# Dielectric study of the crystal–amorphous interphase in poly(vinylidene fluoride)/poly(methyl methacrylate) blends

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We investigated the dielectric properties of crystalline poly(vinylidene fluoride) (PVDF)/poly(methyl methacrylate) (PMMA) blends in a wide range of frequency $f$ at various temperatures $T$. A large peak of the dielectric loss $\varepsilon''(f)$ due to the interfacial polarization was found in the blend below the frequency region of the $\alpha_c$ process. Such a peak was not observed in neat PVDF. The difference may be ascribed to the existence of a large amount of PMMA at the crystal–amorphous interphase in the blend. We also demonstrated that a low $T$peak in $\varepsilon''(T)$, which was thought of as an interfacial peak, is not related to the $\alpha_a$ process of PVDF in the interphase, but to the $\beta$ process of PVDF.

**(Keywords: dielectric properties; blends; interphase)**

## INTRODUCTION

Recently, the existence of a crystal–amorphous interphase, which is comprised of an amorphous state of a purely crystalline polymer, was demonstrated in crystalline/non-crystalline polymer blends by dielectric relaxation studies[1–4]. Typical examples are seen in poly(vinylidene fluoride) (PVDF)/poly(methyl methacrylate) (PMMA) blends[1,2]. A peak, which is assigned to the glass transition of PVDF, was found in the spectra of the temperature dependence of the dielectric loss (about −20°C at 1 kHz) in the blend in spite of the change in the glass transition with blend composition. Based on this result, it was concluded that this low temperature peak is not related to the liquid-like amorphous phase, but rather arises from the crystal–amorphous interphase. That is, the existence of an interphase peak was suggested. However, Runt *et al.*[3] found a lack of constancy for the location of the interphase peak with blend composition in poly($\varepsilon$-caprolactone)/poly(vinyl chloride) and poly(butylene terephthalate)/polyarylate blends.

The intention of this study is to gain a deeper understanding of the interphase peak of the PVDF/PMMA blend. Dielectric relaxation measurements were carried out in a wide frequency range at various temperatures.

## EXPERIMENTAL

The polymer samples used in this study were commercial polymers. PVDF was supplied by Polyscience, Inc., $M_w = 60\,000$. PMMA was supplied by Röhm GmbH, $M_w = 58\,000$.

PVDF and PMMA were dissolved at 10 wt% of total polymer in *N*,*N*-dimethylacetamide. The solution was cast onto a cover glass. After the solvent had been evaporated at room temperature, the cast film was dried further under vacuum ($10^{-4}$ mmHg) for 3 days at room temperature. A stack of thin-cast films was then compression-moulded at 210°C into a sample of about 0.13 mm thickness. The film was then cut into a circular shape of 20 mm diameter. The specimen was kept between two gold-plated copper electrodes, with a spacing of 0.125 mm maintained by a polyimide film (Kapton, Du Pont). The specimens were melted at 210°C for 10 min to allow adhesion between specimen and electrodes, and then cooled to a desired crystallization temperature $T_c$. Here $T_c$ is 160°C for neat PVDF and 145°C for the blend. After crystallizing for 24 h, the specimen was cooled rapidly to room temperature.

The dielectric measurements were carried out with a Schlumberger 1260 Impedance Analyzer equipped with an impedance transformer (Chelsea Dielectric Interface, Pugh Dielectric Instruments). The dielectric measurements covered the frequency range of 0.1 Hz–1 MHz and the temperature range of −100 to 200°C. The sample temperature was raised in steps after frequency-dependent runs at fixed temperature. The whole set-up operated under microcomputer control and allowed automatic data collection for various temperatures and frequencies.

## RESULTS AND DISCUSSION

*Figure 1* shows the dielectric loss $\varepsilon''$ as a function of temperature $T$ at different frequencies for neat PVDF and a PVDF/PMMA 60/40 blend. A low temperature peak, which was thought of as an interphase peak, is observed in this temperature range in both neat PVDF and the

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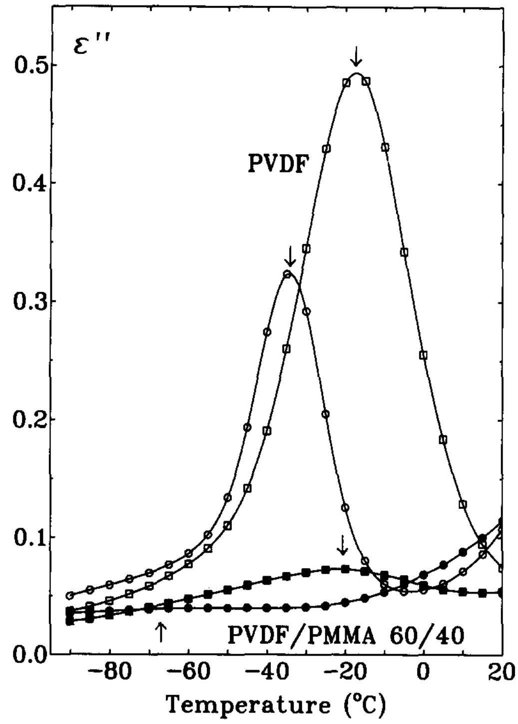

**Figure 1** Dielectric loss $\varepsilon''$ *versus* temperature: ○, PVDF; ●, PVDF/PMMA 60/40 at 100 Hz; □, PVDF; ■, PVDF/PMMA 60/40 at 10 kHz

blend. The peak location of the blend is nearly equal to that of neat PVDF at 10 kHz. This result is in agreement with that demonstrated by Hahn *et al.*[1,2]. However, the peak height of the blend is too small and the location is different from that of neat PVDF at 100 Hz, i.e. the location of the peak is at about −35°C for neat PVDF while that of the blend is at about −65°C. Thus the nature of the low temperature peak may be more complicated than previously thought. In the following we will discuss the frequency and the temperature dependence of this peak and elucidate the underlying relaxation.

The frequency, $f$, dependence of the dielectric loss, $\varepsilon''$, of neat PVDF at the low temperature region, demonstrated above, is shown in *Figure 2*. A diffuse peak appears at low temperature. This peak is assigned to the $\beta$ process characteristic for a local conformational transition of the frozen main chain in the amorphous region[5,6]. At higher temperatures, above −20°C, a large peak appears. This peak is assigned to the $\alpha_a$ process characteristic for the micro-Brownian motions of amorphous main chains that freeze at the glass transition[5,6]. As shown in *Figure 3*, these peaks can be well resolved by fitting the Havriliak-Negami (HN) equation to the data[7]:

$$\varepsilon^*(\omega) = \varepsilon_\infty + (\varepsilon_\infty - \varepsilon_s)/[1 + (i\omega\tau)^\alpha]^\gamma \qquad (1)$$

where $\varepsilon^*$ is the complex dielectric permittivity $\varepsilon^* = \varepsilon' - i\varepsilon''$, $\omega$ is the angular frequency, $\omega = 2\pi f$, $\varepsilon_s$ and $\varepsilon_\infty$ are the limiting low- and high-frequency permittivities, respectively, $\Delta\varepsilon = \varepsilon_\infty - \varepsilon_s$ is the dielectric strength, $\tau$ is the relaxation time, and the parameters $\alpha$ and $\gamma$ are fit parameters $(0 \leqslant \alpha, \gamma \leqslant 1)$ describing the broadening and the asymmetry of the relaxation time distribution. Each relaxation, $\beta$ and $\alpha_a$, is represented as a (HN) type function in the fit. From the fitting procedure, the mean relaxation rate $\nu_\tau = 1/(2\pi\tau)$ was obtained. The temperature dependence of the $\nu_\tau$ is shown by using an Arrhenius plot in *Figure 4*. The $\beta$ process exhibits an Arrhenius behaviour while the temperature dependence of the $\alpha_a$ process is described by the Vogel equation:

$$\log \nu_\tau = A + B/(T - T_0) \qquad (2)$$

where $A$ is related to the relaxation rate at infinitely high temperature, $B$ is an activation parameter, and $T_0$ is related to the glass transition temperature. Thus the low

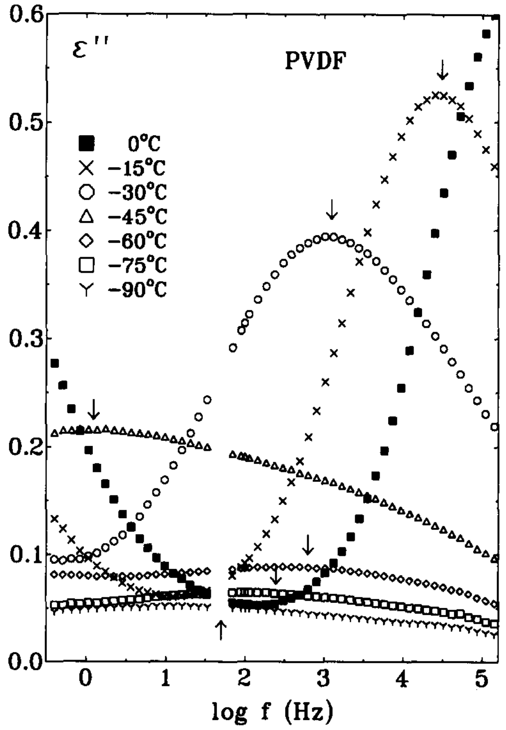

**Figure 2** Dielectric loss $\varepsilon''$ *versus* frequency in the low temperature region for PVDF

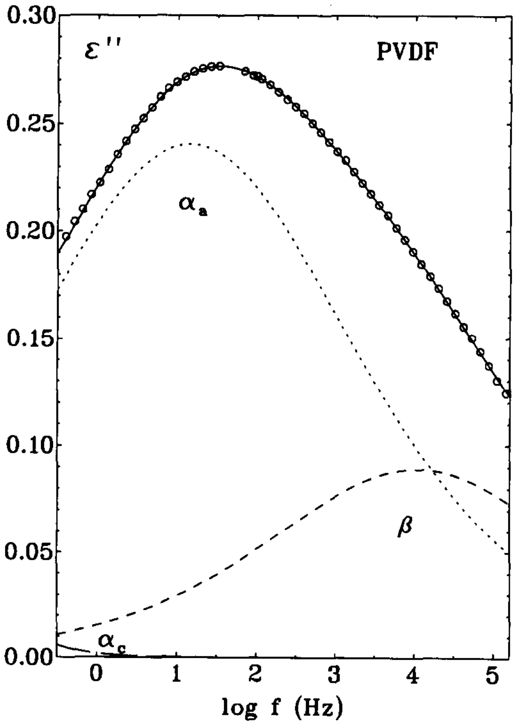

**Figure 3** Dielectric loss $\varepsilon''$ *versus* frequency for PVDF at −40°C. The curve was fitted by equation (1) with $\Delta\varepsilon = 2.00$, $\log \nu_\tau = 1.16$, $\beta = 0.30$, $\gamma = 1$ for the $\alpha_a$ process and $\Delta\varepsilon = 0.69$, $\log \nu_\tau = 4.0$, $\beta = 0.32$, $\gamma = 1$ for the $\beta$ process

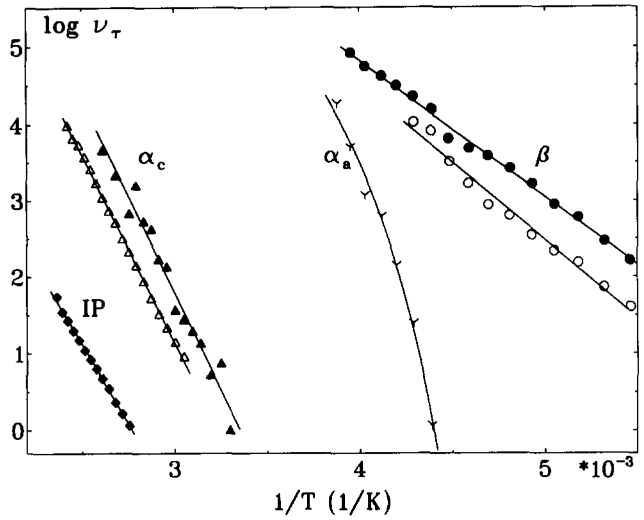

**Figure 4** Arrhenius plot of the mean relaxation rate $\nu_\tau$ for PVDF (open symbols) and PVDF/PMMA 60/40 (solid symbols). A curve representing the $\alpha_a$ process of PVDF is a fit of equation (2) with $A = 8.45$, $B = 272.8$, $T_0 = 195.1$ K. IP denotes the interfacial polarization (see text)

temperature peak in $\varepsilon''(T)$ of neat PVDF is ascribed to both the $\alpha_a$ and the $\beta$ process.

On the other hand, only one broad unstructured peak appears in the blend, as shown in *Figure 5*. This peak could not be resolved (*Figure 6*) and the temperature dependence of the $\nu_\tau$ exhibits a similar behaviour to that of the $\beta$ process of PVDF (*Figure 4*). The dielectric strength $\Delta\varepsilon$ of the blend is about 0.6 times that of the $\beta$ process of neat PVDF, which is equal to the fraction of PVDF in the blend. Thus we can assign this peak to the $\beta$ process of PVDF. Based on this result, we conclude that the low temperature peak in $\varepsilon''(T)$ of the blend is not related to the $\alpha_a$ process of PVDF in the interphase, but is rather ascribed to the $\beta$ process of PVDF. This also explains the low peak height of the blend and the inconsistency of the peak location between neat PVDF and the blend, as demonstrated in *Figure 1*.

Our preliminary interest had been in the $\alpha_a$ process of the blend. A peak of the $\alpha_a$ process appears in neat PMMA above 130°C in our frequency range[8]. Thus, if the dissimilar polymers of this blend are homogeneously mixed in the interlamellar amorphous phase, a single peak of the $\alpha_a$ process is expected to appear at higher temperatures than those shown in *Figure 2*.

The $\varepsilon''(f)$ of the blend in the high temperature regime is shown in *Figure 7*. A broad shoulder appears at 45°C (*Figure 7a*). At higher temperatures (above 80°C), a large peak appears (*Figure 7b*). The observed curves were successfully resolved into two peaks by equation (1), as shown in *Figure 8*. The temperature dependence of the $\nu_\tau$ of both peaks exhibits Arrhenius behaviour (*Figure 4*). The $\alpha_a$ process, however, is described by the Vogel equation. It could not be detected at any temperature. We could not detect the peak of the $\alpha_a$ process even in a blend sample that was prepared to be non-crystalline. Concentration fluctuations of the dissimilar polymers that differ widely in their glass transition temperatures may cause a broadening of the peak of the $\alpha_a$ process[9], so that the peak is hidden by other peaks.

In neat PVDF, a peak appears above 30°C, as shown in *Figures 9* and *10*. This peak is assigned to the $\alpha_c$ process of the crystalline phase characterized by the conformational change $TGT\bar{G} \Leftrightarrow \bar{G}TGT$ along the chain axis[10–12]. The temperature dependence of the $\alpha_c$ process exhibits an Arrhenius behaviour (*Figure 4*). This behaviour is similar to that of the shoulder of the blend in *Figure 7a*. Thus we can assign the shoulder of the blend to the $\alpha_c$ process of PVDF.

We remark that the side group rotation of PMMA gives rise to a $\beta$ process[8], which may contribute to the

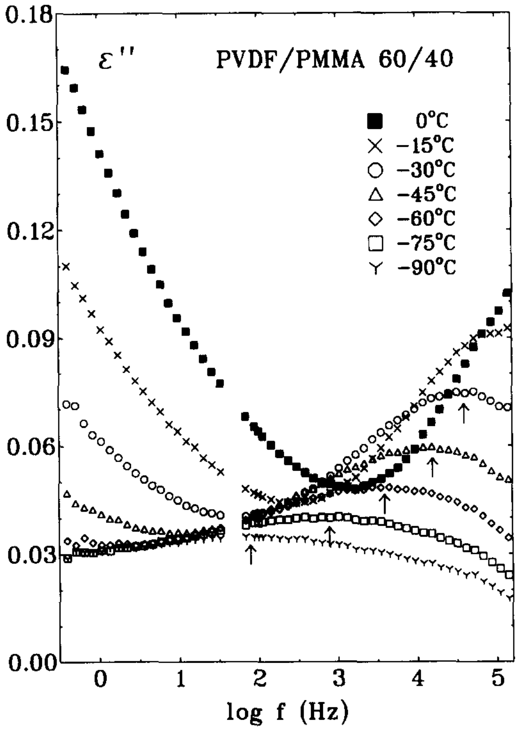

**Figure 5** Dielectric loss $\varepsilon''$ *versus* frequency at the low temperature region for PVDF/PMMA 60/40

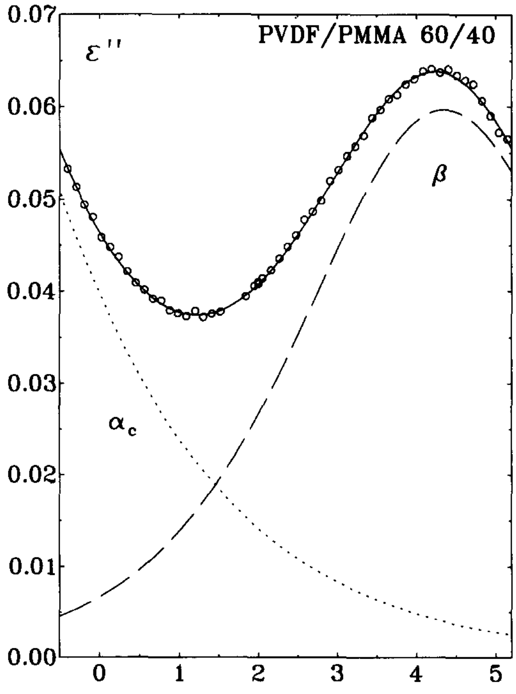

**Figure 6** Dielectric loss $\varepsilon''$ *versus* frequency for PVDF/PMMA 60/40 at $-40$°C. The curve is a fit of equation (1) with $\Delta\varepsilon = 0.43$, $\log \nu_\tau = 4.3$, $\beta = 0.34$, $\gamma = 1$ for the $\beta$ process

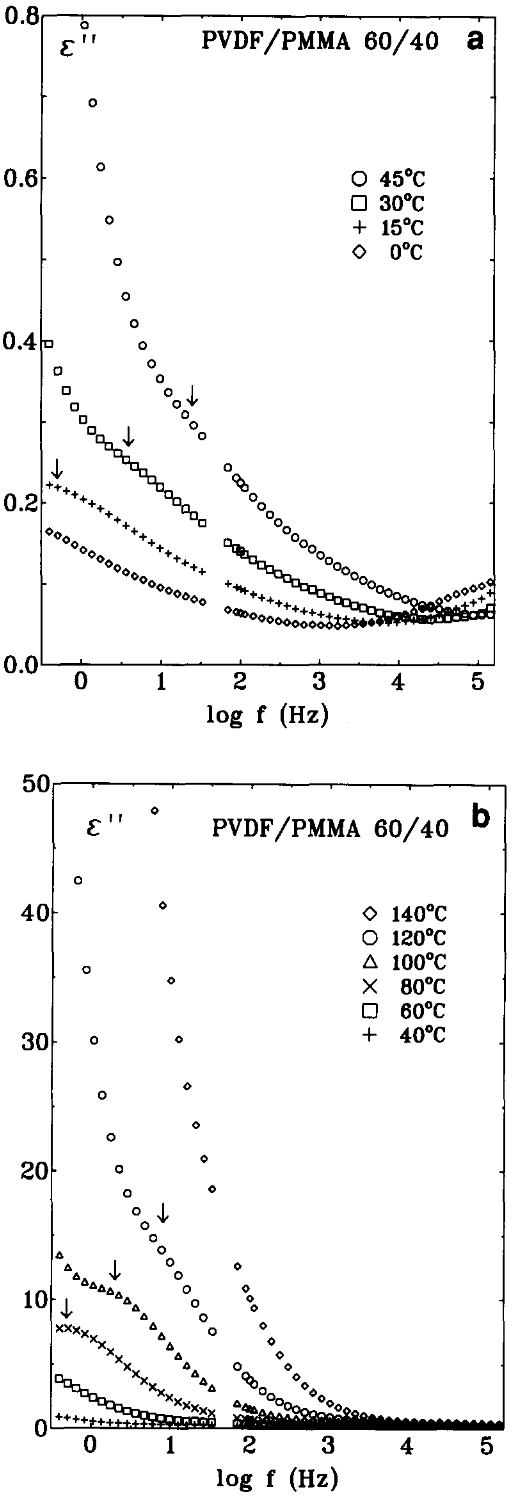

**Figure 7** Dielectric loss $\varepsilon''$ *versus* frequency at the high temperature region for PVDF/PMMA 60/40

above-described shoulder in $\varepsilon''$ observed in the blend (cf. *Figures 7a* and *8*). However, the shape of the peak, as resolved in *Figure 8*, is quite different from that of the $\beta$ process in PMMA. We obtain parameters $\beta = 0.62$ and $\gamma = 1$ (see equation (1)) for the resolved curve whereas $\beta = 0.52$ and $\gamma = 0.54$ are found in neat PMMA. On the other hand, the $\alpha_c$ process in neat PVDF has exactly the same shape parameters. The broad peak of the $\beta$ relaxation of PMMA is hidden underneath the $\alpha_c$ process of PVDF.

A further interesting observation is that a large peak appears below the frequency region of $\alpha_c$ process in the blend (*Figure 7b*), while such a peak is not observed in neat PVDF (*Figure 9*). $\Delta\varepsilon$ of the peak is too large compared to that of the $\alpha_c$ process and the peak disappears above the melting temperature. Thus we assign this peak to the relaxation of interfacial

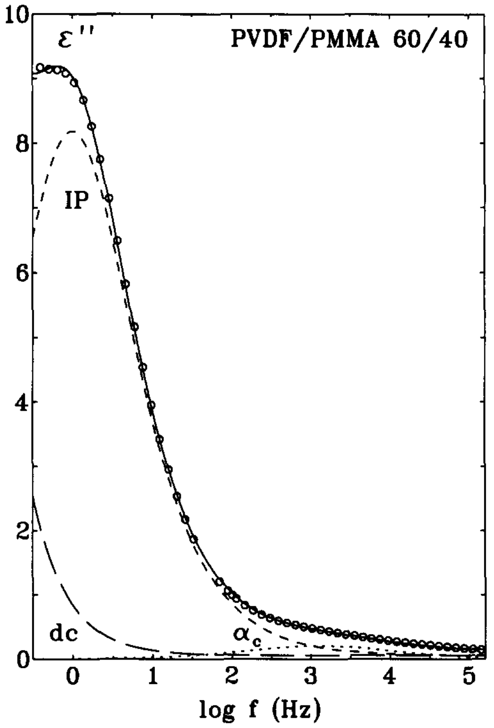

**Figure 8** Dielectric loss $\varepsilon''$ *versus* frequency at 90°C for PVDF/PMMA 60/40. The curve is a fit of equation (1) with $\Delta\varepsilon = 0.8$, $\log \nu_\tau = 3.1$, $\beta = 0.62$, $\gamma = 1$ for the $\alpha_c$ process, and $\Delta\varepsilon = 22.5$, $\log \nu_\tau = 0$, $\beta = 0.72$, $\gamma = 1$ for interfacial polarization (IP). dc is the contribution of direct current conductivity

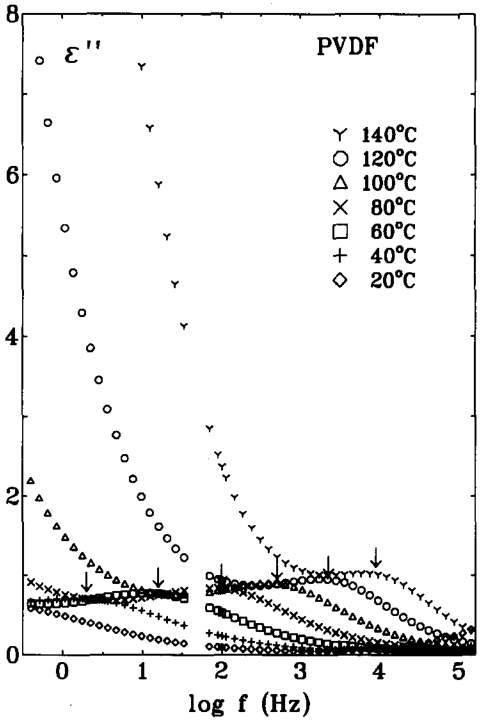

**Figure 9** Dielectric loss $\varepsilon''$ *versus* frequency at the high temperature region for PVDF

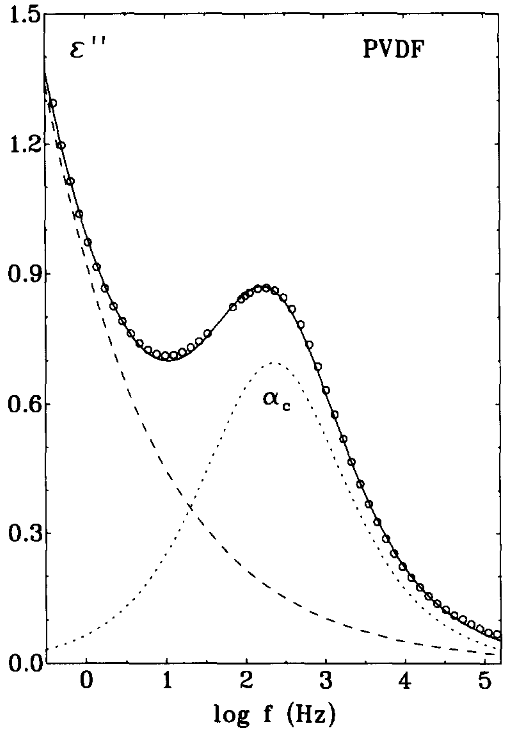

**Figure 10** Dielectric loss $\varepsilon''$ *versus* frequency at 90°C for PVDF. The curve is a fit of equation (1) with $\Delta\varepsilon = 2.5$, $\log \nu_r = 2.4$, $\beta = 0.64$, $\gamma = 1$ for the $\alpha_c$ process

polarization caused by trapping of charge carriers at the crystal–amorphous interphase (see *Figure 4*). According to Yano *et al.*[13], the steep increase of the $\varepsilon''$ with decreasing $f$ in neat PVDF, shown in *Figure 9*, is also attributed to the interfacial polarization. Thus the peak due to the interfacial polarization is expected to exist at lower $f$ region in neat PVDF, so that the peak position of neat PVDF seems to shift to much higher $f$ with blending. The shift of peak position may arise from the different mobility of the charge carriers in the diffused interphase[14,15], and the difference of the relative permittivity of each phase at the interphase[16]. This suggests that the nature of the interphase of the blend differs from that of neat PVDF. The difference may be ascribed to the existence of a large amount of PMMA at the interphase, caused by the exclusion of PMMA from lamellae during crystallization.

## CONCLUSION

We have shown that a low temperature peak in $\varepsilon''(T)$, which was thought of as an interphase peak, is not related to the $\alpha_a$ process of PVDF in the interphase. The peak of the $\alpha_a$ process could not be detected in the blend. A large peak of the $\varepsilon''(f)$ due to the interfacial polarization was found in the blend below the frequency region of the $\alpha_c$ process. We believe that such an interfacial polarization may provide a key to understanding the unsolved problem of the effect of the exclusion on the crystallization kinetics[17] and the crystalline structure of polymer blends[18].

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