation in Pure PVAc

Figure 1 shows the loss factor ( $\tan \delta$ ) curves obtained for PVAc in the temperature range from 50 to 90°C. The relaxation parameters corresponding to the dielectric loss ( $\epsilon'' \cdot C_0$ ) curves are presented in Table I. The results are consistent with the previously published studies on pure PVAc and correspond to the behavior of a normal  $\alpha$ -process. In fact, it can

**Table I** Parameters of the  $\alpha$  Relaxation of PVAc

$T$ (°C)	$f_{\max}$ (kHz)	$\tau_0$ (s)	$\epsilon''_{\max} \cdot C_0$ (pF)	$(\epsilon_0 - \epsilon_\infty) \cdot C_0$ (pF)	$\beta$
50	0.092	1.73e-3	120.2	450.7	0.55
60	1.100	1.45e-4	118.8	421.6	0.56
65	3.250	4.90e-5	116.3	406.9	0.58
70	8.500	1.87e-5	114.1	395.6	0.58
75	19.000	8.38e-6	112.3	377.4	0.58
80	45.000	3.54e-6	111.4	363.2	0.60
85	80.000	1.99e-6	112.2	357.9	0.62
90	170.000	9.36e-7	115.9	356.9	0.62



**Figure 2** Loss factor ( $\tan \delta$ ) as a function of the frequency for pure PEMA at different temperatures: 1–60°C, 2–80°C, 3–100°C, 4–120°C, 5–130°C, and 6–140°C.

be seen from the data in Table I that the frequency of maximum loss increases (and the relaxation time,  $\tau_0$ , decreases) with increasing temperature (also, the loss factor curves shown in Fig. 1 illustrate this behavior). This is a general behavior (also observed for PEMA and for the studied blends) and is a consequence of the increased mobility of the polymer chains at higher temperatures. On the other hand, the maximum of intensity of the dielectric loss ( $\epsilon''_{\max} \cdot C_0$ ) decreases slightly with increasing temperature (Table I). Because the shape of the loss curves remains unchanged (a single master curve is obtained from the different normalised dielectric loss curves), we must conclude that the dielectric relaxation strength,  $\epsilon_0 - \epsilon_\infty$ , also decreases with increasing temperature (see Table I where the  $\epsilon_0$  and  $\epsilon_\infty$  values were obtained from the Cole–Cole plots). The  $\beta$  parameter (also shown in Table I), which is the Kohlrausch–Williams–Watts response function for the

dielectric polarization, do not show any significant dependence on the temperature. This  $\beta$  parameter, which describes the distribution of relaxation times, was determined by fitting our dielectric loss data to the numerical tables of Koizumi and Kita.<sup>11</sup> Our dielectric results on pure PVAc are well fitted by the Williams–Landel–Ferry (WLF) equation and the activation energy at 70°C is 42 kcal mol<sup>-1</sup>.

### The $\alpha\beta$ Relaxation in Pure PEMA

Figure 2 shows the loss factor ( $\tan \delta$ ) peaks obtained for PEMA in the temperature range from 60 up to 140°C. The relaxation parameters are presented in Table II. From the results presented in Figure 2 (very similar to the dielectric loss curves) and Table II, it comes out that we can distinguish two different temperature regions: from 60 to 90°C, where the intensity of the loss peaks increases markedly with increasing temperature and the dielectric strength,  $\epsilon_0 - \epsilon_\infty$  also increases, and from 90 to 140°C, where  $\epsilon_0 - \epsilon_\infty$  decreases with increasing temperature and the loss peak intensity increases with  $T$  but not markedly so as in the former. The behavior observed in the lower temperature region is characteristic of the  $\beta$  process, whereas the behavior above 90°C suggests that the relaxation process of PEMA is mainly an  $\alpha$ -process. The Arrhenius plot of  $\log f_m$  versus  $1/T$  (see ref. 8) shows very explicitly those two temperature regions: the activation energy in the lower temperature domain is 19 kcal mol<sup>-1</sup> (Hideshima et al.<sup>12</sup> obtained this same value for the separated  $\beta$ -process, whereas it is 30 kcal mol<sup>-1</sup> in the higher temperature region.

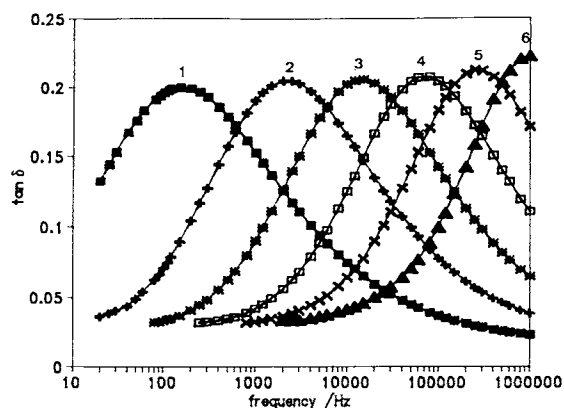
### The Relaxation in PEMA/PVAc Blends

Figures 3–5 show the loss factor ( $\tan \delta$ ) curves at different temperatures for PEMA/PVAc blends

**Table II** Parameters of the  $\alpha\beta$  Relaxation of PEMA

$T$ (°C)	$f_{\max}$ (kHz)	$\tau_0$ (s)	$\epsilon''_{\max} \cdot C_0$ (pF)	$(\epsilon_0 - \epsilon_\infty) \cdot C_0$ (pF)	$\beta$
50	0.110	1.45e-3	7.93	—	—
60	0.275	5.79e-4	9.44	75.0	—
70	0.550	2.89e-4	10.94	81.1	0.32
80	1.250	1.27e-4	12.76	92.6	0.32
90	3.000	5.31e-5	14.66	93.0	0.33
100	9.000	1.77e-5	16.19	88.5	0.37
110	27.000	5.89e-6	17.47	84.0	0.41
120	57.000	2.79e-6	18.30	81.0	0.44
130	140.000	1.15e-6	18.91	79.0	0.46
140	370.000	4.30e-7	19.62	76.5	0.46

—, not enough data for the calculation of the parameter.

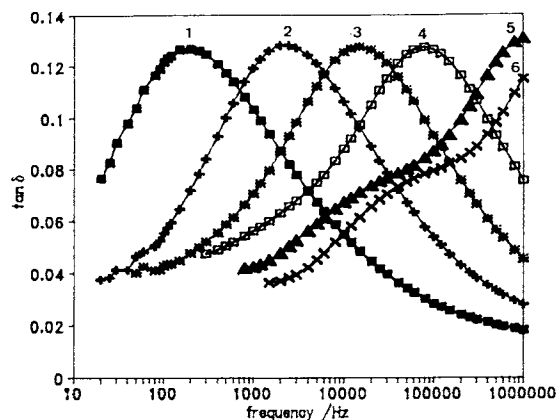


**Figure 3** Loss factor ( $\tan \delta$ ) as a function of the frequency for the 25% PEMA/PVAc blend at different temperatures: 1–50°C, 2–60°C, 3–70°C, 4–80°C, 5–90°C, and 6–100°C.

with compositions of 25, 50, and 75% (w/w percent in PEMA), respectively. The parameters corresponding to those relaxations (pure polymers and blends) are presented in Table III.

It is to be noted that the amplitude of the peaks decreases (accompanied by an increase of their broadness) as the PEMA content increases. The broadening of the curves (increase of the half-height width), to which corresponds a decrease of the  $\beta$  parameter shown in Table III, is ascribed to an heterogeneity of the environment of the relaxing dipoles in the blend.<sup>1,2</sup> From Figures 4 and 5, a second peak can also be observed that becomes apparent in the curves obtained at temperatures above 90°C. This second peak observed in the blends with higher PEMA content causes a broadening of the lower frequency side of the dielectric spectra and is, as will be shown later, a manifestation of the independent relaxation of PEMA in the blend. Figure 6 shows the representation of the peak's maximum intensity ( $\tan \delta_{\max}$ ) and of the dielectric strength ( $\epsilon_0 - \epsilon_\infty$ ) as a function of the blend composition.

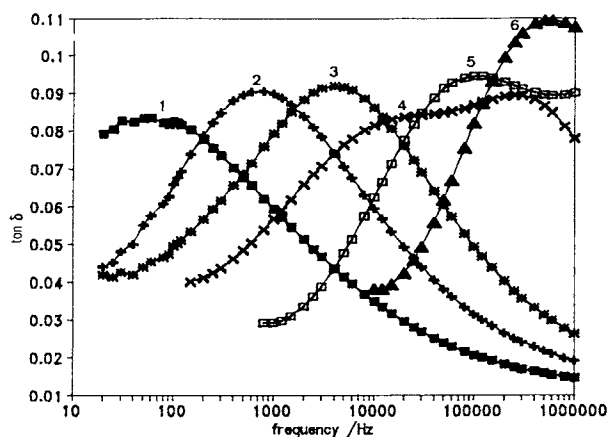
Figure 6 shows that the intensity of the peaks increases nearly linearly with the PVAc content, whereas the dielectric strength shows an even more marked increase. These results suggest that the PVAc dipole moment has a stronger contribution to the global dielectric loss. This behavior can also be inferred from the analysis of Figures 3–5. In fact, from Figure 3 (which corresponds to the 25% blend) the observed relaxations are dominated by the PVAc  $\alpha$ -process and the peaks show a location in the frequency axis similar to that observed for pure PVAc (Fig. 1). In Figure 4 (50% blend), the peaks also appear as being dominated by the  $\alpha$ -process of PVAc



**Figure 4** Loss factor ( $\tan \delta$ ) as a function of the frequency for the 50% PEMA/PVAc blend at different temperatures: 1–50°C, 2–60°C, 3–70°C, 4–80°C, 5–100°C, and 6–110°C.

but now it becomes clear, for the dielectric spectra obtained above 90°C, the appearance of the relaxation process of PEMA in the lower frequency side (we see later how the DSC thermograms illustrate this behavior). It is interesting to note in this context that the activation energy calculated at 70°C for the main process in the 25 and 50% blends has the same value of 42 kcal mol<sup>-1</sup> that was reported before for pure PVAc.

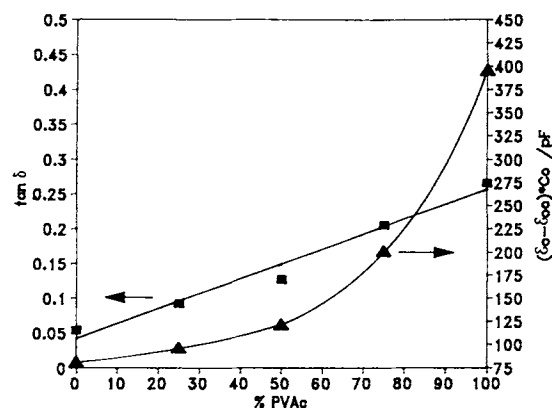
The behavior of the 75% blend is markedly different from the other two blends. The corresponding loss peaks are shown in Figure 5, and it can be observed that the frequency of maximum loss of the peaks in the lower temperature region ( $T < 90^\circ\text{C}$ ) is located between those corresponding to the pure polymers (an activation energy of 38 kcal mol<sup>-1</sup> was



**Figure 5** Loss factor ( $\tan \delta$ ) as a function of the frequency for the 75% PEMA/PVAc blend at different temperatures: 1–50°C, 2–60°C, 3–70°C, 4–100°C, 5–120°C, and 6–140°C.

found at 70°C for this lower temperature process). At higher temperatures ( $T > 90^\circ\text{C}$ ), the behaviour of the blend is similar to that of the main component (PEMA). The behavior described before is illustrated in Figure 7, which shows the loss factor at a fixed frequency (10 kHz) as a function of the temperature [Fig. 7(a)] and the loss factor at a fixed temperature (70°C) as a function of the frequency [Fig. 7(b)].

It can be seen from Figure 7 that the relaxation process in the 25 and 50% blends is unchanged relatively to pure PVAc, which is an indication of immiscibility in these blends. For the 75% blend, on the other hand, a shift of the location of the peaks is observed, which can be considered as indicative of some degree of miscibility between PVAc and PEMA. The activation energy also changes, as reported before, showing a decrease relatively to that observed for pure PVAc. Moreover, it can be observed from Figure 7(a) that the behavior of the 75% blend in the higher temperature region is, as



**Figure 6** Maximum intensity ( $\tan \delta_{\max}$ ) and dielectric strength [expressed as  $(\epsilon_0 - \epsilon_\infty) \cdot C_0$ ] at 70°C as a function of blend composition (% w/w of PVAc).

pointed out before, similar to that of the main component (PEMA).

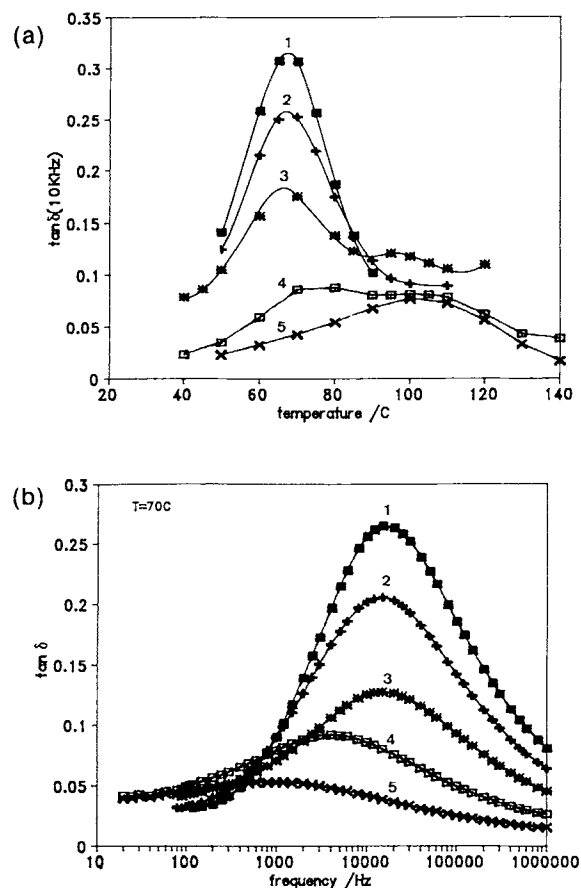
The study by DSC seems to confirm the previous interpretation of the dielectric data. Figure 8 shows

**Table III** Parameters of the Dielectric Relaxation of Poly(vinyl acetate), Poly(ethyl methacrylate), and Some of the Corresponding Blends

	$T$ ( $^\circ\text{C}$ )	PEMA	75% PE	50% PE	25% PE	PVAc
$\tan \delta_{\max} \times 10$	50	0.390	0.836	1.270	2.000	2.585
	60	0.463	0.905	1.283	2.046	2.643
	70	0.532	0.920	1.275	2.055	2.650
	80	0.614	0.909	1.274	2.071	2.662
	90	0.700	0.901	1.300	2.120	2.704
	100	0.772	0.895			
	110	0.834	0.888 <sup>a</sup>			
	120	0.878	0.945 <sup>a</sup>			
	130	0.914	1.011 <sup>a</sup>			
	140	0.948	1.095 <sup>a</sup>			
$f_{\max}$ (kHz)	50	0.15	0.06	0.19	0.16	0.19
	60	0.4	0.75	2.25	2.25	2.25
	70	0.9	4.0	14.0	15.0	16.0
	80	2.0	22.0	80.0	75.0	80.0
	90	5.0	75.0	280.0	225.0	275.0
	100	13.0	250.0			
	110	35.0	40.0 <sup>a</sup>			
	120	90.0	100.0 <sup>a</sup>			
	130	225.0	250.0 <sup>a</sup>			
	140	500.0	550.0 <sup>a</sup>			
$\beta^b$	50	—	—	0.45	0.47	0.55
	60	—	0.40	0.45	0.50	0.56
	70	0.32	0.32	0.41	0.51	0.58
	80	0.32	0.27	0.34	0.53	0.60
	90	0.33	0.24	0.29	0.55	0.62
	100	0.37			0.58	

<sup>a</sup> Parameter of the overlapping peak.

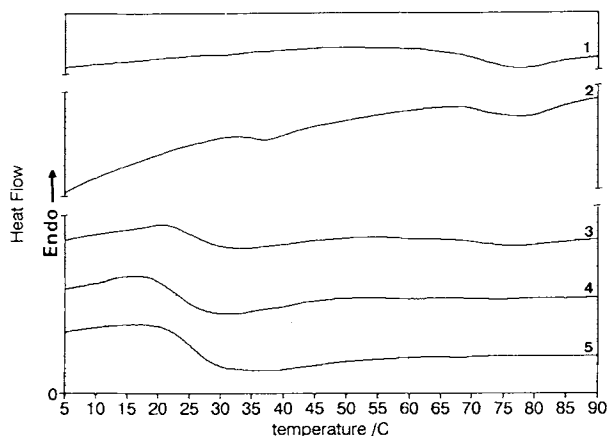
<sup>b</sup> Determined from the dielectric loss curves; in overlapping curves, the parameter was calculated by the expression  $\beta = 1.14/\Delta\log_{10}f$ .<sup>13</sup> —, not enough data for the calculation of the parameter.



**Figure 7** (a) Dielectric loss factor at 10 kHz as a function of the temperature: 1-pure PVAc; 2-25% PEMA blend; 3-50% PEMA blend; 4-75% PEMA blend; 5-pure PEMA (to make the figure clearer, curves 1, 2, and 3 were shifted 0.05 up in the ordinate axis). (b) Dielectric loss factor at 70°C as a function of the frequency: 1-pure PVAc; 2-25% PEMA blend; 3-50% PEMA blend; 4-75% PEMA blend; 5-pure PEMA.

the traces of the DSC thermograms for the pure polymers and for the three studied blends. It is clear from Figure 8 that for the 25 and 50% blends, the glass transitions are unchanged relatively to those of the pure polymers, indicating that there is immiscibility (incompatibility) in this concentration range. For the 75% blend, on the other hand, a marked shift of the lower temperature transition is observed and, simultaneously, the glass transition of pure PEMA is always present. These results suggest that the 75% blend is a two-phase system where one phase is (nearly) pure PEMA and the other phase is an "homogeneous" mixture of both polymers. A similar situation has been found for other polymer mixtures.<sup>5</sup>

A phase-separated system usually shows an interfacial polarization, the so-called Maxwell-Wag-

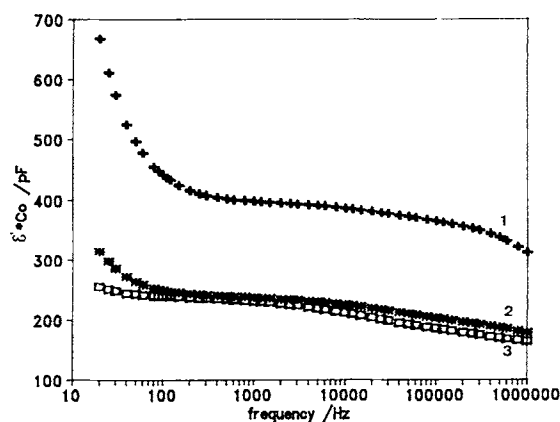


**Figure 8** DSC thermograms for pure polymers and corresponding blends: 1-pure PEMA; 2-75% PEMA blend; 3-50% PEMA blend; 4-25% PEMA blend; 5-pure PVAc. The heating rate was 10 K min<sup>-1</sup>.

ner-Sillars (MWS) effect, which causes an increase of the dielectric constant with decreasing frequency. Figure 9 shows a plot of the quantity  $\epsilon' \cdot C_0$  (see experimental part) as a function of the frequency of the applied electric field. It is clear from Figure 9 that the intensity of the MWS effect is stronger for the 25% blend, and we can conclude from these results that the incompatibility between the two polymers increases with decreasing PEMA content.

## CONCLUSIONS

From the reported results, it can be concluded that the PVAc-rich PVAc/PEMA blends show incompatibility that is manifested by the fact that the re-



**Figure 9**  $\epsilon' \cdot C_0$  as a function of the frequency, at 110°C, for the blends: 1-25% PEMA blend, 2-50% PEMA blend, 3-75% PEMA blend.

laxations observed in these blends are unchanged relatively to the pure polymers. In this situation, a strong MWS effect is observed and the glass transitions monitored by DSC are those characteristic of the pure polymers. In PEMA-rich blends, on the other hand, some degree of miscibility is observed that causes the appearance of a new relaxation whose location in the frequency axis is intermediate between that of the relaxations corresponding to the pure polymers. In this context, the DSC thermograms show a glass transition that is clearly different and located at an intermediate temperature from those observed for the pure polymers, and the MWS effect is weaker than in PVAc-rich blends. The PEMA-rich PEMA/PVAc blends seem thus to be composed of two separated phases, one of them being constituted by nearly pure PEMA and the other by an homogeneous mixture of the two polymers.

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